41<sup>st</sup> Conference on the Physics & Chemistry of Surfaces & Interfaces

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January 12-16, 2014, Santa Fe, New Mexico, USA

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# Abstract Book & Schedule

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# **PCSI 41 General Information**

## **Conference Hotel:**

La Fonda Hotel, Santa Fe, New Mexico

### **Program Committee:**

- Chagaan Baatar, Office of Naval Research
- Anand Bhattacharya, Argonne National Lab
- Leonard Brillson, The Ohio State University
- Alex Demkov, University of Texas, Austin
- Helen Farrell
- Michael Flatté, University of Iowa
- Rachel S. Goldman, University of Michigan
- Jessica Hilton, Mantis Deposition
- Harold Hwang, Stanford University
- Hisao Ishiii, Chiba University
- Karen Kavanagh, Simon Fraser University
- Roland Kawakami, The Ohio State University
- William Lampert, Sustema Research LLC
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- Rudy Ludeke
- Matthew R. Libera, Stevens Institute of Technology
- Chris McConville, Warwick University
- Anders Mikkelsen, Lund University
- Roberto Myers, Ohio State University
- Chris J. Palmstrøm, University of California, Santa Barbara
- Henning Riechert, Paul Drude Institute
- Jack Rowe
- Nitin Samarth, Penn State University
- Masaaki Tanaka, University of Tokyo
- Akira Toriumi, University of Tokyo
- Pani Varanasi, Army Research Office
- Robert Wallace, University of Texas, Dallas
- Roland Wiesendanger, University of Hamburg
- Ed Yu, University of Texas at Austin

### Chair:

### **Roland Kawakami**

The Ohio State University E-mail: <u>kawakami.15@osu.edu</u>

# **General Chair:**

Chris Palmstrøm University of California, Santa Barbara E-mail: <u>cpalmstrom@ece.ucsb.edu</u>

## **JVST Special Issue Editor:**

Rudy Ludeke E-mail: <u>rudy\_ludeke@msn.com</u>

## **Registration:**

Della Miller/Heather Korff AVS, 110 Yellowstone Dr., Suite 120 Chico, CA 95973 E-mail: <u>della@avs.org /heather@avs.org</u> Phone: 530-896-0477

Conference Website: <u>www.pcsiconference.org</u>

## **Presentation Formats:**

Invited Talks—35 minute oral presentation, 5 minute discussion, <u>plus poster</u> Upgraded Talks—17 minute oral presentation, 3 minute discussion, <u>plus poster</u> Contributed Talks—4 minute oral presentation (max 3 slides, 1 minute discussion, <u>plus poster</u>) Posters—Displayed all week (46 inches tall x 44 inches wide)

# **PCSI 41 Sponsors**



# **PCSI 41 Schedule Overview**

### Sunday:

- Su1400 Registration
- Su1455 Welcome Remarks
- Su1500 Sunday Afternoon Session: Topological Insulators
- Su1705 Poster Setup
- Su1730 Welcome Reception
- Su1930 Sunday Evening Session: Oxides I

### Monday:

- Mo0730 Registration and Continental Breakfast
- Mo0830 Monday Morning Session: Semiconductors I
- Mo0940 Coffee Break and Poster Viewing
- Mo1100 Monday Morning Session: Energy Storage and Generation I
- Mo1150 Lunch and Poster Viewing
- Mo1400 Monday Afternoon Session: Spintronics and Spin Transport
- Mo1540 Coffee Break and Poster Viewing
- Mo1610 Monday Afternoon Session: Graphene
- Mo1800 Dinner

### **Tuesday:**

- Tu0730 Registration and Continental Breakfast
- Tu0830 Tuesday Morning Session: Oxides II
- Tu1005 Coffee Break and Poster Viewing
- Tu1045 Tuesday Morning Session: New Imaging and Spectroscopy Tools
- Tu1200 Free Afternoon
- Tu1930 Tuesday Evening Rump Session: Single Atom Devices

### Wednesday:

- We0730 Registration and Continental Breakfast
- We0830 Wednesday Morning Session: Energy Storage and Generation II
- We0940 Coffee Break and Poster Viewing
- We1040 Wednesday Morning Session: Semiconductors II, Epitaxy, and Surface Microscopy
- We1200 Lunch and Poster Viewing
- We1400 Wednesday Afternoon Session: Graphene Analogs and Novel 2D Materials I
- We1535 Coffee Break and Poster Viewing
- We1630 Wednesday Afternoon Session: Nanostructures for Electronics and Photonics
- We1805 Poster Viewing
- We1900 Conference Banquet

## Thursday:

- Th0730 Continental Breakfast
- Th0830 Thursday Morning Session: Oxides and Semiconductors
- Th0925 Coffee Break and Poster Viewing
- Th1000 Thursday Morning Session: Graphene Analogs and Novel 2D Materials II
- Th1130 Poster Viewing
- Th1200 Conference Ends

Sunda	y Afterno	oon:								
Su1400	Su1400 2:00 p.m. Registration									
Su1455	2:55 p.m.	Welcome Remarks								
Topologi	cal Insulator	S		Session Chair: M. Flatté						
Su1500	3:00 p.m.	INVITED: Direct Measurement of Surface Transport on a Topological Insulator		<u>P. Hofmann,</u> Aarhus Univ.						
Su1540	3:40 p.m.	INVITED: Mapping the Spin Texture of Topological Insulators		<u>A. Lanzara,</u> Univ. of California, Berkeley						
Su1620	4:20 p.m.	UPGRADED: Interfacing 3D Topological Insulators with Ferromagnetism and Superconductivity		<u>A. Richardella</u> , A. Kandala, J.S. Lee, D. Zhang, T. Flanagan, N. Samarth, W. Dai, Q. Li, The Pennsylvania State Univ.; S. Xu, Z. Hasan, Princeton Univ.; F. Chou, National Taiwan Univ.; J. Heron, D. Schlom, Cornell Univ.						
Su1640	4:40 p.m.	Unusual Surface Termination of the 3D Topological Insulator Bi <sub>2</sub> Se <sub>3</sub>		<u>A. Hewitt</u> , J. Wang, J. Bolterdorf, T. Guan, P. Maggard, D. Dougherty, D. Dougherty, North Carolina State Univ.						
Su1645	4:45 p.m.	UPGRADED: Probing Spin Orbit Interaction in Inas/Ingaas Gate-defined Quantum Point Contact		<u>J. Shabani</u> , T. Mcfadden, A. Liaghat, Y. Kim, R.M. Lutchyn, C.J. Palmstrøm, Univ. of California, Santa Barbara						
Su1705	5:05 p.m.	Poster Setup								
Su1730	5:30 p.m.	Welcome Reception								
Sunda	y Evenin	g:								
Oxides I				Session Chair: D. Schlom						
Su1930	7:30 p.m.	INVITED: Two-dimensional Electron Gases at Oxide Interfaces		<u>S. Stemmer</u> , Univ. of California, Santa Barbara						
Su2010	8:10 a.m.	Integration of Ferroelectric BaTiO <sub>3</sub> on Ge (001)		K.D. Fredrickson, P. Ponath, A.B. Posadas, The Univ. of Texas; M.R. Mccartney, D.J. Smith, Arizona State Univ.; <u>A.A. Demkov,</u> The Univ. of Texas						
Su2015	8:15 p.m.	INVITED: Electric Field Induced Metallization of Correlated Electron Oxides		<u>S. Parkin</u> , IBM						

Monda	ay Mornir	ng:									
Mo0730	Mo0730 7:30 a.m. Registration and Continental Breakfast										
Semicon	ductors I		Session Chair: J. Wong								
Mo0830	8:30 a.m.	INVITED: Design and Applications of GaN Tunnel Junctions	<u>S. Rajan</u> , The Ohio State Univ.								
Mo0910	9:10 a.m.	III-V Nitride Heterojunctions by Atomic Layer Epitaxy	<u>C.R. Eddy, Jr.</u> , U.S. Naval Research Lab; N. Nepal, Sotera Defense Solutions; T. Anderson, A. Koehler, M. Mastro, J. Hite, U.S. Naval Research Lab								
Mo0915	9:15 a.m.	Metamorphic Growth of Insb Quantum Wells on (110) Oriented GaAs	<u>A. Podpirka</u> , M.E. Twigg, J.G. Tischler, R. Magno, B.R. Bennett, U.S. Naval Research Lab								
Mo0920	9:20 a.m.	Dynamic Strain Measurements of Ge on Si Using Spectroscopic Ellipsometry	A. Ghosh, Univ. of Michigan-Flint; N. Fernando, C.M. Nelson, A.A. Medina, New Mexico State Univ.; S.C. Xu, Arizona State Univ.; J. Menendez, J. Kouvetakis, <u>S. Zollner</u> , New Mexico State Univ.								
Mo0925	9:25 a.m.	Micro Reflectance Difference Spectroscopy of $Si_3N_4/N$ -Si (111), GaP/Si/GaP (100) 4° $\rightarrow$ (111) and GaP/AsGaP/Si (100) structures	R. Herrera-Jasso, L.F. Lastras-Martínez, R.E. Balderas Navarro, A. Lastras-Martínez, N.A. Ulloa Castillo, Instituto de Investigación en Comunicación Óptica, Universidad Autónoma de San Luis Potosí; Sergey Nikishin, Texas Tech. Univ.; A.C. Lin, J.S. Harris, M.M. Fejer, Stanford Univ.								
Mo0930	9:30a.m.	Different Orientation of AgGaTe <sub>2</sub> and AgAITe <sub>2</sub> Layers Grown on A-plane Sapphire Substrates by a Closed Space Sublimation Method	<u>A. Usui</u> , A. Uruno, M. Kobayashi, Waseda Univ.								
Mo0935	9:35 a.m.	Characterization of Surface Defects on Be Implanted GaSb Caused by Rapid Thermal Annealing	<u>N. Rahimi</u> , A.A. Aragon, O.S. Romero, T.J. Rotter, T. Busani, O. Lavrova, G. Balakrishnan, Univ. of New Mexico; L.F. Lester, Virginia Polytechnic Institute and State Univ.								
Mo0940	9:40 a.m.	Coffee Break and Poster Viewing	·								
Energy S	storage and (	Generation I	Session Chair: E. Alarcon-Llardo								
Mo1100	11:00 a.m.	INVITED: Metal-insulator-semiconductor Tunnel Diodes for Efficient Solar Hydrogen Production	<u>A. Talin</u> , Sandia National Labs								
Mo1140	11:40 a.m.	Efficient and Stable Photoelectrochemical Water Splitting with Metal-Insulator- Semiconductor Photoelectrodes grown by Molecular Beam Epitaxy	<u>L. Ji</u> , M.D. McDaniel, S. Wang, A.B. Posadas, A.A. Demkov, J.G. Ekerdt, A.J. Bard, E. Yu, The Univ. of Texas at Austin								
Mo1145	11:45 a.m.	Optical Properties of Sm-doped Ceria Films Prepared by Liquid Solution Deposition	<u>K. Mitchell</u> , C. Rodriguez, T. Willett-gies, Y. Li, S. Zollner, New Mexico State Univ.								
Mo1150	11:50 a.m.	Lunch and Poster Viewing									

Monda	ay Afterr	100n:	
Spintron	ics and Spi	n Transport	Session Chair: S. Crooker
Mo1400	2:00 p.m.	INVITED: Spin Filtering at Metal-organic Interfaces	<u>M. Aeschlimann</u> , Univ. of Kaiserslautern
Mo1440	2:40 p.m.	Spin Accumulation Detection of FMR Driven Spin Pumping in Silicon-based Metal-oxide- semiconductor Heterostructures	Y. Pu, The Ohio State Univ.; P.M. Odenthal, Univ. of California, Riverside; R. Adur, J. Beardsley, The Ohio State Univ.; A.G. Swartz, Univ. of California, Riverside; D.V. Pelekhov, R.K. Kawakami, J. Pelz, P.C. Hammel, <u>E. Johnston-Halperin</u> , The Ohio State Univ.
Mo1445	2:45 p.m.	Effect of Oxides on Fe/Gaas Spin Resistance	<u>S. Majumder</u> , D. Hohertz, Simon Fraser Univ.; A. Springthrope, National Science Council; K.L. Kavanagh, Simon Fraser Univ.
Mo1450	2:50 p.m.	Cr <sub>2</sub> O <sub>3</sub> Films on Graphite for Magnetoelectric Gate Applications	D.B. Dougherty, <u>S. Stuart</u> , E. Sachet, J.P. Maria, J.E. Rowe, M. Ulrich, NC State Univ.
Mo1500	3:00 p.m.	INVITED: Fluorination of Graphene: Engineering Charge Transport and Spin-flip Scattering	<u>J. Zhu</u> , Penn State Univ.
Mo1540	3:40 p.m.	Coffee Break and Poster Viewing	
Graphen	e		Session Chair: J. Shan
Mo1610	4:10 p.m.	Heating-induced Disorder of Graphene Transferred to a Substrate	<u>S. Suzuki</u> , NTT Corporation
Mo1615	4:15 p.m.	Giant Seebeck Coefficients of the Graphene/H-bn Superlattices	Y. Yokomizo, The Univ. of Electro-Communications (UEC-Tokyo) (UEC- Tokyo); <u>J. Nakamura</u> , The Univ. of Electro-Communications (UEC-Tokyo)
Mo1620	4:20 p.m.	Atomic Layer Deposition on Carbon-based Nanostructures: The Importance of Surface Modification and Nucleation	V. Wheeler, N. Garces, L. Nyakiti, R. Myers-ward, Z. Robinson, U.S. Naval Research Lab; A. Nath, George Mason Univ.; N. Nepal, M. Mastro, U.S. Naval Research Lab; E. Self, P. Pintauro, Vanderbilt Univ.; D.K. Gaskill, C.R. Eddy, Jr., U.S. Naval Research Lab
Mo1625	4:25 p.m.	INVITED: Exploring Atomically-Engineered Graphene Nanostructures	M. Crommie, Univ. of California, Berkeley
Mo1705	5:05 p.m.	Effect of Oxygen on Graphene Growth by Low Pressure Sublimation of C-face SiC	Z.R. Robinson, G.G. Jernigan, K.M. Bussmann, R.L. Myers-Ward, V.D. Wheeler, U.S. Naval Research Lab; S. Oida, J.B. Hannon, IBM T.J. Watson Research Lab; C.R.E. Jr, D.K. Gaskill, U.S. Naval Research Lab
Mo1710	5:10 p.m.	Oxidation of epitaxial graphene on SiC substrate: STM/STS, XPS and Raman characterization	<u>Z. Hossain</u> , M.B.A. Razak, Gunma Univ.
Mo1715	5:15 p.m.	Coupled Chemisorption and Physisorption of Oxygen on Single Layer Graphene Devices	<u>H. Wen</u> , A.G. Swartz, D.J. O'Hara, P.M. Odenthal, J. Chen, R.K. Kawakami, Univ. of California, Riverside
Mo1720	5:20 p.m.	INVITED: 2D Materials: Characterization and Device Application	R. Feenstra, Carnegie Mellon Univ.
Mo1800	6:00 p.m.	Dinner	

Tuesd	Tuesday Morning:							
Tu0730	7:30 a.m.	Registration and Continental Breakfast						
Oxides II			Session Chair: L. Brillson					
Tu0830	8:30 a.m.	UPGRADED: Control of Interlayer-coupling in $SrTiO_3$ Bilayer Delta-doped Structures	<u>H. Inoue</u> , Stanford Univ.; M. Kim, C. Bell, Y. Hikita, SLAC National Accelerator Lab; S. Raghu, SLAC National Accelerator Lab/Stanford Univ.; H.Y. Hwang, Stanford Univ./SLAC National Accelerator Lab					
Tu0850	8:50 a.m.	Band Alignment Control of Anatase-TiO <sub>2</sub> Heterojunctions Using Oxide Dipole Layers	<u>T. Tachikawa</u> , M. Minohara, Y. Hikita, C. Bell, H.Y. Hwang, SLAC National Accelerator Lab					
Tu0855	8:55 a.m.	Modulation of Over 1014 cm-Â-â€2 Electrons in SrTiO₃/GdTiO₃ Heterostructures	<u>M. Boucherit</u> , S. Rajan, C. Polchinski, The Ohio State Univ.; C. Jackson, S. Raghavan, S. Stemmer, Univ. of California, Santa Barbara; O.F. Shoron, The Ohio State Univ.					
Tu0900	9:00 a.m.	UPGRADED: Persistent Optically Induced Magnetism in Oxygen-deficient Strontium Titanate	<u>W.D. Rice</u> , Los Alamos National Lab; P. Ambwani, Univ. of Minnesota; M. Bombeck, Technische Universitat Dortmund; J.D. Thompson, Los Alamos National Lab; C. Leighton, Univ. of Minnesota; S.A. Crooker, Los Alamos National Lab					
Tu0920	9:20 a.m.	UPGRADED: Spin Injection and Detection in La- and Nb-Doped Strontium Titanate	<u>W. Han</u> , X. Jiang, IBM Almaden Research Center; A. Kajdos, UC Santa Barbara; SH. Yang, IBM Almaden Research Center; S. Stemmer, UC Santa Barbara; S. Parkin, IBM Almaden Research Center					
Tu0940	9:40 a.m.	Native Point Defects, Fermi Level Pinning, and Electrostatic Repulsion at MgxZn1- xOAlloys	<u>J. Perkins</u> , The Ohio State Univ.; M. Meyer, Columbus School for Girls; J.M. Chauveau, Universidad Politecnica de Madrid; A. Redondo-Cubero, A. Hierro, Univ. of Nice Sophia Antipolis; L.J. Brillson, The Ohio State Univ.					
Tu0945	9:45 a.m.	Hafnia-hafnium Interface in RRAM Devices: Theoretical Investigation	A. O'hara, The Univ. of Texas; G. Bersuker, SEMATECH; <u>A.A. Demkov</u> , The Univ. of Texas					
Tu0950	9:50 a.m.	Theoretical Investigation of the Strong Interaction on the Interface Between the Rh and CeO <sub>2</sub> Surface	<u>A. Suzuki</u> , R. Miura, N. Hatakeyama, A. Miyamoto, Tohoku Univ.					
Tu0955	9:55 a.m.	Morphology and Magnetic Properties of Thick- film Yttrium Iron Garnet Deposited by the Aerosol Deposition Method	<u>S.D. Johnson</u> , E.R. Glaser, S.F. Cheng, F.J. Kub, C.R. Eddy, Jr., U.S. Naval Research Lab					
Tu1000	10:00 a.m.	In-Situ Electronic Characterization of thin LaNiO <sub>3</sub> films via Scanning Tunneling Micropscopy and X-ray Photoemission Spectroscopy	<u>N. Wilson</u> , C.J.Palmstrøm, Univ. of California, Santa Barbara					
101005	10.00 a.iii.	CONCE DIEak and FUSIEL VIEWING						

New Imag	ging and Spe	ectroscopy Tools	Session Chair: P. Koenraad
Tu1045	10:45 a.m.	INVITED: Synchrotron X-ray STM	V. Rose, Argonne National Lab
Tu1125	11:25 a.m.	UPGRADED: Photoemission Electron Microscopy Using High Intensity, Ultrashort Laser Pulses	E. Mårsell, C.L. Arnold, E. Lorek, D. Guenot, E. Witting-Larsen, H. Xu, A. L'Huillier, <u>A. Mikkelsen</u> , Lund Univ.
Tu1145	11:45 a.m.	Nanocrystal Surface Structure and Ligand Bonding Probed by Surface-specific X-ray Spectroscopy	E.L. Rosen, K. Gilmore, A.M. Sawvel, A.T. Hammack, B.E. Cohen, J.J. Urban, D.J. Milliron, D. Prendergast, B.A. Helms, <u>D.F. Ogletree,</u> Lawrence Berkeley National Lab
Tu1150	11:50 a.m.	SERS and Gap-mode TERS Investigations of Phthalocyanine Molecules on Nanostructured Gold Substrates	<u>E. Sheremet</u> , R.D. Rodriguez, Technishche Universität Chemnitz, Germany; A.G. Milekhin, L. Leal, Universidad de Los Andes; A.V. Rzhanov Institute of Semiconductor Physics, Russia; V. Kolchuzhin, Technishche Universität Chemnitz, Germany; E.E. Rodyakina, A.V. Latyshev, A.V. Rzhanov Institute of Semiconductor Physics, Russia; D.R.T. Zahn, Technishche Universität Chemnitz, Germany
Tu1155	11:55 a.m.	Surface Enhanced Raman Scattering by CuxS Nanocrystals	N.A. Yeryukov, A.G. Milekhin, L.L. Sveshnikova, T.A. Duda, L.D. Pokrovsky, A.K. Gutakovsky, S.A. Batsanov, E.E. Rodyakina, A.V Latyshev, Rzhanov Institute of Semiconductor Physics; E. Sheremet, Chemnitz Univ. of Technology; D.R.T. Zahn, Chemnitz Univ. of Technology
Tu1200	12:00 p.m.	Free Afternoon	
Tuesd	ay Eveniı	ng:	
Rump Se	ssion: Single	e Atom Devices	Session Chair: R. Kawakami
Tu1930	7:30 p.m.	INVITED: Introduction to Single Atom Devices	<u>M. Flatté</u> , Univ. of Iowa
Tu1950	7:50 p.m.	INVITED: Single Impurities in Semiconductors Studied by STM	P. Koenraad, Eindhoven Univ. of Technology
Tu2030	8:30 p.m.	INVITED: Spin Qubits in Silicon	A. Dzurak, Univ. of New South Wales

Wedne	esday Mo	rning:		
We0730	7:30 a.m.	Registration and Continental Breakfast		
Energy S	Storage and (	Generation II		Session Chair: A. Talin
We0830	8:30 a.m.	INVITED: III-V Nanowires for Next Generation Solar Cells	<u>[</u>	E. Alarcon-Llardo, EPFL
We0910	9:10a.m.	Optical and Surface Characterization Studies of CdSe Quantum Dots Undergoing Photooxidation	 1 	<u>L. Powell,</u> A. Reinicker, Carnegie Mellon Univ.; L.F. Allard, Oak Ridge National Lab; R. Rosenberg, Argonne National Lab; L. Qu, M. Bootman, Crystalplex Inc; R.F. Davis, Carnegie Mellon Univ.
We0915	9:15 a.m.	The Application of Zinc Oxide Nanosheets in Dye-sensitized Solar Cells	[ 	<u>D.R. Jones</u> , J.D. Mcgettrick, D.T.J. Bryant, A. Tarat, T.G.G. Maffeis, Swansea Univ.
We0920	9:20 a.m.	Enhancing Solar Cell Performance Through the Use of Plasmon Generating Nanocomposite Materials	<u> </u>	<u>D. Joyce</u> , S. Saranu, V. Broadley, Mantis Deposition Ltd.
<del>We0925</del>	<del>9:25 a.m.</del>	WITHDRAWN: Narrowing of Band Gap in Thin Films and Linear Arrays of Ordered TiO <sub>2-</sub> Nanoparticles	/ /   	<u>Y. Liu, J. Taing, Univ. of California, Irvine; C.C. Chen, Argonne National Lab;</u> A.P. Sorini, SLAC National Accelerator Lab; M.H. Cheng, A.M. Margarella, Univ. of California, Irvine; H. Bluhm, Lawrence Berkeley- National Lab; T.P. Devereaux, SLAC National Accelerator Lab;- J.C. Hemminger, Univ. of California, Irvine
We0930	9:30 a.m.	Microdiffraction and Structural Characterization of Nanocrystalline Cu <sub>2</sub> ZnSnSe <sub>4</sub> Thin Films: Indentification Phase Formation Cu <sub>1.8</sub> Se	/	<u>A. Dussan</u> , H.P. Quiroz, N.J. Sena, Universidad Nacional de Colombia
We0935	9:35 a.m.	New Measurement Technique for the Separation of Recombination and Trapping Parameters in Semiconductors	<u> </u>	<u>R.K. Ahrenkiel</u> , S.W. Johnston, National Renewable Energy Lab; D. Kuciauskas, National Renewable Energy Lab
We0940	9:40 a.m.	Coffee Break and Poster Viewing		
Semicon	ductors II, E	pitaxy, and Surface Microscopy		Session Chair: R. Myers
We1040	10:40a.m.	Electrical and Microstructure Characterization of Low-resistance Palladium/Molybdenum Based Ohmic Contacts to N-GaSb on GaAs	1 ( 	<u>N. Rahimi</u> , A.A. Aragon, O.S. Romero, D.M. Shima, T.J. Rotter, G. Balakrishnan, S.D. Mukherjee, Univ. of New Mexico; L.F. Lester, Virginia Polytechnic Institute and State Univ.
We1045	10:45a.m.	Formation and Characterization of an In/Pb Binary Surface Alloy on Ge(111): LEED, STM, ARPES and Core Level Studies	ŀ	H.M. Sohail, R.I.G. Uhrberg, Linköping Univ.
We1050	10:50 a.m.	INVITED: Polarization Doping in Layered Heterostructures	<u>1</u>	<u>M. Ware</u> , Univ. of Arkansas
We1135	11:35a.m.	Effects of Plasma Treatment on Evolution of Surface Step-terrace Structure of Critically Cleaned C-plane Sapphire Substrates: An AFM Study	<u>[</u>	<u>D. Zhang</u> , Y. Gan, Harbin Institute of Technology
We1140	11:40 a.m.	Structural, Morphological and Optoelectrical Characterization of $Bi_2S_3$ Thin Films Grown by Co-evaporation	F	F <u>. Mesa</u> , Universidad Libre
We1145	11:45a.m.	Cationic Two-dimensional Surface States at Epitaxial InAs(111)A Surface Characterized Using Low-temperature Scanning Tunneling Microscopy	ŀ	K. Kanisawa, H. Tamura, NTT Corporation
We1150	11:50 a.m.	Cold Tip SPM -A New Generation of Variable Temperature SPM for Spectroscopy	(	C. Troeppner, J. Koeble, <u>B. Uder</u> , Oxford Instruments Omicron NanoScience
We1155	11:55 a.m.	Novel Applications in Surface Science In Situ Sample Analysis in Extreme Environments		T. Schulmeyer, SPECS Surface Nano Analysis, Inc.
We1200	12:00 p.m.	Lunch and Poster Viewing		

Wedne	esday Af	ternoon:	
Graphen	e Analogs a	nd Novel 2D Materials I	Session Chair: J. Zhu
We1400	2:00 p.m.	INVITED: Atomically Thin MoS <sub>2</sub> Crystals - A New Two-dimensional Semiconductor	<u>J. Shan</u> , Case Western Reserve Univ.
We1440	2:40 p.m.	UPGRADED: Direct Measurement of the Thickness-dependent Electronic Band Structure of MoS <sub>2</sub>	<ul> <li>W. Jin, P. Yeh, N. Zaki, D. Zhang, Columbia Univ.; J.T. Sadowski,</li> <li>A. Al-mahboob, Brookhave National Lab; M.V.D. Zande, D.A. Chenet,</li> <li>J.I. Dadap, Columbia Univ.; I.P. Herman, Columbia University;</li> <li>P. Sutter, Brookhave National Lab; J. Hone, Columbia University;</li> <li><u>R.M.O. Jr</u>, Columbia Univ.</li> </ul>
We1500	3:00 p.m.	UPGRADED: Variability in Exfoliated MoS <sub>2</sub> Generated by Defects	<u>R. Addou</u> , S. Mcdonnell, C. Buie, C.L. Hinkle, R.M. Wallace, The Univ. of Texas at Dallas
We1520	3:20 p.m.	Growth of Single-layer $MoS_2$ , $MoSe_2$ and Their Alloys on Flat and Pre-patterned SiO <sub>2</sub> /Si	J. Mann, E. Preciado, D. Barroso, G.V. Son, A. Nguyen, D. Pleskot, V. Klee, S. Bobek, D. Sun, <u>L. Bartels</u> , Univ. of California at Riverside
We1525	3:25 p.m.	Modification of Monolayer Molybdenum Disulfide Surfaces in UHV	P. Odenthal, Q. Ma, M. Isarraraz, A. Nguyen, K. Yamaguchi, C. Wang, A. Nguyen, D. Barroso, G.V. Son, E. Preciado, J. Mann, G. Powin, Univ. of California Riverside; R. Kawakami, The Ohio State Univ.; L. Bartels, Univ. of California Riverside
We1530	3:30 p.m.	Nanoscale Characterization Study of the Interface Between a Carbon Substrate and Two-dimensional Gallium Selenide Nanoflakes	<u>R.D. Rodriguez</u> , Technische Universität Chemnitz; A. Villabona, ULA; S. Müller, E. Sheremet, J. Kalbacova, Technische Universität Chemnitz; S.A. Lopez-rivera, ULA; D.R.T. Zahn, Technische Universität Chemnitz
We1535	3:35 p.m.	Coffee Break and Poster Viewing	
Nanostru	uctures for E	lectronics and Photonics	Session Chair: A. Mikkelsen
We1630	4:30 p.m.	INVITED: Si/III-V Hybrid Nanowires	<u>M. Hocevar</u> , TU Eindhoven
We1710	5:10 p.m.	INVITED: Radial Growth Surfaces and Interfaces in MOCVD Grown III-V Nanowires	<u>J. Wong</u> , Australian National Univ.
We1750	5:50 p.m.	Polarization-induced UV Nanowire Leds on Silicon and Molybdenum Films	<u>A.G. Sarwar</u> , S.D. Carnevale, T.F. Kent, The Ohio State Univ.; P.J. Phillips, R.F. Klie, Univ. of Illinois at Chicago; R.C. Myers, The Ohio State Univ.
We1755	5:55 p.m.	Surface Studies of Single Heterostructure InAs and GaAs Nanowires with Wurtzite and Zincblende Segments	<u>J. Knutsson</u> , M. Hjort, S. Lehmann, R. Timm, L. Samuelson, K.A. Dick, A. Mikkelsen, Lund Univ.
We1800	6:00 p.m.	Intrinsic Electrical Transport Property Extraction of Zinc Oxide Nanowires Using Non-lithographic Gated Four Probe Measurements	N.A. Smith, A.M. Lord, J. Evans, S.P. Wilks, Swansea Univ.
We1805	6:05 p.m.	Poster Viewing	
We1900	7:00 p.m.	Conference Banquet and Speaker: Behind the Scenes: Forensics and MythBuster	rs, V. Romero, New Mexico Institute of Mining and Technology

Thurs	day Morn	ling:		
Th0730	7:30 a.m.	Registration and Continental Breakfast		
Oxides o	n Semicond	uctors		Session Chair: C. Palmstrom
Th0830	8:30 a.m.	INVITED: Exploiting Dimensionality and Defect Mitigation to Create Tunable Microwave Dielectrics with Record Performance		<u>D. Schlom</u> , Cornell Univ.
Th0910	9:10 a.m.	Spin Dependent Variable Range Hopping in Thin Dielectric Films in MOS and MIM Systems		<u>M. Mutch</u> , P.M. Lenahan, C.J. Cochrane, Pennsylvania State Univ.; S.W. King, B.C. Bittel, Intel Corporation; J.F.C. Jr., N. Alimardani, Oregon State Univ.
Th0915	9:15 a.m.	Gd <sub>2</sub> O <sub>3</sub> Deposited on GaAs(001): Optical Anisotropies with Modulated Reflectance		<u>N.A. Ulloa-Castillo</u> , L.F. Lastras-martinez, R.E. Balderas-Navarro, A. Lastras-martinez, Universidad Autonoma de San Luis Potosi
Th0920	9:20 a.m.	On the Structure of the SiC/SiO <sub>2</sub> Boundary		<u>M.A. Anders</u> , C.J. Cochrane, P.M. Lenahan, Penn State Univ.; S.D. Arthur, J. Mcmahon, L. Yu, X. Zhu, GE Global Research; A.J. Lelis, U.S. Army Research Center
Th0925	9:25 a.m.	Coffee Break and Poster Viewing		
Graphen	e Analogs ar	nd Novel 2D Materials II		Session Chair: W. Han
Th1000	10:00 a.m.	INVITED: Mechanical Routes to Thermodynamic Stabilization of the Elusive Metallic Phase of Monolayer Mo- and W- Dichalcogenides		<u>E. Reed</u> , Stanford Univ.
Th1040	10:40 a.m.	UPGRADED: Spin Polarization of Monolayer Hexagonal Boron Nitride on Ni(111) Studied by Spin-polarized Metastable De-excitation Spectroscopy		<u>M. Ohtomo</u> , P.V. Avramov, S. Entani, Y. Matsumoto, H. Naramoto, Japan Atomic Energy Agency; Y. Yamauchi, National Institute for Materials Science; S. Sakai, Japan Atomic Energy Agency
Th1100	11:00 a.m.	Computer Simulation of Point Defects In Graphane		<u>I. Yadgarov</u> , V. Stelmakh, Institute of Ion-Plasma and Laser Technologies; A.A. Dzhurakhalov, Univ. of Antwerp
Th1105	11:05 a.m.	A Multi-walled Carbon Nanotube Sheet Based Flexible Conductive Film		<u>D. Jung</u> , M. Han, G.S. Lee, The Univ. of Texas at Dallas
Th1110	11:10 a.m.	A Multi-walled Carbon Nanotube Sheet Based Infrared Thermal Detector		<u>M. Han</u> , D. Jung, G.S. Lee, The Univ. of Texas at Dallas
Th1115	11:15 a.m.	Tuning the Oxidation States and Crystallinity of Copper Oxide Nanofibers by Calcination		<u>J. Park</u> , S. Koh, S. Seo, Y. Kang, Pukyong National Univ.
Th1120	11:20 a.m.	P-Type Conductivity in $MoS_2$ and $WS_2$ by Nb doping		<u>E.W. Lee II</u> , M.R.Laskar, D.N. Nath, L. Ma, C.H. Lee, T. Kent, Z. Yang, The Ohio State Univ.; R. Mishra, M.A. Roldan, JC. Idrobo, S.T. Pantelides, S.J. Pennycook, Oak Ridge National Lab; R. Myers, Y. Wu, S. Rajan, The Ohio State Univ.
Th1125	11:25 a.m.	Epitaxial Co-deposition Growth of CaGe2 Films by Molecular Beam Epitaxy for Large Area Germanane		I. Pinchuk, The Ohio State Univ.; P. Odenthal, Univ. of California, Riverside; A. Ahmed, J. Goldberger, <u>R. Kawakami</u> , The Ohio State Univ.
Th1130	11:30 a.m.	Poster Viewing		
Th1200	12:00 p.m.	Conference Ends	L	

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# Sunday

- Su1400 Registration
- Su1455 Welcome Remarks
- Su1500 Sunday Afternoon Session: Topological Insulators
- Su1705 Poster Setup
- Su1730 Welcome Reception
- Su1930 Sunday Evening Session: Oxides I

# **Topological Insulators**

## Direct measurement of surface transport on a topological insulator

# Philip Hofmann

# Department of Physics and Astronomy, Aarhus University

The so-called topological insulators are well-known, off-the-shelf materials, but they have a previously overlooked and profound "topological" property that forces their surfaces and edges to be metallic, in contrast to the insulating bulk. Moreover, the existence of the one-dimensional (two-dimensional) metal at the edge (surface) of a topological insulator was shown to be inherently robust against disturbances, and to possess special transport properties linked to the electron's spin, leading to many exciting predictions for new physics and potential applications.

These properties suggest that the electronic transport in these materials is dominated by the surfaces states and this would also be an essential condition for exploiting the surface states' unique transport properties. Alas, due to the high remaining bulk conductivity, surface contributions to transport have so-far only been singled out indirectly via quantum oscillations, or for devices based on gated and doped topological insulator thin films, a situation in which the surface carrier mobility could be limited by defect and interface scattering. Here we present the first direct measurement of surface-dominated conduction on an atomically clean surface of bulk-insulating Bi<sub>2</sub>Te<sub>2</sub>Se. Using nano-scale four point setups with variable contact distance, we show that the transport at 30 K is two-dimensional rather than three-dimensional and by combining these measurements with angle-resolved photoemission results from the same crystals, we find a surface state mobility of 390(30) cm<sup>2</sup>/(Vs) at 30 K and a carrier concentration of 8.71x10<sup>12</sup> cm<sup>-2</sup>.

# Mapping the Spin texture of topological insulators

Alessandra Lanzara<sup>1,2</sup>

<sup>1</sup>Physics Department, University of California, Berkeley, USA <sup>2</sup>Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley USA

The helical spin texture of surface electrons in topological insulator has attracted a great deal of interest in the past few years. Although this texture was predicted with the discovery of topological insulators and experimentally confirmed in in few points in the momentum space, its full experimental verification has been non trivial because of the low efficiency of spin resolved experiments.

In this talk I will present new results<sup>1,2</sup>, obtained by using an innovative ultra-high efficiency spin-resolved photoemission instrument<sup>3</sup>, which provide a complete map of the spin texture in a Bi2Se3 topological insulator. Moreover we show that the spin texture of photoelectrons can be fully manipulated by light, paving the way of use of these materials for spintronics applications.

**1.**"Photoelectron spin-flipping and texture manipulation in a topological insulator." C. Jozwiak, et al. *Nature Physics* **9**, 293 (2013)

**2.** "Widespread spin polarization effects in photoemission from topological insulators." C. Jozwiak, et al. *Phys. Rev. B* **84**, 165113 (2011)

**3.** "A high-efficiency spin-resolved photoemission spectrometer combining time-of-flight spectroscopy with exchange-scattering polarimetry." C. Jozwiak et al. *Rev. Sci. Instrum.* 81, 053904 (2010)

#### Interfacing 3D Topological Insulators with Ferromagnetism and Superconductivity

Anthony Richardella, Abhinav Kandala, Joon Sue Lee, Duming Zhang<sup>\*</sup>, Thomas Flanagan, Nitin Samarth, Wenqing Dai, Qi Li,

Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802, USA Su-Yang Xu, M. Zahid Hasan,

Joseph Henry Laboratory, Department of Physics, Princeton University, Princeton, New Jersey 08544, USA Fangcheng Chou,

Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan John Heron, Darrell Schlom

Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853, USA

\*Current address: Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA.

Topological Insulators (TI) are a novel class of materials that are insulating/semiconducting in their bulk but have spin-polarized, conducting states with Dirac-like dispersion on their surfaces. Coupling these surface states with materials that break symmetries, such as ferromagnets or superconductors, is predicted to lead to a host of exotic effects.<sup>1</sup> Among these is the recently observed quantum anomalous Hall effect (QAHE) in Cr doped (BiSb)<sub>2</sub>Te<sub>3</sub>.<sup>2</sup> Similarly, proximity induced superconductivity in the surface states are expected to lead to realizations of Majorana fermions. To test these predictions, we have used molecular beam epitaxy to synthesize a variety of heterostructures that interface TIs with ferromagnetism and superconductivity. Samples were characterized by spin- and angle-resolved photoemission (ARPES), x-ray magnetic circular dichroism, high resolution transmission electron microscopy, SQUID magnetometry, polarized neutron reflectivity, ferromagnetic resonance, point contact Andreev reflection and magneto-transport. Angle- and spin- resolved photoemission spectroscopy in Mn-doped Bi<sub>2</sub>Se<sub>3</sub> revealed that breaking time reversal symmetry opens a gap at the Dirac point accompanied by the development of a hedgehog spin texture.<sup>3</sup> This is accompanied by a crossover from weak anti-localization to weak localization in magneto-transport.<sup>4</sup> TI heterostructures with insulating magnetic layers have been used to study the coupling to the surface states while varying the position of the Fermi energy across the Dirac point using either top gating or back gating with SrTiO<sub>3</sub> substrates.<sup>5</sup> Simultaneously, we have been able to measure the superconducting proximity effect in Bi<sub>2</sub>Se<sub>3</sub>/NbSe<sub>2</sub> heterostructures which indicates pairing occurs in the surface states.<sup>6</sup> Possibilities for functional TI devices based on these structures are discussed. This work is funded by ARO-MURI, ONR, DARPA and SRC.

- 1. M. Z. Hasan, C. L. Kane, Rev. Mod. Phys. **82**, 3045 (2010).
- 2. C.-Z.Chang, et al., Science 340, 167 (2013).
- 3. S.-Y. Xu, et al., Nature Physics 8, 616 (2012).
- D. Zhang *et al.*, Phys. Rev. B 86, 205127 (2012).
- 5. A. Kandala et al., Appl. Phys. Lett. (accepted).
- 6. S.-Y. Xu et al., submitted.



Figure 1: a) ARPES of Mn- $Bi_2Se_3$  showing spin texture. b) AHE in Cr- $(BiSb)_2Te_3$ . c) Gating across the Dirac point in  $(BiSb)_2Te_2Se/GaMnAs$  heterostructures. d) BTK fitting of point contact spectroscopy of  $Bi_2Se_3/NbSe_2$ .

### Unusual surface termination of the 3D Topological Insulator Bi<sub>2</sub>Se<sub>3</sub>

A.S. Hewitt<sup>1</sup>, J. Wang<sup>1</sup>, J. Boltersdorf<sup>2</sup>, T. Guan<sup>1</sup>, P. Maggard<sup>2</sup>, D.B. Dougherty<sup>1</sup>
 <sup>1</sup> Department of Physics, North Carolina State University, Raleigh, NC
 <sup>2</sup>Department of Chemistry, North Carolina State University, Raleigh, NC

The strong three-dimensional topological insulator (TI) Bi<sub>2</sub>Se<sub>3</sub> is of great research interest to the spintronics community. TIs are a class of materials which have a topological invariant associated with their 3D band structure that results in unique "topological surface states" (TSS) [1]. Experimental characterization of the surface of Bi<sub>2</sub>Se<sub>3</sub> has revealed enormous complexity including the coexistence of the TSS with both bulk bands [2] and with more traditional 2D quantum well states [3]. Most surprisingly, recent ion scattering experiments have shown evidence for Bi bilayer-terminated surface, challenging the common assumption that mechanical cleavage of Bi<sub>2</sub>Se<sub>3</sub> results in a bulk-like Se surface termination [4].

We have observed the occurrence of both metallic Bi and Se terminated surfaces on Bi<sub>2</sub>Se<sub>3</sub> single crystals grown in-house by established techniques and purchased from commercial suppliers. X-ray Photoelectron Spectroscopy of Bi 4f core levels with an extra low binding energy component indicative of the presence of a Bi-Bi bond (Figure 1). This occurs in approximately 50% of samples cleaved in air and is observed by ultraviolet photoelectron spectroscopy to result in unusual valence band electronic structure. These observations further point out the complexity of the "simplest" 3D TI particularly in the context of understanding surface transport for samples cleaved from single crystals.

Hasan and Kane *Rev. Mod. Phys.* 82, 3045 (2010)
 Analytis et al. *Phys. Rev. B* 81, 205407 (2011)
 Bahramy et al., *Nature Comm.* 3, 1159 (2012)

[4]He et al., Phys. Rev. Lett., 110, 156101 (2013)



Figure 1. Example XPS spectrum of Bi 4f core levels showing a low binding energy component attributed to metallic Bi at the surface of cleaved  $Bi_2Se_3$ . (Mg K $\alpha$  X-ray source).

Probing spin orbit interaction in InAs/InGaAs gate-defined quantum point contact

J. Shabani<sup>1</sup>, T. McFadden<sup>2</sup>, A. Liaghat<sup>3</sup>, Y. Kim<sup>3</sup>, R. M. Lutchyn<sup>4</sup>, and C. J. Palmstrøm<sup>1,2,5</sup>

[1] California NanoSystems Institute, University of California, Santa Barbara
 [2] Department of Electrical and Computer Engineering, University of California, Santa Barbara
 [3] Department of Physics, University of California, Santa Barbara
 [4] Microsoft Research, Station Q, University of California, Santa Barbara
 [5] Materials Department, University of California, Santa Barbara

Control and manipulation of the spin-orbit interaction in materials that lack inversion symmetry is considered the basis for novel spintronic devices. These devices utilize the fact that the inversion asymmetry of the confining potential can be tuned with electric field applied via external gates. This structural inversion asymmetry, along with the bulk inversion asymmetry of the zinc-blende structure, leads to a lifting of the spin degeneracy of the energy bands even in the absence of an applied magnetic field. It is therefore important to study spin orbit interactions and the ability control their influence on the electron transport in semiconductor channels

Epitaxially grown heterostructures containing InAs layers are trusted to be a suitable platform to study spin orbit interaction. We have grown InGaAs-InAs-InGaAs (x=0.75) quantum wells bounded on both sides by undoped InAIAs (x=0.75) barrier layers using molecular beam epitaxy machine. In this heterostructure, the electron wavefunction mainly resides in the InAs layer, which has strong spin orbit interaction. We probe the strength of this interaction in two dimensions by analyzing the weak antilocalization peak within lordanskii, Lyanda-Geller and Pikus (ILP) model. Additional confinement is introduced by fabrication of a quantum point contact (QPC) to form a quasi 1D channel in the middle of a Hall bar. We study spin orbit interaction by measuring the magnetoconductance of the Hall bar as a function of QPC gate bias. We find an increase in Rashba parameter when the constriction is formed. By directly measuring the width of the channel (from the onset of Shubnikov de Haas oscillations) we relate this enhancement to the confined potential. As the channel is further pinched off, we find a geometrical suppression of spin orbit signal in the constriction when the length of channel becomes comparable to the spin orbit length. We also observe universal conductance fluctuations when the conductance of the channel is about e^2/h and examine their amplitudes as a function of channel widths.

Part of this work is funded by Microsoft Station Q, University of California, Santa Barbara. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490, the State of Florida, and the U.S. Department of Energy.



### Two-dimensional electron gases at oxide interfaces

#### **Susanne Stemmer**

Materials Department, University of California, Santa Barbara

Two-dimensional electron gases (2DEGs) at interfaces between two insulating oxides have attracted significant attention because they can exhibit unique properties, such as strong electron correlations, superconductivity and magnetism. In this presentation, we will discuss emergent properties at interfaces and quantum wells formed between Mott insulating rare earth titanates (SmTiO<sub>3</sub> and GdTiO<sub>3</sub>), and the band insulator SrTiO<sub>3</sub>. Such interfaces exhibit a high-density 2DEG, of approximately  $\frac{1}{2}$  electron per surface unit cell, providing ~  $3 \times 10^{14}$  cm<sup>-2</sup> mobile charge per interface. We will start with an overview of the basic properties of these materials, their physics, and recent advances in controlling growth and interface properties. We show that the subband structure can be probed using quantum oscillations and resonant tunneling studies. We investigate electron correlation effects due to short-range Coulomb interactions and metal-insulator transitions in narrow quantum wells bound by two such interfaces, and the role of coupling to the lattice.

This work was performed in collaboration with Clayton Jackson, Santosh Raghavan, Pouya Moetakef, Jack Zhang, Jinwoo Hwang, Evgeny Mikheev, Adam Kajdos, Leon Balents, and Jim Allen.

#### Integration of ferroelectric BaTiO<sub>3</sub> on Ge (001)

Kurt D. Fredrickson<sup>1</sup>, Patrick Ponath<sup>1</sup>, Agham B. Posadas<sup>1</sup>, Martha R. McCartney<sup>2</sup>, David J. Smith<sup>2</sup> and Alexander A. Demkov<sup>1</sup>

<sup>1</sup>Department of Physics, The University of Texas at Austin, Austin, Texas 78712, USA <sup>2</sup>Department of Physics, Arizona State University, Tempe, Arizona 85287, USA

#### Abstract

BaTiO<sub>3</sub> (BTO) is a ferroelectric oxide that can be grown on Si and Ge substrates with the use of an appropriate buffer. The interest in putting BTO on semiconductors stems from the potential for realizing a ferroelectric field effect transistor (FeFET), which is advantageous over regular transistors; the state of the transistor is nonvolatile and does not require any standby power<sup>1,2</sup>. However, one of the key requirements for achieving this is that the ferroelectric must be single crystalline with a single domain over the entire size of the device. Typical deposition techniques that can achieve single crystalline BTO are normally done at temperatures above 600°C, which is higher than the ferroelectric transition temperature of the material. This means that the BTO is grown in a paraelectric state and becomes ferroelectric during the cool down process. Achieving a single domain state requires that the lattice and thermal expansion matching be favorable. The formation of an epitaxial interface between BTO on Ge is the focus of our study.



Figure 1. Annular-dark-field electron micrograph showing abrupt nature of BTO/Ge interface

N-type Sb-doped (001)-oriented Ge substrates (0.029-0.054  $\Omega$ cm) were used in this study. The substrate is first degreased, then wet-etched and oxidized using a combination of hydrochloric acid (HCl) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The substrate is then outgassed in vacuum at 120°C and exposed to oxygen plasma in the MBE growth chamber. A subsequent annealing in vacuum removes the oxide layer and results in a clean 2x1 reconstruction<sup>3</sup>. To minimize the oxidation of Ge during the initial BTO deposition, <sup>1</sup>/<sub>2</sub> monolayer (ML) of Sr was first deposited at 600 °C on the clean germanium surface. On top of this layer, an initial two unit cells of BTO are deposited using alternate monolayer dosing with the BaO layer first in the presence of  $1.5 \times 10^{-7}$  Torr molecular oxygen at a temperature of 600°C. The oxygen pressure is then increased to  $6.0 \times 10^{-7}$  Torr and an additional three unit cells of BTO are deposited. Finally, the oxygen pressure is increased to  $5.0 \times 10^{-6}$  Torr and additional BTO is deposited to the desired thickness. The substrate temperature is kept constant throughout the entire growth process. After growth, the BTO film is cooled down to room temperature in oxygen at a rate of 5°C/min.

An aberration-corrected, high-angle, annular-dark-field electron micrograph of BTO on Ge is shown in Fig. 1. The atomically sharp interface between the two materials is evident. An x-ray diffraction symmetric  $2\theta$ - $\omega$  scan of a 40-nm film of BTO on germanium reveals an out of plane lattice constant of 3.97 Å. This indicates that the BTO film is *a*-axis (100) oriented, implying that the ferroelectric polarization lies in the plane of the BTO film. The valence band offset (VBO) between a thin (five unit cells) BTO layer and Ge was measured using x-ray photoelectron spectroscopy and was found to be  $2.7\pm0.1$  eV (Figure 2). Adding the experimentally measured band gaps of Ge and BTO gives us a conduction band offset (CBO) of -0.2\pm0.1 eV, with the conduction band of Ge being higher than that of BTO.



Figure 2. Measured valence band offsets for the Ge/BTO interface.

Using density functional theory (DFT) in the local density approximation, we examine multiple interfaces between BTO and Ge, and calculate the band offsets for each of them. We consider variations in the polarization of BTO, including inplane (in the a- and b- directions), out-of-plane (in the cdirection), and un-polarized configurations. Depending on the interface, either in-plane or out-of-plane polarization is preferred; for the non-preferred polarizations, we set them by hand. To calculate the VBO we use the reference potential method<sup>4</sup>. As the band gaps calculated by DFT are typically smaller than measured in experiment, we add the experimentally measured band gap to the calculated valence band top to place the conduction band edge for our interface. Due to the underestimated band gap of BTO, in certain cases there is an unphysical charging of the oxide due to its

calculated conduction band being incorrectly placed below the valence band of Ge. In these cases, we add an on-site Hubbard correction U of 8.0 eV on the Ti d-states in order to open the gap and prevent this unphysical charging<sup>5</sup>.



Figure 3. The Ge-O bonded interface.

We find that the band offset depends strongly on the chemical nature of the interface and the polarization state of BTO. Depending on these factors, the VBO ranges from 0.73 to 2.50 eV, and the CBO ranges from 0.03 to 1.80 eV. For the Ge-O bonded interface shown in Figure 3, we find that, for in-plane polarized BTO, the VBO is 2.50 eV and the CBO is 0.03 eV. These values match well with the experimentally measured VBO of 2.7 and CBO of -0.2 eV. This interface has a  $\frac{1}{2}$  monolayer of Sr and the interfacial BTO begins with BaO, as - expected from experiment, so we - have identified a possible

interfacial model of BTO epitaxially grown on Ge. For comparison, using the Schottky limit<sup>6</sup> and experimentally measured electron affinities of 3.9 eV for BTO and 4.0 eV for Ge gives us a 2.4 eV VBO and a -0.1 eV CBO. That the offsets are quite close to the Schottky limit suggests that there is only a very small shift in the energy of the band offsets due to an interfacial dipole.

In conclusion, we have prepared epitaxial BTO on Ge using a  $\frac{1}{2}$  ML Sr Zintl buffer<sup>7</sup>, polarized in-plane. The VBO for this configuration is measured to be 2.7 eV, matching well with the theoretical value of 2.5 eV for the in-plane polarized BTO with  $\frac{1}{2}$  ML Sr and BaO layer first. The agreement between the calculated and measured VBOs confirm the high degree of control MBE growth has over the formation of the interface. Though in-plane polarization is not desirable in a FeFET, the material is very promising for microwave device applocations<sup>8</sup>.

<sup>&</sup>lt;sup>1</sup> M. Dawber, K.M. Rabe, and J.F. Scott, Rev. Mod. Phys. 77, 1083 (2005).

<sup>&</sup>lt;sup>2</sup> J.F. Scott, Ferroelectrics **183**, 51 (1996).

<sup>&</sup>lt;sup>3</sup> P. Ponath, A.B. Posadas, R.H. Hatch and A.A. Demkov, J. Vac. Sci. Technol. B **31**, 031201 (2013).

<sup>&</sup>lt;sup>4</sup> L. Kleinman, Phys. Rev. B 24, 7412 (1981).

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# Electric field induced metallization of correlated electron oxides

## Stuart S.P. Parkin

IBM Research – Almaden, 650 Harry Road, San Jose, California 95120-609, USA, <u>stuart.parkin@us.ibm.com</u> or <u>stuart.parkin@icloud.com</u>

The electric field induced metallization of insulating oxides is a powerful means of exploring and creating novel electronic states. Recently large internal electric fields from polar surfaces have been used to create emergent metallic, superconducting and magnetic states at interfaces between two insulating oxides. However, the origin of the metallicity is a subject of considerable debate, especially as to whether charged carriers are induced electrostatically. We show that by placing various oxide surfaces and thin films in contact with charged fluids these nominally insulating materials can be transformed into metallic conductors and that the mechanism is rather due to the flow of ionic currents of oxygen to and fro between the oxide surface and the liquid<sup>1-3</sup>. We discuss, in particular, the electrolyte gating of epitaxial films of vanadium dioxide  $(VO_2)$ . VO<sub>2</sub> exhibits a transition from an insulating to a metallic state above a metalinsulator transition temperature, T<sub>MIT</sub>, that depends on strain induced in the film by epitaxy with underlayers and/or the substrate material and crystal orientation<sup>4</sup>. Using in-situ gating we use x-ray diffraction to show that the out-of-plane lattice constant can be reversibly changed by more than 3.5% using ionic liquid gating. The possibility of novel, highly energy efficient "liquid" electronics is discussed.

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# Monday

Mo0730 Registration and Continental Breakfast Monday Morning Session: Semiconductors I Mo0830 Coffee Break and Poster Viewing Mo0940 Monday Morning Session: Mo1100 **Energy Storage and Generation I** Mo1150 Lunch and Poster Viewing Monday Afternoon Session: Mo1400 Spintronics and Spin Transport Mo1540 Coffee Break and Poster Viewing Mo1610 Monday Afternoon Session: Graphene Mo1800 Dinner
## **Semiconductors I**

### **Design and Applications of GaN Tunnel Junctions**

Siddharth Rajan<sup>a</sup>, Sriram Krishnamoorthy<sup>a</sup>, and Fatih Akyol<sup>a</sup> <sup>a</sup> Electrical and Computer Engineering, The Ohio State University, USA, rajan@ece.osu.edu.

We report on the demonstration of the lowest resistance III-Nitride inter-band tunnel junctions (TJ) and the potential of a new class of GaN optoel ectronic devices based on tunneling. Tunnel junctions can be used to inject holes into p-type GaN, and to cascade multiple active regions for multi-active region LEDs and solar cells. While the large band gap of GaN and AlGaN makes tunneling inefficient, we show two approaches using polarization [1-3] and midgap states [4] that can enhance tunneling by several orders of magnitude. We discuss device applications of these tunnel junctions junctions, and show that they could provide a solution to the long-standing challenge of efficiency droop in solid state lighting, and enable a new class of tunnel-based optoelectronic devices in the ultra-violet wavelength regime.

Polarization engineering [1-3] can be used to create large band-bending over nanoscale lengths to enhance tunneling by several orders of magnitude, overcoming fundamental limits of homojunction P-N tunnel diodes. Such tunnel junctions were incorporated in a GaN P- N junction as a n-type tunneling contact to p-GaN. 4 nm of 25% InGaN inserted between degenerately doped GaN aligns the conduction and valence bands of GaN, owing to the high polar ization charge dipole at the GaN/InGaN interface, resulting in a high current density even close to zero bias across the tunnel junction. As the P-N junction is forward biased, the TJ gets reverse biased, tunne l injecting holes into p-GaN. The tunneling resistivity is extracted by subtracting the contact and series resistances from the overall forward bias resistance to be  $1.2 \times 10^{-4} \cdot \text{ cm}^2$ . This is the lowest reported tunneling resistivity in GaN.

The second approach to enhance tunneling in III nitrides is to introduce m id gap states in a G aN  $p^+ n^+$  junction, to reduce the tunneling ba rrier width. GdN nano-islands embedded in heavily doped GaN P-N junctions were used to inject holes into a GaN P-N junction. Tunnel junction specific contact resistivity of GdN-based tunnel junction has been de-embedded fr om the overall device resistance to be 1. 3 X 10<sup>-3</sup> • cm<sup>2</sup> [4]. Our work represents the lowest tunneling resistance achieved in GaN. Low resistance tunnel junctions were also integrated into commercial bl ue LED (450 nm) structures enabling p-contact free LEDs. Excellent current spreading and enhanced light output power was observed in the TJ LED devices. The voltage drop in the T J LED devices are the low est reported till date (4 V @ 20 m A, 5.4 V @ 100mA).

Tunnel junctions can be used to achieve carrier regeneration in cascaded p-n junction/LED structures. Multiple (n=1,2,4) pn junctions were stacked epitaxially using TJ interconnects and the turn-on voltage was found to scale with the num ber of junctions. This low resistance TJ interconnects enable a cascaded LED device structure. Such a device can be operated in the low current regime wherein there are minimal or no efficiency droop effects, while still achieving high brightness due to multiple photon emission from the multiple LEDs that are cascaded. Calculations i ndicate enhanced wall plug efficiency and lowered joule heating in high brightness cascaded LEDs when the tunnel junctions are efficient [5].

In conclusion, state-of-the-art polarization engineered GaN/InGaN/GaN tunnel junctions  $(1.2 \times 10^{-4} \cdot cm^2)$  and GdN nanoislands embedde d tunnel junctions  $(1.3 \times 10^{-3} \cdot cm^2)$  have been demonstrated. Tunnel junctions were also integrated with commercial blue LED resulting in a p -contact free LED. Record low voltage drop is reported for TJ LED ( 450 nm) devices. Cascaded p-n junctions have been demonstrated. The proposed cascaded LED structure holds promise in circumventing the efficiency droop bottleneck. The authors acknowledge funding from the NSF (DMR-1106177) and the ONR DATE MURI program (Program manager: Paul Maki). We also thank Prof. James Speck, SSLEC, UCSB, for providing LED wafers used in this work.

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### III-V Nitride Heterojunctions by Atomic Layer Epitaxy

C.R. Eddy, Jr.<sup>1</sup>, N. Nepal<sup>2</sup>, T.J. Anderson<sup>1</sup>, A.D. Koehler<sup>1</sup>, M.A. Mastro<sup>1</sup> and J.K. Hite<sup>1</sup> <sup>1</sup>U.S. Naval Research Laboratory, Washington DC 20375 <sup>2</sup>Sotera Defense Solutions, 2200 Defense Hwy Suite 405, Crofton, MD 21114

For the past 25 years, compound semiconductors comprised of elements from group IIIB of the periodic table and nitrogen (III-N) have attracted sustained, high-level research focus. This family of quarternary nitrides aluminum indium gallium nitride (AlInGaN), and soon to be expanded to quinternary with the addition of boron (BAlInGaN), offers significant potential based not only on the properties of the binary semiconductors (associated with their non-centrosymmetric crystal structure), but also on the ability to employ bandgap engineering methods for advanced devices using heterostructures of binaries, ternaries and quarternaries. Such heterostructures are at the core of several modern III-N commercial device technologies including the light emitting diodes (LEDs) that are the basis of white light LEDs, blue laser diodes and high power and high frequency transistors. These latter applications involve evermore-complex barrier structures to ensure high on-state performance in normally-off devices. These barrier structures often involve several very thin semiconductor layers and, more recently, a dielectric at the top to reduce gate leakage currents during operation. Such structures begin to challenge the abilities of conventional growth approaches. Here we present the first developments on heterojunctions grown by atomic layer epitaxy.

Atomic layer epitaxy (ALE) has recently been shown [1,2] to be a promising method for growing ultra-thin binary (InN, AlN, GaN) and ternary (AlGaN, InAlN) nitride layers with good crystallinity under conditions that allow the elimination of miscibility gaps that plague conventional growth at higher temperatures. This is made possible by the non-equilibrium growth process inherent in atomic layer epitaxy that is comprised of two surface-limited half-reactions separated by a purge of the growth chamber. In this manner, films are grown "layer-by-layer" with the group III atom first, then the group V atom second and so on.

Here we report on AlGaN/GaN and InAlN/GaN heterojuctions grown by ALE with and without a high-k dielectric cap. Ternaries are accomplished through a ratio of pulse sequences for the group III precursors and x-ray photoelectron spectroscopy (chemical) and optical reflectance measurements (bandgap) show the ability to cover the entire stoichiometry range for both ternaries. AFM measurements show that the morphology of the ALE heterostructures retains or improves on that of the GaN template substrate. Al<sub>0.83</sub>In<sub>0.17</sub>N/GaN and Al<sub>0.27</sub>Ga<sub>0.73</sub>N/GaN heterostructures have been synthesized by ALE and characterized by Hall Effect measurements to show clear indication of a two-dimensional electron gas (2DEG) with the latter demonstrating a density in the low  $10^{12}$  cm<sup>-2</sup> range and a carrier mobility in excess of 1000 cm<sup>2</sup>/V-s. This first-ever demonstration also highlights key issues that remain to be addressed, namely impurity control (carbon and oxygen). Similar characterizations of MISHEMTs with a Al<sub>2</sub>O<sub>3</sub>/Al<sub>0.27</sub>Ga<sub>0.73</sub>N/GaN structure will be presented.

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### Abstract PCSI-41

### Metamorphic Growth of InSb Quantum Wells on (110) Oriented GaAs

Adrian Podpirka\*, Mark E. Twigg, Joseph G. Tischler, Richard Magno and Brian R. Bennett U.S. Naval Research Laboratory, 4555 Overlook Ave. SW; Washington, D.C. 20375

\*corresponding author/presenter: adrian.podpirka.ctr@nrl.navy.mil

Growth of III-V compound semiconductors by molecular beam epitaxy (MBE) has traditionally focused on (100) substrates due to the wide range of growth conditions which result in good epitaxial quality arising from the polar nature of the surface. Despite being the natural cleavage plane in the zinc-blende structure, growth on the nonpolar (110) surface has often been overlooked due to the difficulty in growing smooth epitaxial layers. Growth on the (110) surface would allow the development of new devices based on novel physical phenomena associated with strong spin orbital coupling with applications to Majorana Fermions and spin based devices due to the electron spin relaxation times of several nanoseconds at room temperature.<sup>1,2,3</sup> In this work, we report on a three step buffer layer preparation (shown schematically in supporting Figure 1A) for metamorphic growth of the InSb quantum well on the (110) GaAs surface. At each surface, conditions were optimized in order to produce the smoothest surface possible. By varying growth rates, group V/III flux, substrate temperature, and the addition of in situ annealing, we are able to achieve a high-quality metamorphic buffer layer of In<sub>0.85</sub>Al<sub>0.15</sub>Sb. Atomic force microscopy and cross sectional TEM (supporting Figure 1B) were used in order to analyze surface morphology, dislocation formation and filtering at the interfaces of the buffer layers. Optimized growth conditions resulted in a surface roughness of 2.1 nm, capable of accommodating a 13 nm InSb QW (supporting Figure 2). Electron confinement in the quantum well was confirmed by photoluminescence measurements. These results are an important step toward realizing antimonide-based electronic and spin devices utilizing novel physical phenomena of the (110) orientation.

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### Dynamic Strain Measurements of Ge on Si using Spectroscopic Ellipsometry

### Ayana Ghosh,<sup>1</sup> Nalin Fernando,<sup>2</sup> Cayla M. Nelson,<sup>2</sup> Amber A. Medina,<sup>2</sup> Seth Chi Xu,<sup>3</sup> Jose Menendez,<sup>3</sup> John Kouvetakis,<sup>4</sup> Stefan Zollner<sup>2</sup>

<sup>1</sup>Department of Physics, University of Michigan, Flint, MI

<sup>2</sup>Department of Physics, New Mexico State University, Las Cruces, NM

<sup>3</sup>Department of Physics, Arizona State University, Tempe, AZ

<sup>4</sup>Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ

Strain is an important parameter in semiconductor band engineering because it modifies the electronic band structure. Strain can be static or dynamic (i.e., tunable by an external stimulus). In the present work, we estimate the dynamic strain of a Ge layer grown on a Si (001) substrate, which can be modified by temperature because of the difference in thermal expansion coefficients between Si and Ge. At the growth temperature (at 700 K), our Ge layer grown by CVD is almost completely relaxed. As temperature decreases, the Ge layer experiences a tensile biaxial stress, since bulk Ge shrinks more than Si as T decreases. This effect can be modeled since the thermal coefficients of Si and Ge are known very precisely (Robert Reeber, Materials Chemistry and Physics, 1996). We calculate in-plane tensile strain values of 0.12% at 300 K or 0.19% at 77K for our Ge on Si films, which compares very well with an in-plane strain of 0.11% derived from shifts of the Ge (004) lattice reflection at 300 K. We can also determine the strain in our films through precision measurements of the E<sub>1</sub> and E<sub>1</sub>+ $\Delta_1$  band gaps using spectroscopic ellipsometry. We find shifts in these gaps for Ge on Si up to 20 meV (comparing spectra at 77 and 700 K), consistent with the known deformation potentials for the E<sub>1</sub> gaps.

### Micro reflectance difference spectroscopy of Si3N4/n-Si (111), GaP/Si/GaP (100) $4^{\circ} \rightarrow$ (111) and GaP/AsGaP/Si (100) structures

R. Herrera-Jasso<sup>1</sup>\*, L. F. Lastras-Martínez<sup>1</sup>, R. E. Balderas Navarro<sup>1</sup>, A. Lastras-Martínez<sup>1</sup>, N.A. Ulloa Castillo<sup>1</sup>, Sergey Nikishin<sup>2</sup>, Angie C. Lin<sup>3</sup>, J. S. Harris<sup>3</sup> and M. M. Fejer<sup>4</sup>

1.- Instituto de Investigación en Comunicación Óptica, Universidad Autónoma de San Luis Potosí,

Álvaro Obregón 64, 78000 San Luis Potosí, SLP, México

2.-Dept. ECE, Texas Tech. University

3. - Solid State and Photonics Laboratory, Stanford University, Stanford, California 94305 U.S.A.
4. - E.L. Ginzton Laboratory, Stanford University, Stanford, California 94305 U.S.A.

\* rafaelherreraj84@gmail.com

#### Abstract

Reflectance Differential Spectroscopy (RDS) is a useful optical tool for the control and monitoring of growth of semiconductor materials and devices by Molecular Beam Epitaxy MBE [1], due to its high sensitivity to different surface conditions [2, 3, 4]. The development of the RDS as an optical probe for the characterization of surfaces and interfaces has suggested its extension to a microscopic scale ( $\mu$ -RD) as it could further increase the potential of the technique. In particular, the characterization of the strain induced by lineal defects [5] and novel III-V structures grown on Si. Microscopic resolution is possible using a charge coupled device (CCD) instead of a detector (phototube or photodiode) as in the existing experimental arrangements. Illuminating the simple with a spot using a CCD and a microscope, it is possible to spatially resolve the RDS signal to the area on the order of 3  $\mu$ m x 3  $\mu$ m. Here, we report on RDS spectroscopy, along with both  $\mu$ -RD and reflectance (R) spectra of semiconductor III/V and IV structures at photon energies comprising E<sub>0</sub>, E<sub>1</sub> and E<sub>1</sub> +  $\Delta_1$  critical points. We focus on Si3N4/n-Si (111), GaP/Si/GaP (100) 4°  $\rightarrow$  (111), GaP/AsGaP/Si (100). Also GaSb (001) substrates with preferential mechanical polishing along [110] and [110] directions and heterostructures formed by Gap/AlGaP (001) grown on vicinal Si (100) 4°  $\rightarrow$  (110) and GaP (100) 4°  $\rightarrow$  (111) substrates grown by MBE.

#### Results



Fig 1. - Open black circles are the RDS spectra and solid lines are the fits to RDS for the samples (a) GaP/AsGaP/Si (100)  $4^{\circ} \rightarrow (110)$  and (b) GaP/AsGaP/Si (100)  $6^{\circ} \rightarrow (110)$ .



Fig 2. -  $\mu$ -RD spectra of different areas of the Si3N4/n-Si (111). Each spectra correspond to an area of 64 x 64  $\mu$ m<sup>2</sup>. Note that the amplitude of the spectra depends strongly on the specific surface area considered.



Fig 3. - Density of lineal defects along the surface of GaSb (001) determined by using the CCD-based spectrometer [5]. The spatial resolution is 24  $\mu$ m. (a) GaSb surface after rubbing along [110] direction. (b) GaSb surface after rubbing along [110] direction.

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### Different orientation of AgGaTe<sub>2</sub> and AgAlTe<sub>2</sub> layers grown on a-plane sapphire substrates by a closed space sublimation method

<u>Ayaka Usui</u><sup>1\*</sup>, Aya Uruno<sup>1</sup>, and Masakazu Kobayashi<sup>1, 2</sup> <sup>1</sup>Department of Electrical Engineering and Bioscience, Waseda University, Tokyo, JAPAN <sup>2</sup>Kagami Memorial Research Institute for Materials Science and Technology, Waseda University, Tokyo, JAPAN \*a-usui@asagi.waseda.jp

Recently, chalcopyrite I-III-VI<sub>2</sub> compound semiconductors have been focused on because of their appropriate properties for fabricating solar cells. Among them, CuInSe<sub>2</sub> has been widely used for solar cells. Te based compounds, however, have not been extensively studied. Among them, AgGaTe<sub>2</sub> has a relatively suitable bandgap for the fabrication of solar cells (around 1.3 eV) at room temperature, and has been grown on a-plane sapphire substrates by a closed space sublimation (CSS) method [1, 2]. The bandgap value of AgGaTe<sub>2</sub> is slightly lower than the optimum value (around 1.4 eV) for fabricating solar cells. In order to control the bandgap, forming solid solutions of AgAITe<sub>2</sub> (Eg = 2.2 eV) and AgGaTe<sub>2</sub> would be attractive. In this study, AgGaTe<sub>2</sub> and AgAITe<sub>2</sub> layers were grown by the CSS method, and the orientation characteristic of layers grown on a- plane sapphire substrates were studied. The source used was 4N AgGaTe<sub>2</sub> powder and 4N AgAITe<sub>2</sub> powder, and the source temperature during the growth was around 800 °C. The crystallinity of grown layers was compared mainly by theta-2theta profiles of the x-ray diffraction (XRD) measurement.

The XRD spectrum of the AgGaTe<sub>2</sub> starting material (powder) and the grown layer were summarized. The 112 peak was the dominant peak for the starting material, whereas a strong 103 peak along with a 220 peak were observed from the grown layer. The lattice arrangement at the substrate/layer interface was investigated, and parallelograms of the sapphire substrate surface atoms and parallelogram of (103) AgGaTe<sub>2</sub> atoms exhibited about 3.5% of the mismatch. The lattice arrangement mismatch between the a-plane sapphire and (110) AgGaTe<sub>2</sub> could be as low as 7.7%. Based on these lattice arrangements, the film exhibited strong preferences for (103) and (110) orientations [1, 2].

The XRD spectrum of the AgAlTe<sub>2</sub> starting material and the grown layer were also compared. Because both AgGaTe<sub>2</sub> and AgAlTe<sub>2</sub> have the same crystal structure, theoretical peak intensity variations exhibited the similar profile. The XRD spectra of two staring materials also exhibited the similar profile. On the other hand, the grown layer of AgAlTe<sub>2</sub> exhibited a spectrum different from the AgGaTe<sub>2</sub> layer, and a strong peak was observed only at the 112 diffraction. Since (112) is a close packing surface for these materials, (112) orientation was not surprising, but the AgAlTe<sub>2</sub> layer scarcely exhibited other diffraction peaks, indicating very strong orientation to (112). The variation of the substrate/epilayer interface chemistry has resulted in the variation of orientations of those layers.

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### Characterization of Surface Defects on Be Implanted GaSb Caused by Rapid Thermal Annealing

N. Rahimi<sup>1</sup>, A. Aragon<sup>1</sup>, O. S. Romero<sup>1</sup>, T. J. Rotter<sup>1</sup>, T. Busani<sup>1</sup>, Olga Lavrova<sup>1</sup>, G. Balakrishnan<sup>1</sup>, L. F. Lester<sup>2</sup> (1) Center for High Technology Materials, University of New Mexico, 1313 Goddard SE,

Albuquerque, NM 87106, USA.

(2) Virginia Polytechnic Institute and State University, 910 Drillfield Drive, Blacksburg, VA 24061 Tel: (415)-637-2704, Fax: (505)-846-2290, email: nrahimi@unm.edu

GaSb and the family of III-V semiconductor that can be grown on it, are very important for optoelectronic devices in the MWIR and LWIR including - lasers, photodetectors and thermophotovoltaics<sup>1</sup>. The ability to selectively dope areas of such devices is crucial for high performance ohmic contacts and planar p-n junctions.

Ion implantation is an attractive method to achieve local doping profiles. The use of ion implantation in III-V semiconductors and especially in GaSb introduces damage to the crystalline structure, which is difficult to remove<sup>2</sup>. This is due to a limitation on the maximum annealing temperature that can be used for this material imposed by a low incongruent evaporation temperature of 370 °C and a low melting point of 710 °C. To date only a few reports on ion-implantation doping of GaSb have been published and in these publications there is a limited discussion of thermal activation methods and their effect on the device surface quality.

In this study, we performed Be ion implantation to define p-type regions in an n-GaSb substrate. We perform simulations to determine dose and energy according to the intended doping and depth of junction formation. This has a great importance to avoid the amorphization of III -V semiconductors at the near-surface region due to the damage of high energy and dose of ion implantation. The thermal activation of the Be ions is done using a rapid thermal annealing (RTA) process with the intent to both activate the implanted doping as well as to remove some of the damage caused to the crystalline structure from the implantation. The low melting temperature of GaSb can lead to issues with the annealing process since a significant loss of the more volatile lattice constituent, in this case antimony, occurs at the surface. This leads to concentrations of vacancies resulting in the aggregation of group III on the surface. A protective encapsulant is a typical solution to this issue and we have made use of a deposited Si<sub>3</sub>N<sub>4</sub> capping film to protect the underlying GaSb surface.

The investigation of the GaSb based diodes based on the above technique of ion implantation,  $Si_3N_4$  encapsulation and RTA is studied using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). Initially the  $Si_3N_4$  film was chosen to be 850 Å thick as an arbitrary starting point. In this case, the  $Si_3N_4$ /GaSb interface showed out-diffusion of Sb and Ga clusters after annealing due to the formation of pinholes in the  $Si_3N_4$  capping film. This led to degradation of GaSb surface making it unsuitable for use with devices. In order to prevent the creation of pinholes, a new recipe for  $Si_3N_4$  deposition was created and a double-sided, front and back deposition of  $Si_3N_4$  was also tested. Furthermore, the thickness of the  $Si_3N_4$  capping film was increased by 3 times (~2600Å) to offer better protection to the GaSb device. We have been able to determine that a better recovery of the damaged layer and a defect free  $Si_3N_4$ /GaSb interface is obtained when the annealing temperature is at 600°C for 10 s. However increasing annealing temperature above 650°C or annealing time over 60s, initiates great degradation of  $Si_3N_4$ /GaSb interface.

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# Energy Storage and Generation I

### Metal-Insulator-Semiconductor Tunnel Diodes for Efficient Solar Hydrogen Production

Daniel V. Esposito<sup>1</sup>, Igor Levin<sup>1</sup>, Thomas P. Moffat<sup>1</sup> and <u>A. Alec Talin<sup>2,1</sup></u>

<sup>1</sup>National Institute of Standards and Technology 100 Bureau Drive, Gaithersburg, MD 20899 <sup>2</sup>Sandia National Laboratories Livermore, CA 94551-0969

Photoelectrochemical (PEC) water splitting represents a promising route for renewable production of hydrogen, but trade-offs between photoelectrode stability and efficiency have greatly limited the performance of PEC devices. In this work, we employ a metal-insulator-semiconductor (MIS) photoelectrode architecture that allows for stable and efficient water splitting using narrow band gap semiconductors. Substantial improvement in the performance of Si-based MIS photocathodes is demonstrated through a combination of a high-quality thermal SiO<sub>2</sub> layer and the use of bilayer metal catalysts. Scanning probe techniques are used to simultaneously map the photovoltaic and catalytic properties of the MIS surface and reveal the spillover-assisted evolution of hydrogen off of the SiO<sub>2</sub> surface and lateral photovoltage driven minority carrier transport over distances that can exceed 2 cm.<sup>1</sup> The latter finding is explained by the photo- and electrolyte-induced formation of an inversion channel immediately beneath the SiO<sub>2</sub>/Si interface. These findings have important implications for further development of MIS photoelectrodes and offer the possibility of highly efficient PEC water splitting.



Figure 1. Simultaneously-recorded SPCM/SECM images of standard MIS photocathode. a.) Schematic side-view of the SPCM/SECM set-up. b.) Optical image of standard 20/30 nm Pt/Ti collectors on MIS photocathode surface immersed in 0.5 M H<sub>2</sub>SO<sub>4</sub> with dashed lines marking the region mapped in SPCM/SECM measurements. Inset shows a Pt ultramicroelectrode (UME) with effective tip radius of  $\approx 12 \,\mu\text{m}$  and a 532 nm laser beam (23.5 μW) positioned next to a collector. c-d.) SPCM EQE images and e-g.) SECM UME tip current images recorded with the photocathode held at three different applied potentials. In SPCM images, the EQE is lower when the laser beam is positioned directly over the collector because the metal absorbs/reflects a large fraction of the incident light.

1. D. V. Esposito, I. Levin, T. P. Moffat, and A. A Talin, Nature Materials, 12, 562 (2013)

### Efficient and Stable Photoelectrochemical Water Splitting with Metal-Insulator-Semiconductor Photoelectrodes grown by Molecular Beam Epitaxy

Li Ji<sup>1,3</sup>, Martin D. McDaniel<sup>2</sup>, Shijun Wang<sup>3</sup>, Agham B. Posadas<sup>4</sup>, Alexander A. Demkov<sup>4</sup>, John G. Ekerdt<sup>2</sup>, Allen J. Bard<sup>3</sup> and Edward T. Yu<sup>1\*</sup>

<sup>1</sup>Microelectronics Research Center, the University of Texas at Austin 10100 Burnet Road, Building 160, Austin TX 78758

<sup>2</sup>Department of Chemical Engineering, the University of Texas at Austin 200 East Dean Keeton Street, Stop C0400, Austin TX 78712

<sup>3</sup>Center for Electrochemistry, Department of Chemistry and Biochemistry 105 East 24th Street Stop A5300, Austin, TX 78712

> <sup>4</sup>Department of Physics, the University of Texas at Austin 2515 Speedway, Building C1600, Texas 78712

Photoelectrochemical (PEC) water splitting has been proposed for hydrogen production using solar energy<sup>1</sup>. One possible approach is to use a metal-insulator-semiconductor (MIS) structure as the photoelectrode<sup>2</sup>, which has been shown to provide high efficiency and good electrochemical stability. In this structure, the catalytic metal is deposited on oxide-covered semiconductor. The metal serves as a cocatalyst to reduce the required kinetic energy for water splitting and the oxide is used to protect the semiconductor from corrosion but allow photogenerated minority carriers to tunnel between the metal and semiconductor. Since the oxide serves as a tunneling layer, it must be sufficiently thin to allow efficient tunneling, yet thick enough to protect the semiconductor from corrosion. Use of Si as the semiconductor is also desirable due to its relatively low cost and the availability of highly developed processing technology.

In this work, single crystalline SrTiO<sub>3</sub> (STO) thin films were grown on p-type (100) Si wafers by Molecular Beam Epitaxy (MBE) to form a MIS photocathode. As shown in Figure 1, STO provides a small conduction band offset with Si, facilitating tunneling, and the lattice mismatch between (111) STO and (100) Si is very small. The photogenerated electrons in the Si substrate will face a minimal barrier when tunneling through the STO layer hence a high current density could be obtained. For the catalytic metal design, a major problem is adhesion issue between platinum, a widely used catalyst, and STO. We found that Pt will easily come off the STO surface after several minutes' operation. A Ti layer inserted between Pt and STO both provides the adhesion and contributes to performance due to its low work function<sup>2</sup>. In addition, the catalytic metal are structured into arrays of dots structure with 1-400 um diameters. For comparable surface coverage densities, the smallest diameter dots were found to yield the highest fill factors.

The electrochemistry measurement was conducted on a standard CHI 660D potentistat (CH In, Austin TX, USA). 100 mW/cm<sup>2</sup> light was obtained using Xeon Arc Lamp. All experiments were in 0.5M H<sub>2</sub>SO<sub>4</sub> solution. The measured photocurrent density is shown in Figure 2 (a). A 0.4V photovoltage and 30mA/cm<sup>2</sup> were achieved for 4 unit cells (u.c) STO on Si with 30nmTi/20nmPt 1um diameter dots. The light was chopped during the measurement to show the dark current, which is zero. For visible light measurement, all wavelength smaller than 420nm were cut off. The difference between VL and UV-VL arises from the different power density of light. Figure 2 (b) shows linear sweep voltammetry conducted without chopping the light in order to calculate the applied bias photo-to-current efficiency (ABPE). The photocurrent density and bias voltage at maximum power point are 15.9mA/cm<sup>2</sup> and 0.182V, respectively. The calculated ABPE is 2.9%.

Another key property for photoelectrochemical water splitting cells is stability. A 10 hour stability measurement was conducted in  $0.5M H_2SO_4$  with -0.23V vs NHE (0V vs Ag/AgCl) bias. Results in Figure 3 indicated the device showed very good stability, with small variations in photocurrent coming from bubble formation at the sample surface. STO grown on Si by atomic layer deposition (ALD), which yield polycrystalline STO, was found to exhibit poorer stability and photocurrent density than MBE-grown structures. We believe MBE growth yields single crystal STO on Si that improves stability and performance of very thin STO layers compared to that attainable in polycrystalline ALD grown STO layers.

<sup>&</sup>lt;sup>1</sup>A. Fujishima and Kenichi Honda, *Nature* **238**, 37-38 (1972).

<sup>&</sup>lt;sup>2</sup>D. V. Esposito, I. Levin, T. P. Moffat and A. A. Talin, *Nature Materials* 12, 562-568 (2013).

### Mo1145

### Optical properties of Sm doped CeO<sub>2</sub> thin films prepared by liquid solution deposition

K. Mitchell, C. Rodriguez, T. Willett-Gies, Y. Li, and S. Zollner

New Mexico State University, Las Cruces, NM

Cerium(IV) oxide, also known as CeO<sub>2</sub> or ceria, is a transparent (insulating) oxide of the rare earth metal cerium. It is an ionic conductor with applications in fuel cells, as a catalyst, or for photovoltaic water splitting (hydrogen production). Thin films of ceria produced by RF magnetron sputtering on sapphire at 770C have been studied extensively by Arwin's group (S. Guo et al., J. Appl. Phys. 77, 5369, 1995). They found changes in grain size, surface morphology (visible in AFM images), and optical constants varying with the film thickness. By contrast, we report analysis results for relatively thick (300-500 nm) ceria films prepared by liquid solution deposition (dip-coating) followed by annealing. We also investigate the effect of samarium doping (up to 20at.%) of ceria. The rare earth metal samarium usually forms a sesquioxide Sm<sub>2</sub>O<sub>3</sub>. Therefore, doping ceria with Sm is expected to lead to the formation of oxygen vacancies, which enhances the ionic conductivity of ceria. Our ellipsometry spectra (ellipsometric angles and depolarization) can be described very well in the transparent region (below 3 eV) using a Tauc-Lorentz dispersion model for ceria, if small amounts of surface roughness and thickness non-uniformity across the wafer are taken into account. Once these thickness parameters have been determined for our films, we obtain the optical constants of CeO<sub>2</sub>:Sm using a basis spline expansion. We find the typical dispersion expected for an insulator with a direct band gap near 3.7 eV. Samarium doping causes a significant decrease of the refractive index in the transparent region. Most likely, the films with high Sm content are less dense (have more voids, perhaps due a smaller crystallite size) than pure ceria films. An increase in disorder due to Sm doping was also found in x-ray diffraction studies of electrodeposited ceria films (Phok and Bhattacharya, phys. status solidi (a) 203, 3734, 2006). As expected from Kramers-Kronig consistency, we find a significant reduction of the height of the main absorption peak at 4 eV. The direct band gap, however, remains at 3.7 eV, independent of Sm content. There is, however, a significant decrease in the slope of the onset of absorption with increasing Sm content. In addition to ellipsometry results, we will also report AFM, XRD, Raman, and (perhaps) FTIR ellipsometry results for our Sm-doped ceria films.

# Spintronics and Spin Transport

### **Spin Filtering at Metal-Organic Interfaces**

Martin Aeschlimann

Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Germany ma@physik.uni-kl.de

Interfaces between ferromagnetic materials and organic molecules represent one of the most intriguing and at the same time promising material systems for advanced spintronics applications [1]. Indeed, the hybridization between the molecular orbitals and the spin-split bands of the ferromagnet occurring at such interfaces leads to the formation of hybrid states, whose spin properties can, in principle, be easily tuned by acting on the electronic structure of the molecules. This can be achieved, for example, by using electron doping, as we recently demonstrated for the Co-CuPc interface [2]. Thus, the great potential of hybrid interfaces is that they can be used as tunable spin-filters.

Although the spin-filtering properties of organic molecules on ferromagnetic substrate have been demonstrated by spin-resolved scanning tunnelling spectroscopy and spin resolved photoemission [3,4], it is still unknown how organic spin filters work from a microscopic point of view. Thus, in order to fully exploit the potential of hybrid interfaces, we need to go beyond their static characterization by accessing their dynamical properties.

Here, we will show our recent dynamical characterization of the Co-Alq<sub>3</sub> interface, obtained by combining different time-resolved spectroscopy methods. The results show the presence of an unoccupied hybrid interface state (uHIS) characterized by a flat angular dispersion, a very broad linewidth and inelastic electron lifetimes in the order of some hundreds of



*Microscopic understanding of spin filtering in a hybrid interface state obtained by time-resolved spectroscopy.* 

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femtoseconds. Remarkably, both the measured linewidths and lifetimes turn out to be spin-dependent. We find that both elastic and inelastic scattering processes leading to energy and spin-relaxation from the uHIS into the cobalt substrate are spin dependent, which means that the uHIS acts as spin-dependent scattering barrier at the Co-Alg3 interface, as schematically depicted in the figure [5].

### Spin accumulation detection of FMR driven spin pumping in silicon-based metal-oxide-semiconductor heterostructures

Y. Pu<sup>1</sup>, P. M. Odenthal<sup>2</sup>, R. Adur<sup>1</sup>, J. Beardsley<sup>1</sup>, A. G. Swartz<sup>2</sup>, D. V. Pelekhov<sup>1</sup>, R. K. Kawakami<sup>2</sup>, J. Pelz<sup>1</sup>, P. C. Hammel<sup>1</sup>, E. Johnston-Halperin<sup>1</sup>

<sup>1</sup>Department of Physics, The Ohio State University, Columbus, Ohio 43210

<sup>2</sup>Department of Physics and Astronomy, University of California, Riverside, California 92521

The use of the spin Hall effect and its inverse to electrically detect and manipulate dynamic spin currents generated via ferromagnetic resonance (FMR) driven spin pumping has enabled the investigation of these dynamically injected currents across a wide variety of ferromagnetic materials. However, while this approach has proven to be an invaluable diagnostic for exploring the spin pumping process it requires strong spin-orbit coupling, thus substantially limiting the materials basis available for the detector/channel material (primarily Pt, W and Ta). Here, we report FMR driven spin pumping into a weak spin-orbit channel through the measurement of a spin accumulation voltage in a Si-based metal-oxide-semiconductor (MOS) heterostructure. This alternate experimental approach enables the investigation of dynamic spin pumping in a broad class of materials with weak spin-orbit coupling and long spin lifetime while providing additional information regarding the phase evolution of the injected spin ensemble via Hanle-based measurements of the effective spin lifetime.

### Effect of oxides on Fe/GaAs spin resistance

Sarmita Majumder<sup>1</sup>, Donna Hohertz<sup>1</sup>, Anthony SpringThorpe<sup>2</sup> and Karen L. Kavanagh<sup>1</sup> <sup>1</sup>Simon Fraser University, Department of Physics, Burnaby, BC V5A 1S6 Canada <sup>2</sup>National Research Council, Canada

Spin accumulation at an individual, ferromagnetic metal/semiconductor (FM/SM) tunnel contact is achievable by simply applying a bias. The spin polarization state of the FM is transported into the semiconductor with some reduction due to interfacial spin relaxation. Any voltage measured with respect to another unbiased contact, can then be interpreted as being proportional to the spin accumulation in the semiconductor at the biased contact. Measuring this voltage as a function of a perpendicular applied magnetic field is a simple test of the spin precession phenomena called a 3-terminal (3-T) Hanle measurement. Given the area of the contact and the applied current, the spin contact resistance,  $R_s$ , is defined and can be compared to the normal contact resistance,  $R_c$ . In early results from MBE-grown Fe/GaAs tunnel junctions<sup>1</sup>  $R_s$  of 5×10<sup>-7</sup>  $\Omega$ cm<sup>2</sup> were reported for an  $R_c$  of 0.1  $\Omega$ cm<sup>2</sup>. Since then many groups have found much larger  $R_s$ , two to three orders of magnitude larger than the theoretical expectations, particularly when an oxide is added to the junction<sup>2-4</sup>. At present there is not an adequate explanation for these results, although spin trapping at interfacial states is one possibility that has been proposed.

Electrodeposited (ED) Fe/GaAs tunnel barriers have allowed us to experiment with a lower cost method to fabricate spin diodes. We have reported a higher spin accumulation than for equivalent tunnel contacts fabricated via MBE<sup>5</sup>. We proposed via a qualitative quantum model that a magnetic oxide layer at the interface might be responsible for this enhanced spin voltage and reduced spin diffusion time,  $\tau_s$ , compared to their MBE counterpart. In this report, we will show evidence of Fe oxide at our tunnel junction interfaces that depends on the junction doping concentration. We will demonstrate that  $R_s$  (6×10<sup>-4</sup>  $\Omega$ cm<sup>2</sup>) from 3-T Hanle measurements and  $R_c$  (101  $\Omega$ cm<sup>2</sup>), are correlated with the concentration of this interfacial oxygen.

Our ED contacts were fabricated in an aqueous Fesulphate electrolyte using a constant current source $^{6,7}$ . The substrate was an epitaxially-grown (MOCVD)  $n^{+}/n$ -GaAs (2 or 5×10<sup>18</sup> cm<sup>-3</sup>/10<sup>16</sup> cm<sup>-3</sup>) layer on a semiinsulating bulk (001) wafer. We probed the composition of the electrodeposited samples using Ar ion beam milling to gradually remove the Fe layer and expose the GaAs interface while collecting XPS spectra. Figure 1 shows a typical high-resolution XPS scan of the O 1s peak, from the interfacial region of one of the electrodeposited tunnel diode samples. Deconvolution of the oxygen peak gives one peak centered on  $529.9 \pm$ 0.1 eV, characteristic of iron oxides and two minor peaks at 531.0  $\pm$  0.2 and 532.0  $\pm$  0.2 eV associated with Ga<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>3</sub>, respectively. The estimated oxygen concentration is  $4.5 \pm 0.2\%$  to be compared with that of a bulk reference n-type wafer with  $1.18 \pm 0.04\%$ . Meanwhile, the spin life time,  $\tau_s$ , (8.5 ± 0.4 ns to 1.8 ± 0.4 ns for 20 K to 150 K) extracted from 3-T Hanle measurements

comparable with their 4-terminal counterpart  $(7.8 \pm 0.4)$  ns to  $3.2 \pm 0.4$  ns for 25 K to 77 K)<sup>5</sup>, both decreasing with temperature.



Fig. 1. XPS scan of O 1s peak of interfacial region of electrodeposited Fe/GaAs (001) tunnel junction.

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Corresponding author: Karen L. Kavanagh, e-mail: kavanagh@sfu.ca

### Cr<sub>2</sub>O<sub>3</sub> Films on Graphite for Magnetoelectric Gate Applications

<u>S. C. Stuart<sup>1</sup></u>, E. Sachet<sup>2</sup>, J. P. Maria<sup>2</sup>, M. J. E. Rowe<sup>1</sup>, M. Ulrich<sup>1,3</sup> and D. B. Dougherty<sup>1</sup> 1.Department of Physics, North Carolina State University, Raleigh, NC 27695 USA 2 Department of Materials Science, North Carolina State University, Raleigh, NC 27695 USA 3.Army Research Office, Physics Division, Research Triangle Park, NC 27709 USA

Email: scstuart@ncsu.edu

Graphene's high carrier mobility and low spin-orbit scattering allow for efficient spin transport , which has been demonstrated by several publications over useful length scales (1,2). Further progress toward more sophisticated spintronics devices requires controllable manipulation of spin polarized charge carriers. A graphene Spin-Field Effect Transistor has been proposed by Semenov et al (3) that manipulates the spin of charge carriers in a graphene channel by an exchange interaction with a hypothetical ferromagnetic dielectric. As an alternative to this simple picture, we have identified Cr2O3 as a material whose magnetoelectric properties would enable voltage controlled switching of the exchange interaction. The Magnetoelectric properties of  $Cr_2O_3$  have been extensively studied (4), including recent reports of a robust electrically switched magnetic surface state (5,6).

We used pulsed laser deposition to grow thin  $Cr_2O_3$  films directly on HOPG. AFM shows closely packed  $Cr_2O_3$  islands, with a smooth surface interrupted by grain boundaries. X-Ray Diffraction shows that the film has a (0001) texture for films grown at ~ 650°C, which is ideal for magnetoelectric gating. X-Ray Photoelectron Spectroscopy on incomplete films suggest strong chemical interactions between the graphite and  $Cr_2O_3$  films which will be further discussed at the psci meeting.



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### Fluorination of graphene: engineering charge transport and spin-flip scattering

Jun Zhu, Department of Physics, The Pennsylvania State University, University Park, PA 16801, USA

Graphene is a zero-gap material with intrinsically weak spin-orbit coupling and long spin coherence time. I will discuss our work on using fluorine adatoms to modify the charge transport and spin-related properties of graphene. Magneto-transport measurements show that with a dilute coverage of F:C ratio less than 0.1%, fluorine adatoms introduce spin-flip scattering in graphene and bilayer graphene. Remarkably, in bilayer graphene, the spin-flip rate is in situ tunable via an electric field perpendicular to the sample plane. We discuss the possible explanations of the observed phenomena and its implications for spin manipulations in graphene. In the regime of heavy fluorination, where the F:C ratio is of order 0.1-1, fluorinated graphene (FG) becomes highly insulating and a band gap opens, accompanied by luminescence and reduced absorption. Our studies reveal highly non-uniform spatial distribution of the fluorine adatom in FG derived from graphene sheets grown by chemical vapor deposition. FG may be promising as an ultra-thin tunnel barrier and/or dielectric layer in electronics assembled from layered materials but several challenges need to be overcome before its application potentials can be realized.

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# Graphene

### Heating-induced disorder of graphene transferred to a substrate

Satoru Suzuki, Carlo M. Orofeo, Shengnan Wang, Fumihiko Maeda, Makoto Takamura, and Hiroki Hibino

NTT Basic Research Laboratories, NTT Corporation, 3-1, Morinosato Wakamiya, Atsugi, Kanagawa 243-0198, Japan

Graphene is generally considered to be thermally stable owing to the robust  $sp^2$  bonding. In fact, a heating treatment is commonly used in graphene research to remove adsorbates and resist materials from graphene. Heating graphene followed by air exposure is also known to result in heavy hole doping in graphene, although the role of heating has not been clarified. Here we show that a practical graphene film transferred to a SiO<sub>2</sub>/Si substrate using the commonly used transfer technique is unstable against heating in a high vacuum.

In this study, we only used very common techniques for both CVD growth and transfer unless otherwise mentioned. A Raman spectrum of a single layer graphene film transferred to a  $SiO_2/Si$  substrate is shown in Figure 1. The graphene film was heated in a vacuum at a certain temperature for 30 min and the spectra were measured at room temperature in air. By heating in a vacuum, the Raman selection rule is largely relaxed and a disorder-induced broad spectrum appeared in the G and D band regions. The structural disorder was found to coincide with the heating-induced hole doping. Our results also showed that more severely defective graphene is more easily disordered, and that less disorder is observed when



Figure 1. Raman spectra before and after heating of a graphene sample.

a graphene film transferred to a hydrophobic substrate was heated. XPS analyses of a graphene/Au sample also showed that a considerable number of oxygen-containing molecules are unintentionally inserted between graphene and the substrate and that the molecules can not be eliminated even in an ultrahigh vacuum and at a high temperature of 700 °C. Based on these experimental results, we propose that the disorder can be ascribed to defect formation caused mainly by graphene's reacting with water and oxygen molecules inevitably inserted beneath it during the transfer process. The hole doping caused by air-exposure after heating is explained by gas adsorption at the defect sites.

### Giant Seebeck coefficients of the graphene/h-BN superlattices

Yushi Yokomizo<sup>1,2</sup> and \*Jun Nakamura<sup>1,2</sup>

<sup>1</sup>The University of Electro-Communications (UEC-Tokyo), Tokyo, Japan <sup>2</sup>JST-CREST, Saitama, Japan

The thermoelectric conversion has been of interest for many researchers since Hicks and Dresselhaus showed that the introduction of quantum well structures would significantly enhance the dimensionless figure of merit [1]. The dimensionless thermoelectric figure of merit, ZT, which is a standard index for the efficiency of thermoelectric conversion, is defined by

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

where S is the Seebeck coefficient,  $\sigma$  the electric conductivity,  $\kappa$  the thermal conductivity, and T the absolute temperature. Graphene is a two-dimensional, mono-layer material having honeycomb lattice of carbon atoms [2,3]. It has been suggested that the graphene-based device can be a novel thermoelectric material because of its potential giant Seebeck coefficient larger than 30 mV/K [4]. On the other hand, graphene nanoribbon (GNR) is a one-dimensional (1D) material, a strip of graphene, which has also been investigated theoretically as thermoelectric materials. A molecular dynamics study has shown that the high ZT >1 can be obtained for the zigzag GNR (ZGNR) [5]. This surprising result implies that the introduction of 1D structural modulation makes graphene into novel thermoelectric materials. We hereby propose, in this study, superlattice models consisting of ZGNR and zigzag BN nanoribbon (ZBNNR) [6]. Figure 1 shows the structure of a ZGNR/BNNR superlattice. We have investigated the Seebeck coefficients of ZGNR/BNNRs within the Boltzmann transport theory. It has been confirmed that the Seebeck coefficients of ZGNR/BNNRs are drastically enhanced from those of ZGNRs as shown in Fig. 2 [7]. It has been revealed that the giant Seebeck coefficients of the superlattices stem from the so-called pudding mold band with a finite energy gap

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Fig. 1: Structure of (4,4)ZGNR/BNNR; Black, white, and gray balls indicate C, N, and



Fig. 2: Seebeck coefficients as a function of the chemical potential for (a) the 2D ZGNR/BNNR superlattices and (b) 1D ZGNRs.

### Atomic layer deposition on carbon-based nanostructures: The importance of surface modification and nucleation

Virginia Wheeler<sup>1</sup>, Nelson Garces<sup>1</sup>, Luke Nyakiti<sup>1</sup>, Rachael Myers-Ward<sup>1</sup>, Zachary Robinson<sup>1</sup>, Anindya Nath<sup>2</sup>, Neeraj Nepal<sup>1</sup>, Michael Mastro<sup>1</sup>, Peter Pintauro<sup>3</sup>, Ethan Self<sup>3</sup>, D. Kurt Gaskill<sup>1</sup>, Charles Eddy Jr<sup>1</sup>.

<sup>1</sup>U.S. Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, DC 20375 <sup>2</sup> Department of Electrical and Computer Engineering, George Mason University, Fairfax, VA 22030

3Dept. of Chemical and Biological Engineering, Vanderbilt University, Nashville, TN 37235

Carbon-based nanomaterials, such as graphene, carbon nanotubes, and carbon black, have attracted considerable attention due to their good thermal and electrical conductivity, mechanical and chemical stability, and high surface area which can enable new device structures in sensing, high frequency field-effect transistors, energy storage, and thermal management. To realize such technologies, integration of scalable thin films onto carbon-based nanostructures is required. Atomic layer deposition (ALD) is the preferred method to conformally coat planar as well as complex, high surface area nanostructures with abrupt interfaces and angstrom-scale control of thickness. However, the inert nature of high-quality graphitic carbon inhibits direct application of ALD films. Several methods have been investigated which render these carbon surfaces more amenable to precursor bonding <sup>[1,2]</sup> and while each method has had some success in obtaining uniform ALD films, it is often at the expense of deleterious structural damage and degradation of intrinsic properties. In this work, we will discuss the importance of ex-situ surface functionalization and/or in-situ surface modifications, as well as the initial ALD pulse sequence on the ability to obtain thin, conformal, high-quality films on graphene and carbon fibers.

We have developed a novel dry chemical functionalization approach using XeF<sub>2</sub> that results in thin, conformal, high- $\kappa$  ALD oxide films, such as HfO<sub>2</sub> ( $\epsilon_{HfO2}$ =18.5) and Al<sub>2</sub>O<sub>3</sub> ( $\epsilon_{Al2O3}$ =8.9), on graphene, without degrading transport properties desired for low power, high frequency applications. By using this technique, a 10-25% improvement in graphene mobility and comparably small Dirac voltage shifts (HfO<sub>2</sub>=2V, Al<sub>2</sub>O<sub>3</sub>=0.1V) were observed, indicating the effectiveness of fluorine functionalization <sup>[3]</sup>. A systematic study performed on a normalized set of graphene samples indicated that the optimal XeF<sub>2</sub> pretreatment results in ~6% fluorine surface coverage, as measured by x-ray photoelectron spectroscopy (XPS), in the form of semi-ionic C-F bonds <sup>[4]</sup> (F1s ~687eV) only, which provided sufficient additional ALD reaction sites to obtain uniform oxide films. The semi-ionic nature of the C-F bond is desirable because it permits the graphene lattice to maintain planarity <sup>[3]</sup> and we show that it minimizes degradation to transport properties. The fluorination technique explored here is not limited to ALD oxide films and has been used to deposited 2-5 nm of uniform, conformal ALD AIN, GaN, or InN directly on EG, which opens the possibility of such heterostructures for more complex device applications.

Electrospun carbon fiber mats, typically used for battery electrodes, were exposed to three to ten pulses of water, ozone or trimethylaluminum (TMA) prior to sequential ALD pulsing to elucidate the impact of initial pulse sequence's ability to obtain high quality, conformal 2 nm  $Al_2O_3$  films on carbon-based fibers. XPS showed that the carbon peak at ~283 eV associated with the fiber mat structure was removed with the ozone process, while it was maintained during initial water pulsing. This degradation in the fiber mat with the ozone treatment can alter the intrinsic properties of the fiber and subsequent device performance. Both oxygen precursors resulted in thicker, more conformal films than the sample with initial TMA pulsing, likely resulting from insufficient nucleation with the fiber mat surface which lead to oxide pinholes. These results are consistent with previous results obtained on graphene where optimal films are achieved when several in-situ water pulses are used to initiate ALD growth.

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### Mo1625 Invited

#### **Exploring Atomically-Engineered Graphene Nanostructures**

M. F. Crommie<sup>1\*</sup>, Yang Wang<sup>1</sup>, Dillon Wong<sup>1</sup>, D. Oteyza<sup>1</sup>, Yen-Chia Chen<sup>1</sup>, Hsin-Zon Tsai<sup>1</sup>, V.W. Brar<sup>1</sup>, Sangkook Choi<sup>1</sup>, W. Regan<sup>1</sup>, A. Riss<sup>1</sup>, S. Wickenberg<sup>1</sup>, Z. Pedramrazi<sup>1</sup>, P. Gorman<sup>2</sup>, Chen Chen<sup>2</sup>, D. J. Mowbray<sup>3</sup>, R. Kawakami<sup>4</sup>, A. V. Shytov<sup>5</sup>, L. Levitov<sup>6</sup>, A. Zettl<sup>1</sup>, S. G. Louie<sup>1</sup>, G. Etkin<sup>3</sup>, A. Rubio<sup>3</sup>, Felix Fischer<sup>2</sup>

<sup>1</sup>Department of Physics, University of California at Berkeley, Berkeley, CA 94720, US

<sup>2</sup>Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720, US

<sup>3</sup>Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, E-20018 San Sebastián, Spain

<sup>4</sup>Dept. of Physics and Astron., University of California at Riverside, Riverside, CA 92521, US

<sup>5</sup>School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, UK

<sup>6</sup>Department of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139, US

#### \*Corresponding author

Abstract: Graphene has unique electronic properties that arise from its 2D honeycomb structure and which cause novel behavior at the atomic scale. This can be seen in graphene's response to charged impurities, where graphene's ultra-relativistic nature leads to impurity states that are unlike those found in any other material. We have explored such impurity states across different impurity-charge regimes by building charge centers (i.e., "artificial nuclei") atom-by-atom at the surface of graphene devices and probing them via scanning tunneling microscopy. New results on this topic, including the observation of "atomic collapse" [1], will be discussed. Graphene also exhibits extraordinary properties when it is cut into nanoscale structures having atomically clean edges. While such structures are difficult to fabricate via traditional "top-down" lithography, new "bottom-up" synthesis techniques utilizing molecular self-assembly show great promise for creating flexible, atomically-engineered networks. We have recently made progress at fabricating new graphene nanostructures in this way from chemically engineered precursor molecules. New measurements on these systems will also be discussed.

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### Effect of Oxygen on Graphene Growth by Low Pressure Sublimation of C-Face SiC

Z. R. Robinson<sup>1</sup>, G. G. Jernigan<sup>1</sup>, K. Bussmann<sup>1</sup>, R. L. Myers-Ward<sup>1</sup>, V. D. Wheeler<sup>1</sup>, S. Oida<sup>2</sup>, J. B.

Hannon<sup>2</sup>, C.R. Eddy, Jr.<sup>1</sup>, D. K. Gaskill<sup>1</sup>

<sup>1</sup> U.S. Naval Research Laboratory, Washington, DC <sup>2</sup>IBM T.J. Watson Research Laboratory, Yorktown Heights, NY

Graphene growth on Si-face SiC has been shown to have improved uniformity when synthesized in an argon environment instead of in UHV. For C-face growth, which is expected to yield graphene with superior electronic properties due to the absence of the interfacial layer, it remains unclear whether growth in argon can achieve similar improvements. Therefore, a systematic study of SiC surface preparation by hydrogen etching and subsequent graphene growth in argon has been carried out for nominally on-axis C-face 4H- and 6H- SiC substrates. All of the temperatures and pressures used for graphene growth were found to result in non-uniform graphene films, which in some cases can result in islands containing relatively thick (~20 layers) regions surrounded by regions that have no graphene. It has been suggested that the cause of this nonuniform growth is the unintentional oxidation of the SiC substrate during growth [1]. In order to test this, a second set of experiments were performed in which growth was carried out in a low energy electron microscope (LEEM) so that the morphology and crystal structure of the graphene could be measured throughout the growth process. The base pressure of the LEEM was 1 x 10<sup>-10</sup> Torr, and independent growths were carried out in  $2 \times 10^{-7}$  Torr of both disilane and oxygen. It was found that heating up to the graphene growth temperature in disilane resulted in graphene growth that was controllable to within  $\sim 0.5$  monolayers. In situ  $\mu$ -LEED analysis showed sharp spots corresponding to graphene rotational domains that are  $\sim 1 \mu m$ across. Each rotational domain appeared to be randomly oriented with respect to the substrate. Growth was then carried out in oxygen. During heat up, around 900 °C the surface underwent a 3 x 3 reconstruction that was measured with XPS to be a chemisorbed oxygen layer. The original stepped morphology of the SiC was preserved on the oxygen reconstructed surface, and appeared to roughen as the temperature was increased to induce sufficient Si sublimation for graphene to nucleate (around 1200 °C). µ-LEED analysis showed very diffuse arcs corresponding to rotationally disordered graphene (domain size ~nm) aligned with the underlying substrate in coexistence with the 3 x 3 oxygen reconstruction. These results show that the graphene growth process on C-face SiC is significantly affected by the presence of trace amounts of oxygen.



*Figure 1: LEEM image of graphene grown in 2* x 10<sup>-7</sup> *Torr of oxygen. Steps are from the SiC substrate, and can be seen due to incomplete coverage of small graphene grains. FOV 10μm.* 

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### Oxidation of epitaxial graphene on SiC substrate: STM/STS, XPS and Raman characterization

Md. Zakir Hossain<sup>\*</sup>, Maisarah B. A. Razak

Advanced Scientific Research Leaders Development Unit, Graduate School of Science and Technology, Gunma University, Kiryu City, Gunma 376-8515, Japan \*Corresponding author: Email zakir@gunma-u.ac.jp

To make graphene suitable for many of its potential application, it's extraordinary properties need to be modified. For modifying its properties and interfacial characteristics, the chemical functionalization of graphene is being actively pursued. Recently oxidation of graphene have received enormous interest as a prominent way to chemically modify its properties and make the graphene suitable for application in various technologies, such as high-performance electronics, sensor, renewable energy, optics, etc.[1]. The epitaxial graphene (EG) on SiC has drawn much attention because of the advantage of wafer scale production that can be used for high performance device fabrication[2]. We have employed the controlled aqueous phase oxidation procedures on EG on Si-face SiC surface [3]. The strong oxidizing agent known as Hummers solution (mixture of KMnO4, H2SO4 and NaNO3) was used for aqueous phase oxidation under different reaction conditions. The chemically modified surfaces have been characterized by Raman, scanning tunneling microscope (STM) and spectroscopy (STS), and x-ray photoelectron spectroscopy (XPS) and two-probe surface conductivity measurements. The EG oxidized using Hummers solution in both 'dipped-in' and 'drop-casting' procedures results an inhomogeneous surface with various functional groups such as epoxy, hydroxyl, carbonyl and carboxylic groups. Both the 'drop-casting' and 'dipped-in' procedures are found to be equally effective for oxidizing the graphene. Drastic change of surface resistivity (~ 100x) by aqueous phase oxidation of graphene reflects the significant changes in electronic states. STS measurements before and after aqueous phase oxidation of EG confirm a significant band gap opening (~ 0.4 eV) in graphene's electronic structure. The detailed results obtained by different techniques will be discussed. References:

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Coupled Chemisorption and Physisorption of Oxygen on Single Layer Graphene Devices

Hua Wen, A. G. Swartz, D. J. O'Hara, P. M. Odenthal, J.-R. Chen, and R. K. Kawakami

Department of Physics and Astronomy, University of California, Riverside CA 92521

We investigate adsorption of molecular oxygen on single layer graphene devices and demonstrate that chemisorption of molecular oxygen at low temperatures is strongly coupled to the physisorption process. The experiment is performed in an ultrahigh vacuum environment with oxygen pressure of  $1 \times 10^{-5}$  torr. Through low temperature adsorption and variable-temperature desorption studies, we establish the ability to use electrical measurements to separately identify the physisorption and chemisorption of oxygen on graphene: chemisorption is identified by a change in Dirac point voltage, while physisorption is identified through its increase of the mobility. We also demonstrate, for the first time in single layer graphene, the ability to control chemisorption using electrostatic gates (Fig. 1). With a gate voltage of +50 V the chemisorption is facilitiated, while for gate voltage of -50 V the chemisorption is hindered. We utilize this gate control to demonstrate that chemisorption of oxygen at low temperatures is strongly coupled to the physisorption process. Specifically, the chemisorption at low temperatures is driven by a two-step process in which free oxygen molecules are first captured physisorption, and then onto graphene by the oxygen undergoes а physisorption-to-chemisorption conversion. This is illustrated in the experiment of Figure 2. First, oxygen is adsorbed (both chemisorption and physisorption) at zero gate voltage and with oxygen partial pressure of  $1 \times 10^{-5}$  torr. Next, the gate voltage is set to -50 V to hinder the chemisorption while the oxygen gas is pumped out of the system. Finally, the gate voltage is switched to +50 V and the chemisorption is observed. Because the chemisorption occurs without oxygen gas in the chamber ( $<10^{-8}$  torr), this provides strong evidence for the conversion of physisorbed oxygen into chemisorbed oxygen. Our study provides a better understanding of the effect of gas adsorbates on graphene and could be useful in future applications of graphene-based gas sensors.



### Mo1720 Invited

### 2D Materials: Characterization and Device Application\*

### Randall Feenstra

Dept. Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania

Measurements of the reflectivity of low-energy electrons, typically 0 - 10 eV above the vacuum level, are known to provide a sensitive means of characterizing 2-dimensional (2D) materials such as graphene or hexagonal boron nitride (h-BN). Phenomenologically, it was found that one can determine the *number* of 2D layers on a substrate, and also obtain information concerning the *interface* between the 2D layers and the substrate [1]. However, up to now there has not been a fundamental understanding of how the measured reflectivity is determined by these quantities. A first-principles description of low-energy electron reflectivity spectra has recently been developed, yielding results that compare well with experimental data for both graphene and hexagonal boron nitride (h-BN) on various substrates [2]. Results comparing experiment and theory will be presented, from which the interface structure between the 2D material and the substrate is determined.

2D materials enable the development of a range of novel electronic devices. This presentation will focus on one such device, a SymFET (Symmetric Field-Effect Transistor) that relies on the symmetry between the valence and conduction bands in opposite graphene electrodes of a graphene-insulator-graphene (GIG) junction [3,4]. The state-of-the art in GIG and SymFET fabrication will be described, focusing on recent experimental results [5] in which negative differential resistance was observed in SymFET type devices employing h-BN for the insulator layer. The theory describing SymFET device operation will be discussed, including the aspects of energy and momentum conservation as well as the possible roles of (i) relative orientation of the two graphene electrodes, and (ii) scattering within the insulator layer.

\*Work performed in collaboration with N. Srivastava, P. Mende, Q. Gao, M. Widom (Carnegie Mellon University), T. Roy, E. Vogel (Georgia Inst. Technology), A. Ismaj, R. Ruoff (Univ. Texas – Austin).

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# Tuesday

Tu0730	Registration and Continental Breakfast
Tu0830	Tuesday Morning Session: Oxides II
Tu1005	Coffee Break and Poster Viewing
Tu1045	Tuesday Morning Session: New Imaging and Spectroscopy Tools
Tu1200	Free Afternoon
Tu1930	Tuesday Evening Rump Session: Single Atom Devices


#### Control of Interlayer-Coupling in SrTiO<sub>3</sub> Bilayer δ-Doped Structures

H. Inoue<sup>1</sup>, M. Kim<sup>2</sup>, C. Bell<sup>2</sup>, Y. Hikita<sup>2</sup>, S. Raghu<sup>2,3</sup>, and H. Y. Hwang<sup>1,2</sup>

1. Geballe Laboratory for Advanced Materials, Department of Applied Physics,

2. Stanford Institute for Materials and Energy Sciences,

SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA

3. Department of Physics, Stanford University, Stanford, CA 94305, USA

e-mail: hinoue6@stanford.edu

For several decades, two-dimensional electron systems (2DES) have attracted theoretical and experimental interest in semiconductor heterostructures, metal surfaces, and two-dimensional materials. Many of the observed phenomena, such as high mobility electron transport and the quantum Hall effect are related to sub-band quantization effects due to the quantum confinement. Recently, there has been interest focusing on the interplay between sub-bands and superconductivity [1-4]. However progress has been limited, mainly due to the difficulty in making 2DES superconductors clean enough, and with sufficient control of the sub-band quantization in both the normal and superconducting (SC) states.

By using high quality bulk-like single crystalline  $SrTiO_3$  bilayer  $\delta$ -doped structures, here we demonstrate 2DES superconductors with high mobility electrons in the normal state, with flexible sub-band control. Modulation of the superconductivity could be achieved by controlling the sub-band structure of the superconducting layer over a wide range. The system consisted of two parallel 1 atomic % Nb-doped  $SrTiO_3$  2DES layers separated by an undoped  $SrTiO_3$  spacer layer. The doped layer thickness was kept constant at 5.4±1 nm and the spacer layer thickness ( $d_{inter}$ ) was varied from 3.7 nm to 267 nm.

In the normal state, Hall measurements showed parallel conduction of high and low mobility electrons. We observed systematic enhancement of the high mobility sheet carrier density  $(n_{\text{high}})$  for intermediate  $d_{\text{inter}} \sim 70$  nm (Fig. 1). We attributed this to the modulation of the sub-band structure, where the electrons in the upper sub-bands extend over the doped layers into the cleaner spacer layer, while the electrons in the lower sub-bands were confined around the more disordered doped layers.

In the SC state, we observed coexistence of two different SC length scales at intermediate  $d_{inter}$ , which correspond to the different spatial distributions of the electrons in the upper and the lower sub-bands. At the same time,  $T_c$  was suppressed in this  $d_{inter}$  range (Fig. 1), indicating a crossover from a merged two-dimensional (2D) SC state, where two doped layer are coupled, to two decoupled 2D SC states. The coincidence of the  $n_{high}$  enhancement and the features in SC states suggest that both the upper and the lower sub-bands and their inter-sub-band interactions play important roles in determining the electronic properties. These results are a step towards the realization of recently proposed exotic SC states [5-7].

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Fig. 1 High mobility sheet carrier density ( $n_{\text{high}}$ , red open circles), low mobility sheet carrier density ( $n_{\text{low}}$ , green open triangles) and superconducting transition temperature ( $T_{\text{c}}$ , blue closed squares) as a function of spacer layer thickness,  $d_{\text{inter}}$ . The lines are guides to the eye.

Stanford University, Stanford, CA 94305, USA

# Band alignment control of anatase-TiO<sub>2</sub> heterojunctions using oxide dipole layers <u>T. Tachikawa<sup>1,2</sup></u>, M. Minohara<sup>1</sup>, Y. Hikita<sup>1</sup>, C. Bell<sup>1</sup>, and H. Y. Hwang<sup>1,3</sup>

<sup>1</sup>Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA <sup>2</sup>Department of Advanced Materials Science, The University of Tokyo, Chiba, 277-8561, Japan <sup>3</sup>Department of Applied Physics, Stanford University, Stanford, California 94305, USA

e-mail: rapid@slac.stanford.edu

Metal oxide heterojunctions are widely used in energy related devices, such as solar cells and photoelectrochemical cells [1]. Controlling the band alignments at these interfaces by inserting electrostatic dipoles is an important technique for improving device performance. Polar organic molecules have been widely used to manipulate band alignments, however the presence of interface states generally limit the tunable range [2]. Polar surfaces of ionic oxides can potentially be utilized to tune the band alignments with minimal generation of interface states [3]. Here we demonstrate this approach by tuning the Schottky barrier height (SBH) in a model system, Pt/anatase TiO<sub>2</sub> junctions, using an ultrathin epitaxial layer of the perovskite LaAlO<sub>3</sub> (LAO) as the dipole.

LAO/TiO<sub>2</sub> (60 nm) heterojunctions were grown on LAO (001) substrates by pulsed laser deposition under conditions in which the oxygen vacancies in the TiO<sub>2</sub> are well controlled [4]. Pt Schottky electrodes were deposited by e-beam evaporation and SBH measurements were conducted by electrical impedance measurements.

Figure 1 shows the capacitance-voltage (C-V) data of Pt/TiO<sub>2</sub> Schottky junctions with various LAO interlayer thicknesses, *d*, in unit cells (uc). The extrapolated built-in potential ( $V_{bi}$ ) is clearly monotonically decreasing with *d*, indicating that the LAO interlayer plays the role of an interface dipole (Fig. 1 inset). These results demonstrate that polar surfaces of ionic oxides can be utilized to control band alignments even at interfaces between materials with different crystal structures [5], opening up further possibilities to tailor functionalities in oxide devices.

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Fig. 1.  $1/C^2$ -V plot for Pt/LAO/TiO<sub>2</sub> junctions with various LAO thicknesses. The inset illustrates a schematic band diagram of these junctions and the dipole induced by the LAO. CB and VB are the conduction and valence bands, and  $E_F$  the Fermi energy.

#### Modulation of Over 10<sup>14</sup> cm<sup>-2</sup> Electrons in SrTiO<sub>3</sub>/GdTiO<sub>3</sub> Heterostructures

Mohamed Boucherit<sup>1</sup>, Omor F. Shoron<sup>1</sup>, Craig Polchinski<sup>1</sup>, Clayton Jackson<sup>2</sup>, Santosh Raghavan<sup>2</sup>, Susanne Stemmer<sup>2</sup>, Siddharth Rajan<sup>1</sup>

<sup>1</sup>ECE Department, Ohio State University, Columbus, Ohio

#### <sup>2</sup>Materials Department, University of California Santa Barbara

The polar discontinuity at the SrTiO<sub>3</sub>/GdTiO<sub>3</sub> (STO/GTO) interface<sup>[1]</sup> has been shown to provide a high concentration 2DEG<sup>[2]</sup>. However, It is a challenge to modulate such large charge densities. In this work we discuss the use of advanced energy band and device engineering to enable charge modulation of  $10x10^{14}$  cm<sup>-2</sup>, which represents the highest 2D charge modulated in *any* semiconductor system. The ability to modulate such high charge density could enable a new class of devices that exploit the electronic, plasmonic, and correlated properties of extreme charge density oxide heterostructures.

The epitaxial structures investigated in this work were grown on (001)-oriented  $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7}$  (LSAT) single crystal substrates by molecular beam epitaxy (MBE) using a metal organic precursor (titanium isopropoxide) for Ti . The basic structure consists of a GdTiO\_3/SrTiO\_3 structure, with STO on top. Due to the staggered band line-up between GTO and STO, a 2D electron gas channel with a sheet charge density of  $3x10^{14}$  cm<sup>-2</sup> is formed in the wider bandgap STO layer. This inverted STO/GTO HFET structure provides several advantages including large breakdown strength in the STO cap layer and a back-barrier for confinement.

We have used two approaches to increase charge modulation, which is limited largely by the low permittivity interfacial layer between metal and STO. The first approach uses a thick STO layer to reduce the relative effect of the interfacial layer. The second approach utilizes a new oxide-based design consisting of  $Ba_{0.5}Sr_{0.5}TiO_3$  (BST)/STO/GTO heterostructure field effect transistor layer, with the BST dielectric layer to reduce the gate leakage and improve gate capacitance. Detailed energy band diagrams and vertical transport for this new structure will be reported.

Sub-micron transistors with low contact resistance 0.5  $\Omega$ .mm, as well as several test structures were used to understand the electronic properties of these structures. To study the effect of STO thickness we used three different structures - (28/40/98) nm STO/5 nm GTO/LSAT. From C-V measurements, we found higher charge modulation as the STO was increased, reaching 1.05x10<sup>14</sup> cm<sup>-2</sup> charge modulation. The use of the double heterostructure BST/STO/GTO enabled lower gate leakage and charge modulation of 8.7x10<sup>13</sup> cm<sup>-2</sup>. Details of transistor characteristics, energy diagrams, field dependent dielectric properties, charge-dependent mobility, and high-field transport and velocity saturation in STO will be discussed in detail.

In conclusion, we demonstrated for the first time modulation of 2D carrier density greater than  $10^{14}$  cm<sup>-2</sup> in any material system. The work done here could enable fundamental studies of extreme electron concentration oxide interfaces, as well as new device applications based on these materials.

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#### Tu0900 Upgraded

#### Persistent Optically Induced Magnetism in Oxygen-Deficient Strontium Titanate

W. D. Rice,<sup>1</sup> P. Ambwani,<sup>2</sup> M. Bombeck,<sup>3</sup> J. D. Thompson,<sup>4</sup> C. Leighton,<sup>2</sup> and S. A. Crooker<sup>1</sup>

<sup>1</sup>National High Magnetic Field Laboratory, Los Alamos National Laboratory, Los Alamos, NM 87545, USA; <sup>2</sup>Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA; <sup>3</sup>Experimentelle Physik 2, Technische Universität Dortmund, D-44221 Dortmund, Germany; <sup>4</sup>Materials Physics and Applications, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Strontium titanate (SrTiO<sub>3</sub>) is a foundational material in the emerging field of complex oxide electronics. While its electronic and optical properties have been studied for decades,  $SrTiO_3$  has recently become a renewed materials research focus due the observations of extremely high interfacial charge densities that form between  $SrTiO_3$  and other wide bandgap semiconducting oxides. Investigations of  $SrTiO_3$  heterostructure interfaces were further catalyzed in part by the unexpected discovery of the coexistence of magnetism *and* superconductivity. The formation and distribution of oxygen vacancies, especially in  $SrTiO_3$ , is thought to play an essential but as-yet-incompletely understood role in these effects. Moreover, recent signatures of magnetization in gated bulk  $SrTiO_3$  crystals have further galvanized interest in the emergent properties of this nominally nonmagnetic material.

We observe an optically induced and persistent magnetization in oxygen-deficient  $SrTiO_{3-\delta}$  using magnetic circular dichroism spectroscopy and SQUID magnetometry. An optical absorption peak at  $\sim 430$  nm (Fig. 1b) appears when oxygen vacancies are introduced (*i.e.*, the crystal is reduced by annealing in UHV). Concurrent with the appearance of this absorption feature, we are able to optically induce magnetization at zero magnetic field with sub-bandgap (400-500 nm) circularly polarized light (Fig. 1c); this magnetization inverts when the circular polarization is reversed. As Fig. 1d shows, the optically induced magnetization persists without significant degradation even after the pump light is blocked. Interestingly, we found that the relaxation dynamics strongly depend on temperature: the induced magnetization exhibits hours-long decay times when the temperature is below 10 K, but only persists for seconds near 18 K, the temperature where the magneto-optical effects first appear (Fig. 1e). These remarkable low temperature relaxation times, along with the all-optical control over the magnetization, can be combined to use  $SrTiO_{3-\delta}$  as a data storage device. Figure 1f shows a  $SrTiO_{3-\delta}$  crystal with the acronyms 'LANL' and 'UMN' imaged onto it with each adjacent letter oppositely magnetized by reversing the circular polarization. The images are a demonstration that optically written magnetic information can be stored and optically read from  $SrTiO_{3-\delta}$  wafers using technologically relevant wavelengths (e.g. 405 nm). The magneto-optical phenomena described here, which only occur in oxygen-deficient samples, reveal the detailed interplay between magnetism, lattice defects, and light in an archetypal oxide material and may yield new insights into the physics of oxide interfaces.

#### Tu0920 Upgraded

#### Spin injection and detection in La and Nb doped SrTiO<sub>3</sub>

Wei Han<sup>1</sup>, Xin Jiang<sup>1</sup>, Adam Kajdos<sup>2</sup>, See-Hun Yang<sup>1</sup>, Susanne Stemmer<sup>2</sup>, Stuart Parkin<sup>1</sup>

<sup>1</sup>IBM Almaden Research Center, San Jose, California 95120, USA

<sup>2</sup>Materials Department, University of California, Santa Barbara, California 93106-5050, USA

Email: whan@us.ibm.com

There has been much interest in the injection and detection of spin polarized carriers in semiconductors for the purposes of developing novel spintronic devices. The SrTiO<sub>3</sub> (STO) interfaces and thin films, in particular, have attracted much attention, stimulated especially by the discovery of high mobility two dimensional electron gas (2DEG) at the interface between STO and several other perovskites, as well as in La-doped STO thin films. In this talk, I will present the electrical injection and detection of spin-polarized carriers into Nb-doped STO single crystals and La-doped STO epitaxial thin films. The spin injection is performed using MgO tunnel barriers and the three-terminal Hanle technique. Spin lifetimes of up to ~100 ps are measured at room temperature and vary little as the temperature is decreased to low temperatures. However, the mobility of the STO has a strong temperature dependence. Furthermore, the spin lifetime decreases systematically with increasing dopant concentration, which scales with the concentration of doping induced Ti<sup>3+</sup>. These observations suggest that the spin lifetime is limited by spin-dependent scattering at the MgO/STO interfaces, which is most likely related to the Ti<sup>3+</sup> magnetic centers.

## Native Point Defects, Fermi Level Pinning, and Electrostatic Repulsion at Mg<sub>x</sub>Zn<sub>1-x</sub>O Alloys

J. Perkins,<sup>1</sup> M. Meyer,<sup>2</sup> J.M. Chauveau,<sup>3,4</sup> A. Redondo-Cubero,<sup>5</sup> A. Hierro,<sup>5</sup> and L.J. Brillson<sup>1,6</sup>

<sup>1</sup>Department of Physics, The Ohio State University, Columbus, OH 43210

<sup>2</sup>Columbus School for Girls, 56 S. Columbia Ave., Columbus, OH 43209

<sup>3</sup>Dpto. Ingenieria Electronica and ISOM, Universidad Politecnica de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain

<sup>4</sup>CRHEA-CNRS, 06560 Valbonne, France

<sup>5</sup>University of Nice Sophia Antipolis, Parc Valrose, 06102 Nice Cedex 2, France

<sup>6</sup>Department of Electrical & Computer Engineering, The Ohio State University, Columbus, OH 43210

MgZnO alloys are emerging as exciting UV optoelectronic materials based on their large exciton binding energies, small lattice mismatch with ZnO substrates, and ability to create heterostructures for quantum well and superlattices by varying Mg content. Deep level defects in these materials will impact dipole formation, Schottky barriers and heterojunction band offsets, vet how their physical properties depend on alloy content and lattice structure is only now being explored. We have used depth-resolved cathodoluminescence spectroscopy (DRCLS) and nanoscale surface photovoltage spectroscopy (n-SPS) to measure the dependence of native point defect energies and densities on Mg content, band gap, and lattice structure in non-polar Mg<sub>x</sub>Zn<sub>1</sub>. <sub>x</sub>O (0 $\leq$ x $\leq$ 0.56) alloys grown by molecular beam epitaxy (MBE) on *r*-plane sapphire substrates. These features are of particular interest since MgZnO alloys undergo a lattice transformation from wurtzite to rocksalt crystal symmetry with increasing Mg content. The a-plane, nonpolarity normal to their surfaces and interfaces and their XRD lattice variation with Rutherford backscattering spectrometry (RBS)-measured Mg content can be used to assess the role of electric fields and strain on the native defect distribution near MgZnO interface. In turn, the native point defect type, energies, and densities can be correlated with Schottky barriers measured previously.<sup>1,2,3</sup>

DRCLS spectra exhibit multiple deep level emissions with dominant 1.92 and 2.42 eV features corresponding to zinc and oxygen vacancies (V<sub>Zn</sub> and V<sub>O</sub>), respectively, with relatively constant bulk densities with slight surface segregation. While c-plane, polar ZnO typically has strong Vo near-surface segregation, a-plane nonpolar ZnO exhibits relatively low segregation of both V<sub>Zn</sub> and V<sub>0</sub> defects, suggesting the role of electric fields in near-surface distribution of these electrically-active sites. The linear band gap variation with Mg% up to 52% is consistent with previous measurements. SPS work function changes at photothresholds provided defect level positions with respect to band edges.  $V_O(V_{Zn})$  energy level movements vs. Mg% parallel valence (conduction) band edge variations, consistent with their orbital-derived nature. Both DRCLS defect densities exhibit a pronounced minimum at ~45% Mg corresponding to similar a and cparameter minima at ~52%. The reduced lattice parameters represent a 3.36% volume decrease, which may serve to inhibit defect formation due to electrostatic repulsion as observed in SrTiO<sub>3</sub> and other complex oxides. Likewise, reported Schottky barrier heights decrease from ~1.2 to 1 eV above ~45% Mg,<sup>3</sup> consistent with stronger Fermi level pinning as defect densities rise. These results highlight the coupled electronic and structure changes that occur within the MgZnO wurtzite-to-rocksalt transition region.

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#### Hafnia-Hafnium Interface in RRAM Devices: Theoretical Investigation

Andrew O'Hara<sup>1</sup>, Gennadi Bersuker<sup>2</sup> and Alexander A. Demkov<sup>1</sup>

<sup>1</sup>Department of Physics, The University of Texas at Austin, Austin, TX 78712, USA <sup>2</sup>SEMATECH, Albany, NY 12203 USA

Resistive memory (RRAM) technology presents an attractive option for the embedded non-volatile memory systems<sup>1</sup>. Within a large family of the transition metal oxide dielectrics reported to be used for the RRAM application, hafnia-based devices are especially promising since they employ fab-friendly materials and have demonstrated good endurance and low switching time and operation currents. Generally, the architecture consists of  $HfO_2$  grown between the bottom and top electrodes (e.g., TiN). However, successful RRAM operations require a certain degree of dielectric oxygen deficiency that, in the case of the ALD hafnia process, could be achieved by oxygen gettering using a metal layer overlaying hafnia. In this work, we focus on the architecture, in which there is a layer of hafnium metal between the oxide and electrode, aiming to understand the oxygen gettering process.



Figure 1. Atomistic diagram of the hatnium/hatnia/hatnium slab used for the calculations in this paper and the local potential with band offsets along the z-axis.

To model the oxide-metal interface, we use density functional theory within the local density approximation as implemented in the Ab-initio Simulation Vienna Package  $(VASP)^2$ . We choose (100) oriented m-HfO<sub>2</sub> because the hafnium layer in this orientation  $(11\overline{2}0)$ α-hafnium with matches 5.5% compressive strain along the x-axis and 5.2% tensile strain along the y-axis. The full simulation slab, shown in Fig 1, consists of 6 layers of hafnia with 12 layers of hafnium on each side. This size slab ensures bulk-like density of states and local potential at the center of each region. Slabs are separated by 8.7 Å of vacuum. Using the average local

potential along the z-direction, also shown in Fig 1, we calculate the valence band offset to be 3.5 eV, in agreement with 3.9 eV estimated using metal-induced gap states (MIGS) theory and experimental measurements of oxidized polycrystalline hafnium foil of 4.2 eV. Fundamental to understanding the mechanism of the resistive switching is to understand the role of oxygen vacancies and defects near the interface. Thus, we investigate the formation of oxygen vacancies within the oxide layer and subsequent formation and behavior of vacancy-interstitial complexes (extended Frenkel pairs) across the interface.

We calculate the formation energy for oxygen vacancies within each oxide sub-layer from the center of the oxide to the interface. At the center, the formation energy is close to that of bulk hafnia, while there is a ~1.1 eV drop in formation energy near the interface from bulk values of ~7.5 eV. This indicates that any vacancies formed most likely do so at the interface. We maintain the name Frenkel pair (FP) for a vacancy-interstitial complex, however, when the interstitial resides in the metal across the interface we call this an extended FP<sup>3</sup>. Creation of the extended FP is the first step to oxygen out-diffusion into a metal. The shortest possible extended FP that can be formed is for interfacial oxygen to move across the interface into a tetrahedral coordinated site in Hf metal (see Fig 2). Importantly, this configuration is more stable by 0.31 eV than the pristine interface. Other FPs can be considered allowing oxygen to occupy stable interstitial sites further into the hafnium. We find the formation energy of any extended FP to be lower than the formation energy of an oxygen vacancy in bulk HfO<sub>2</sub>.

After establishing that extended FP formation is favorable, we calculate the energy barrier for FP formation employing the nudged-elastic band method<sup>4</sup> which takes extrapolated images between the initial and final atomic positions and finds the optimized minimum energy pathway. For example, the barrier to form the shortest possible FP (Fig 2) is 1.27 eV. The barrier is lower than the energy needed to form vacancies indicating that during application of the forming voltage, creation of suboxide layers on both sides of the interface is favorable.

Once an FP is formed across the interface, we wish to determine whether oxygen would remain close to the interface or diffuse through the metallic region.



Figure 2. The minimum energy pathway from the initial interface to the shortest possible Frenkel pair.

Within the Hf hcp lattice, there are three stable interstitial sites: the *octahedral, hexahedral*, and *crowdion* sites. The octahedral site is between two layers of Hf at the center of a triangle in each plane; the hexahedral site is within a layer inside a trigonal bipyramid; and the crowdion site is at the center of an edge of the bipyramid. Using the nudged-elastic band method and the Vineyard equation<sup>5</sup>, we compute the transition rate between each type of site and direct diffusion from octahedral to octahedral site. In Fig. 3, we combine these using a multistate diffusion formalism<sup>6</sup> and find nearly isotropic diffusion when comparing diffusion within the basal plane and along the z-axis. We fit a single Arrhenius rate equation with a barrier height of 2.31 eV. While our prefactor is low compared to most experiments, the barrier agrees with several experimental reports<sup>7</sup>.



Figure 3. Plot of the calculated diffusion coefficient in bulk Hf showing stable interstitial sites within the lattice.

In conclusion, using DFT we have built an atomistic model of an HfO2/Hf interface important in RRAM technology, and performed a microscopic study of oxygen gettering at the interface. Our calculations suggest that in hafnia, it is harder to create a bulk oxygen vacancy than one at the interface. More importantly, we find it is easier to create an extended FP across the interface, which is the first step in forming suboxide believed to form a conductive filament. To understand the defect behavior after FP disassociation, we have computed the barrier for diffusion within bulk Hf, the results are in good agreement with the latest experiment.

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## Theoretical Investigation of the Strong Interaction on the interface between the Rh and CeO<sub>2</sub> Surface

Ai Suzuki, Ryuji Miura, Nozomu Hatakeyama, Mark C. Williams, Akira Miyamoto

New Industry Creation Hatchery Center(NICHe), Tohoku University, Sendai, 980-8579, Japan \*Corresponding author: Ai Suzuki, 022-795-7235, <u>ai@aki.che.tohoku.ac.jp</u>

Chemical interaction between noble metals and the cerium oxide is a prerequisite for industrially important catalytic reactions such as the three way catalysts. Especially, there are two prominent important characteristics in the noble metals/cerium oxide system those have been intensively investigated so far, the one is the SMSI (strong metal-support interaction) and the other is the OSC (Oxygen storage and release capacity). The former affects on the tendency of sinterability and durability of supported noble metal catalysts, and the latter governs the reactivity of catalysis. In particular, the combination of the Rh-CeO<sub>2</sub> has the most prominent for both effects among the various possible noble metals-CeO<sub>2</sub> combinations.

The interfacial electronic properties between the Rh clusters and three low index ceria surfaces were studied under the NPT ensemble, at 773 K and 101.343 kPa by using the tight binding-quantum chemical molecular dynamics (TB-QCMD) method. The degree of topmost oxygen mobility was demonstrated as shown in Figure 1 (a) for the unsupported  $CeO_2$  cases, and in Figure 1 (b) for the Rh-supported  $CeO_2$  cases. As the results of comparing the magnitude of the slope of MSD in Figure 1(a), the mobility of topmost oxygen atoms of the unsupported-cerium oxide were following order,  $CeO_2$  (100) >  $CeO_2$  (110) >  $CeO_2$ (111). The (100) plane has the highest surface energy among the low index crystal planes, which originates from the instability of the topmost oxygen located at the bridging positions between two cerium ions<sup>2</sup>. The (111) and (110) surfaces contain a stoichiometric ratio of cations and anions, and they are dipoleless and nonpolar. Whereas, the  $CeO_2$  (100) surface is polar, and the presence of a dipole moment increases the surface Gibbs energy. With other factors being identical, a polar surface is less stable than a nonpolar surface<sup>3</sup>. Therefore it is rational that the mobility of topmost oxygens of the unsupported  $CeO_2$  was the following order; (100) > (110) > (111). However, the presence of the Rh made the topmost oxygen on the (110) facet more mobile as compared with the unsupported  $CeO_2$  (110). In case of the Rh-supported  $CeO_2$ surfaces as shown in Figure 1 (b), the presence of Rh altered the order of topmost oxygen mobility in the cerium oxide as follows;  $Rh/CeO_2$  (110) >  $Rh/CeO_2$  (100) >  $Rh/CeO_2$  (111). It was the same as the order of oxygen vacancy formation energy, which decreases in the order,  $(110) > (100) > (111)^{4-5}$ . This enhancement of the oxygen migration by the Rh was causing with the O-vacant sites on the ceria surface. This is because the topmost oxygens shifted to have stronger affinity with Rh than the Ce where the oxygens originally bonded, and the bond strength of the Rh-O bond became rather stronger than the Ce-O bond.



Fig.1 Time course of MSD of topmost oxygen atoms (a) The unsupported CeO<sub>2</sub>(100), (110) and (111), (b) The Rh-supported CeO<sub>2</sub>(100), (110) and (111).

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#### Morphology and Magnetic Properties of Thick-film Yttrium Iron Garnet Deposited by the Aerosol Deposition Method

We have used the aerosol deposition method (ADM) to direct-write 40  $\mu$ m-thick polycrystalline films of yttrium iron garnet (YIG) (Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>) at room temperature onto sapphire substrates at a deposition rate of 1-3  $\mu$ m/min for integration into microwave magnetic circuits.

YIG is an important magnetic compound with many applications to microwave magnetic devices such as resonators, isolators, circulators, and inductors due to its non-reciprocity, extremely narrow FMR linewidth (< 1 Oe), large saturation magnetization ( $M_s = 1.75$  kG), and small coercivity ( $H_c < 15$  Oe).<sup>1</sup> Accordingly, much effort has been put into creating high-density single-crystal and polycrystalline films. While single crystal films have characteristics that are much improved over polycrystalline films the cost of fabricating these films for low-cost devices is prohibitive. For applications of microwave magnetic devices using polycrystalline materials nano-sized grains of dense defect-free material are essential to minimize loss and achieve a high *Q*-factor. An additional challenge to integrating these films into current semiconductor technology is the high-temperature regime (900 – 1400°C) at which ferrite preparation takes place.

The ability of the ADM to form dense thick films at room temperture over a broad range of material systems makes this a novel method for applications to direct-write electronic circuits with integrated magnetics where low-temperature deposition and thick films are required. There are four main components of the ADM system: 1) an aerosol chamber; 2) a deposition chamber; 3) carrier gas source; and 4) a vacuum pump as shown in Supplemental Figure 1. The aerosol chamber containing an aerosol of fine  $(0.1 - 1 \ \mu m)$  particles is pressurized with nitrogen, helium, or oxygen while the deposition chamber containing a target substrate is pumped to < 1 Torr. The pressure differential  $\Delta P$  (~ kinetic energy) accelerates the aerosolized particles through a nozzle toward the substrate. Previous reports of empirically measured velocities are 150 - 550 m/s for  $Pb(Zr_{0.52},Ti_{0.48})O_3$  (PZT)<sup>2</sup> and 650 m/s for ultrafine silver particles.<sup>3</sup>

As illustrated in Supplemental Figure 2 the film begins to form when incident particles impact, fracture, and embed into the substrate. This impact causes indentation and abrasion of the target area giving rise to an increased surface area which facilitates formation of a well-adhered anchor layer comprised of 10 - 100 nm sized particles. Subsequent impact compacts the underlying film and bonds the crystallites. Since only fracturing occurs, the fabricated film has the same crystal structure as the raw powder, which is comprised of densely packed crystalline nanoparticles held together by what is thought to be close-range mechanical and chemical interactions mediated by fracture, and/or plastic deformation of the particles.<sup>2</sup> The ADM can achieve film density of 95% of the bulk material.<sup>4</sup>

Characterization was conducted on samples deposited under a range of particle velocities. In Supplemental Figure 3 the SEM image shows the surface of a film deposited at  $\Delta P = 300$  Torr (~ 250 m/s) with many particles much less than the average starting size of 0.5  $\mu$ m indicating substantial fracturing. Additionally, the overall particle packing has increased compared with the loose starting powder. Profilometry suggest that a typical film is about 30–40  $\mu$ m thick with an rms roughness of 2–4  $\mu$ m, uniformly deposited, and comprised of nano-crystalline grains with an overall density of about 50% of the theoretical value. Supplemental Figure 4 shows a comparison of XRD intensity (top to bottom) of a pressed YIG puck, as-deposited film, starting powder, and ICDD 01-083-1027 phase card which indicates a single-phase film of polycrystalline cubic YIG with random orientation. VSM measurements give a typical saturation value of 22 emu/g and a coercive field of 27 Oe. FMR measured at 9.78 GHz give an in-plane linewidth of about 360 Oe. While the magnetic properties of the film do not change significantly, the film density is optimized at a pressure gradient of 500 Torr. The main results suggest that the ADM can produce thick, high-purity, nano-crystalline, YIG films that have magnetic properties consistent with the raw starting powder and show promise for applications to direct-write electronic circuits with integrated magnetics where low-temperature deposition and thick films are required.

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#### In-Situ Electronic Characterization of thin LaNiO<sub>3</sub> films via Scanning Tunneling Micropscopy and X-ray Photoemission Spectroscopy

Nate Wilson<sup>1</sup> and Chris Palmstrøm<sup>1,2</sup>

<sup>1</sup>Materials Department, University of California, Santa Barbara, California 93106-5050, USA <sup>2</sup>Department of Electrical and Computer Engineering, University of California, Santa Barbara, California 93106-9560, USA

 $LaNiO_3$  is a metallic paramagnet in the bulk and in the case of thin films with thicknesses greater than a few nanometers. Electrical transport measurements of  $LaNiO_3$  show that thin  $LaNiO_3$  layers on the order of 7 unit cells or less show a transition to insulating behavior. Understanding this behavior is important for incorporating  $LaNiO_3$  into hetero-structures and devices.

LaNiO<sub>3</sub> thin films have been grown using Ozone assisted Molecular Beam Epitaxy (MBE) using a shuttered growth technique alternating La and Ni containing layers. The growth system is connected by ultra-high vacuum transfer chambers to a number of pieces of characterization equipment including a low temperature Scanning Tunneling Microscope (STM) capable of temperatures of 4.5K and an X-ray Photoemission Spectroscopy (XPS) system. This makes it possible to monitor changes in the electrical properties of a single sample at multiple thickness by stopping growth and moving to a characterization chamber performing a measurement and then returning to the growth chamber without ever breaking ultra-high vacuum.

Scanning Tunneling Spectroscopy measurements taken at a temperature of 4.5K shows the opening of a gap in the density of states for LaNiO<sub>3</sub> films grown on Nb doped SrTiO<sub>3</sub> at thicknesses of 3, and 5 unit cells which abruptly closes upon reaching a thickness of 7 unit cells. The gap is on the order of ~1.2 eV with the Fermi level located at mid-gap. The evolution of the valence band was also monitored through the use of in-situ XPS measurements of LaNiO<sub>3</sub> films grown on LaAlO<sub>3</sub> and SrTiO<sub>3</sub> substrates. Resistivity as a function of temperature was measured ex-situ in order to correlate changes in transport behavior to changes in the observed STS and XPS spectra.



(Left) Four point Resistivity was measured as a function of Temperature for several different thicknesses of LaNiO<sub>3</sub> grown on LaAlO<sub>3</sub> substrates. (Right) STS spectra of several different thicknesses of LaNiO<sub>3</sub> grown on Nb doped SrTiO<sub>3</sub> measured at 4.5K.

# New Imaging and Spectroscopy Tools

#### Synchrotron X-ray Scanning Tunneling Microscopy

#### Volker Rose

#### Advanced Photon Source & Center for Nanoscale Materials, Argonne National Laboratory, 9700 S Cass Ave, Argonne, Illinois 60439, USA

In this talk we will discuss the development of a novel high-resolution microscopy technique for imaging of nanoscale materials with chemical, electronic, and magnetic contrast [1,2]. It will combine the sub-nanometer spatial resolution of scanning tunneling microscopy (STM) with the chemical, electronic, and magnetic sensitivity of synchrotron radiation [3]. Drawing upon experience from a prototype that has been developed at the Advanced Photon Source to demonstrate general feasibility, current work has the goal to drastically increase the spatial resolution of existing state-of-the-art x-ray microscopy from only tens of nanometers down to atomic resolution. Key enabler for high resolution is the development of insulator-coated "smart tips" with small conducting apex [4]. After entirely coating sharp tips with insulating films, the coating can be removed from the apex by means of high-resolution focused ion beam milling. Such tips drastically reduce the background of photoejected electrons that would otherwise cause an undesired signal at the sidewall of the tip. The novel microcopy technique will enable fundamentally new methods of characterization, which will be applied to the study of energy materials and nanoscale magnetic systems. A better understanding of these phenomena at the nanoscale has great potential to improve the conversion efficiency of quantum energy devices and lead to advances in future data storage applications.

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#### Webpage

http://www.aps.anl.gov/Xray\_Science\_Division/Sxspm/

#### Photoemission electron microscopy using high intensity, ultrashort laser pulses

Erik Mårsell<sup>1</sup>, Cord L. Arnold<sup>1</sup>, Eleonora Lorek<sup>1</sup>, Diego Guenot<sup>1</sup>, Esben Witting-Larsen<sup>1</sup>, Johan

Mauritsson<sup>1</sup>, Hongxing Xu<sup>1</sup>, Anne L'Huillier<sup>1</sup>, Anders Mikkelsen<sup>1</sup>

<sup>1</sup>Department of Physics, Lund University, Box 118, 221 00 Lund, Sweden

#### Email: anders.mikkelsen@sljus.lu.se

Photoemission electron microscopy (PEEM) in combination intense femtosecond pulses from amplification based laser technology has been suggested to open up for studies of electron dynamics at surfaces using a variety of non-linear processes. One such process is high-order harmonic generation (HHG), which can produce coherent attosecond extreme ultraviolet (XUV) pulses. Using attosecond XUV lasers it has been measured that the excitation of core electrons is  $\sim 100$  attoseconds faster than from the valence band in tungsten and spin dynamics in magnetic materials have been studied [1]. Combining these XUV pulses with PEEM (attoPEEM) opens up for unprecedented spatiotemporal resolution as was theoretically suggested by Stockman et al. [2]. Considerable efforts have since then gone into developing suitable experimental setups for PEEM imaging using XUV radiation from HHG sources [3-5]. Time resolution is achieved using attosecond XUV laser pulses up to 100eV together with laser pulses in the visible to infrared (IR) region in pump-probe experiments. Nanoscale spatial resolution results from imaging electron emission changes by PEEM. Our first experimental developments in this direction, focused on observing plasmon dynamics in metallic nano-structures on their natural time and length scales, were very promising [5], but also demonstrated the severe limitations due to the 1kHz laser repetition rate (based on traditional amplification technology). Space charge problems force us to attenuate the XUV pulse peak intensities at least a factor of 1000 thus limiting the image quality and setting minimum image exposure times in the minutes range at 1kHz rep. rate. To resolve this problem, we recently developed, together with an industrial partner (Venteon, Germany), the worldwide first prototype of a commercial high-repetition rate, few-cycle, CEP-stable Optical parametric chirped pulse amplification (OPCPA) laser. The system delivers pulses of 6 fs duration, 11 µJ pulse energy and repetition rate up to 2 MHz. Combining this laser with the PEEM we performed the first test imaging experiments this autumn. Even with the preliminary test setup, acquisition times are orders of magnitude faster and resolution is estimated to be a factor of 2-3 better than with the 1kHz system. The order of magnitude quantitative improvements are amazing, but importantly this also opens up qualitative new opportunities as we can now for example also do electron energy selective imaging.

Another non-linear concept that can be taken to its extreme with amplified laser technology and PEEM is multiphoton photoemission PEEM using infrared pulses. This has been shown to be a powerful way of mapping out localized field enhancements at surfaces[6], and we show results on both semiconductor and metal nanostructures excited by infrared pulses. By optical frequency mixing in non-linear crystals, we can produce femtosecond laser pulses ranging from 400 nm to 2000 nm, and we demonstrate 6-photon PEEM at the important telecommunication wavelength of 1550 nm.

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#### Nanocrystal surface structure and ligand bonding probed by surface-specific x-ray spectroscopy

E. L. Rosen, K. Gilmore, A. M. Sawvel, A. T. Hammack, B. E. Cohen, J. J. Urban, D. J. Milliron, D. Prendergast and B. A. Helms and <u>D. Frank Ogletree</u>

#### Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

The surface structure and properties of solution-synthesized nanocrystals are directly influenced by ligand chemistry and the nature of ligand-surface bonding, but direct investigation of nanocrystal surface structure and ligand bonding is very challenging. We have developed a novel strategy to directly control and investigate nanocrystal surface structure.[1] After synthesis of PbSe nanocrystals, the original oleaic acid ligands were completely replaced by inorganic ligands bound to the PbSe surface through a unique metal atom such as Fe [2]. As the Fe atoms were present only at the nanocrystal surface, the nature of the surface bonding could be directly investigated though spectroscopic probes target at these "beacon" atoms. X-ray spectroscopic probes include x-ray absorption and XPS at the Advanced Light Source (LBL), deep core level XAS at the Stanford Synchrotron light source (SLAC), and conventional XPS. These studies were complemented by chemical analysis of the nanocrystals by ICP, analytical TEM and Auger microscopy. Experimental spectroscopic studies were supported by theoretical calculations of ligand-surface bonding and theoretical simulations of XAS spectra. Insights into the surface structure and ligand bonding of PbSe nanocrystals will be discussed.

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## SERS and gap-mode TERS investigations of phthalocyanine molecules on nanostructured gold substrates

*E. Sheremet<sup>a</sup>*, *R.D. Rodriguez<sup>a\*</sup>*, *A.G. Milekhin<sup>c</sup>*, *L. Leal<sup>d</sup>*, *V. Kolchuzhin<sup>b</sup>*, *E.E. Rodyakina<sup>c</sup>*, *A.V. Latyshev<sup>c</sup>*, and *D.R.T.Zahn<sup>a</sup>* 

<sup>a</sup> Semiconductor Physics, <sup>b</sup> Microsystems and Precision Engineering, Technishche Universität Chemnitz, Reichenhainer Str. 70, 09126 Chemnitz, Germany

<sup>c</sup> A.V. Rzhanov Institute of Semiconductor Physics, pr. Lavrentieva, 13, Novosibirsk 630090, Russia

<sup>d</sup> Universidad de Los Andes, Merida 05101, Venezuela

Surface-enhanced Raman scattering and tip-enhanced Raman scattering (SERS and TERS) provide drastic enhancement of the Raman signal thus reducing the amount of material which can be detected. It might be expected that combining TERS and SERS could provide a much higher enhancement than what is obtained with each method separately. In this study we address this question in order to find out if it is possible to maximize the Raman enhancement using both techniques simultaneously. The experiments were performed on ultra-thin CoPc (cobalt phthalocyanine) films deposited on specially designed SERS structures. The SERS structures were fabricated by electron-beam lithography and contain nanostructured gold films and gold dimer arrays with controlled size and internanocluster distance. Such structures allowed us to study the effect of nanocluster size or/and internanocluster distance, excitation wavelength, and polarization of the light on the electromagnetic SERS enhancement by CoPc films. Significant enhancement of Raman scattering by CoPc was observed with the 632.8 nm excitation line due to double resonance with the energy of the localized surface plasmon and the electronic transitions in CoPc. SERS by CoPc is further enhanced with decreasing the internanocluster distance. Maximum SERS enhancement was demonstrated for the polarization of the incident light across the dimers (Figure 1a). This is related to the peculiarities of the plasmonic spectrum of gold nanostructures. The SERS enhancement for CoPc deposited on nanostructured gold films was shown to be better or comparable to the enhancement provided by dimers both with 514.5 and 632.8 excitation wavelengths. Then, this structure was probed in TERS conditions in order to realize the socalled "gap-mode TERS" which provides the highest enhancement. The TERS experiment was performed using a customized TERS setup and all-metal atomic force microscopy tips fabricated for this purpose. Our findings show that in terms of ultimate sensitivity in Raman spectroscopy, further enhancement can be achieved by the combination of SERS and TERS pushing up the detection limit.



Figure 1. a) structure layout with key dimensions and polarization direction of the incident light with respect to the dimers; b) enhancement factors for the structures with different dimer dimensions for 632.8 nm excitation line. Red circles (•) show the results for polarization along the dimer, black squares (•) correspond to polarization across the dimer. Solid lines are guides for the eye. Arrows show enhancement factors for a different nanostructured gold film, measured with the same polarizations of the incident light.

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#### Surface Enhanced Raman Scattering by Cu<sub>x</sub>S Nanocrystals

N.A. Yeryukov<sup>1\*</sup>, A.G. Milekhin<sup>1,2</sup>, L.L. Sveshnikova<sup>1</sup>, T.A. Duda<sup>1</sup>, L.D. Pokrovsky<sup>1</sup>,

A.K. Gutakovsky<sup>1</sup>, S.A. Batsanov<sup>1</sup>, E.E. Rodyakina<sup>1</sup>, E. Sheremet<sup>3</sup>,

A.V Latyshev<sup>1</sup> and D.R.T. Zahn<sup>3</sup>.

<sup>1</sup>Rzhanov Institute of Semiconductor Physics, Lavrentiev ave.13, Novosibirsk, 630090 Russia.

<sup>2</sup>Novosibirsk State University, Pirogov str.2, Novosibirsk, 630090 Russia.

<sup>3</sup>Semiconductor Physics, Chemnitz University of Technology, 09126 Chemnitz, Germany.

E-mail : <u>yeryukov@isp.nsc.ru</u>

 $Cu_xS$  nanocrystals (NCs) due to their unique optical and electronic properties are promising candidates for applications in nanoelectronic and photovoltaic devices [1]. Properties of  $Cu_xS$  NCs which can exist in several stable crystal phases can be varied in a wide range. The knowledge of the conditions of phase existence and transformation is of great interest. Therefore, the determination of the conditions of both existence of different phases and the transition from one phase to another is an urgent task.

In this study, the phase transformations, structural, and vibrational properties of  $Cu_xS$  NCs synthesized by Langmuir-Blodgett (LB) technique [2] were under investigation.

The shape, size, and crystal structure of  $Cu_xS$  NCs were determined by scanning and high-resolution transmission electron microscopies as well as reflection high-energy electron diffraction (RHEED). It was found that  $Cu_xS$  NCs possess a spherical shape and a size of 6-8 nm. The crystal structure of  $Cu_xS$  NCs depends on the annealing temperature and is either hexagonal (at 120-150, 350-400 °C) or cubic (at 250°C).

Surface enhanced Raman scattering (SERS) by optical phonons in  $Cu_xS$  NCs with different areal densities placed in the vicinity of ordered (Au) and disordered (Au or Pt) metal nanoclusters was observed and investigated. The SERS spectra of  $Cu_xS$  NCs annealed at different temperatures show a frequency shift of the CuS optical phonons, that indicates the formation of new crystalline phases. RHEED experiments revealed at least three stable phases namely CuS,  $Cu_{1.8}S$  and  $Cu_2S$  upon annealing of  $Cu_xS$  NCs embedded in LB films in the temperature range between 120 and 400 °C. Based on the comparative analysis of SERS and RHEED data, it was established that annealing at annealing at 120-150 °C results in the formation of CuS NCs. Increasing the temperature up to 250°C leads to a lattice rearrangement of the NCs from CuS to  $Cu_{1.8}S$ . Further increasing the temperature to 350-400 °C promotes the formation of  $Cu_2S$  NCs.

This work was supported by the following projects: DFG project ZA146/22-1, 12-02-31412, 13-02-00063), the Presidium of RAS-2010 (grant no. 24.27), and SB RAS (grant no. 134).

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# Rump Session: Single Atom Devices

#### Single impurities in semiconductors studied by STM

#### Paul Koenraad

COBRA, Eindhoven University of Technology, P.O.Box 513, 5600 MB, The Netherlands Email: <u>p.m.koenraad@tue.nl</u>

Single impurities play an increasingly important role in devices and fundamental physics. In the emerging field of solotronics [1], where a solitary dopant determines the optoelectronic functionality, many exciting successes have recently been obtained. We use a Scanning Tunneling Microscope (STM) to examine and manipulate single impurities close to a natural cleavage plane of the semiconductor host to unravel their properties that can be strongly affected by the semiconductor-vacuum interface.

Cross-sectional Scanning Tunneling Microscopy (X-STM) is a unique tool to address single impurities in a III/V semiconductor host. The nearby STM tip allows controlling the ionization state of single impurities and spatially resolving the shape of the wavefunction of a single hole or electron bound to an impurity atom. The X-STM topographic and spectroscopic measurements were performed at room temperature and low (4.2 K) temperature in UHV at the cleaved (110) surface of III/V semiconductor nanostructured materials.

In this presentation I will focus on recent results that we have obtained on bi-stable Si atoms in the outer most layer of GaAs. Si atoms in this outer most layer can occur in two different states: either a deep negatively charged ground state or a meta-stable shallow positively charged state. I will discus how we can electronically and optically control this bi-stable defect and how we can study its switching dynamics. I will demonstrate how we can use a single Si atom as a memory element or photon detector.

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## **Single Atom Spin Qubits in Silicon**

#### Andrew S. Dzurak\*

School of Electrical Engineering & Telecommunications The University of New South Wales Sydney NSW 2052 AUSTRALIA Email: a.dzurak@unsw.edu.au

Spin qubits in silicon are excellent candidates for scalable quantum information processing (QIP) [1] due to their long coherence times and the enormous investment in silicon MOS technology. I will discuss qubits based upon single phosphorus (P) dopant atoms in Si [2]. Projective readout of such qubits had proved challenging until single-shot measurement of a single donor electron spin was demonstrated [3] using a silicon single electron transistor (Si-SET) and the process of spin-to-charge conversion. The measurement gave readout fidelities > 90% and spin lifetimes  $T_1 > 6$  seconds [3], opening the path to demonstration of electron and nuclear spin qubits in silicon.

Integration of an on-chip microwave transmission line enables single-electron spin resonance (ESR) of the P donor electron. We use this to demonstrate Rabi oscillations of the electron spin qubit, while a Hahn echo sequence reveals electron spin coherence times  $T_2 > 0.2 \text{ ms}$  [4]. We also achieve single-shot readout of the <sup>31</sup>P nuclear spin (with fidelity > 99.8%) by monitoring the two hyperfine-split ESR lines of the P donor system. By applying (local) NMR pulses we can demonstrate coherent control of the nuclear spin qubit, giving a coherence time  $T_2 > 60 \text{ ms}$  [5].

Finally, I will discuss very recent experiments on single-atom qubits in isotopically enriched <sup>28</sup>Si devices, in which the near elimination of the background <sup>29</sup>Si nuclear spin bath allows for significantly longer spin coherence times, of order 1 second.

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\* Professor Dzurak leads the Silicon Quantum Computation work-package at the Australian Research Council **Centre of Excellence for Quantum Computation and Communication Technology**.

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# Wednesday

We0730	Registration and Continental Breakfast
We0830	Wednesday Morning Session: Energy Storage and Generation II
We0940	Coffee Break and Poster Viewing
We1040	Wednesday Morning Session: Semiconductors II, Epitaxy, and Surface Microscopy
We1200	Lunch and Poster Viewing
We1400	Wednesday Afternoon Session: Graphene Analogs and Novel 2D Materials I
We1535	Coffee Break and Poster Viewing
We1630	Wednesday Afternoon Session: Nanostructures for Electronics and Photonics
We1805	Poster Viewing
We1900	Conference Banquet and Speaker: Behind the Scenes: Forensics and MythBusters, V. Romero, New Mexico Institute of Mining and Tech.

# Energy Storage and Generation II

#### III-V nanowires for next generation solar cells.

#### Esther Alarcon-Lladó, A. Fontcuberta i Morral<sup>1</sup>

<sup>1</sup>Laboratoire des Materiaux Semiconducteurs, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

#### anna.fontcuberta-morral@epfl.ch

There is an expanding interest in finding novel concepts for increasing the efficiency-to-cost ratio in solar cell devices. Among the different options, semiconductor nanowires provide various paths towards this goal. In this talk, we will discuss different aspects that point out to semiconductor nanowires for next generation photovoltaics: 1) increased device freedom for optimizing the carrier extraction and light absorption, 2) a self-concentrating effect in single nanowires, which provides the potential to surpass the Shockley-Queisser limit [1], and 3) three-dimensional-heterostructure design in up-conversion strategies [2].

References:

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#### We0910

### Optical and Surface Characterization Studies of CdSe Quantum Dots Undergoing Photooxidation

Quantum Dots (QDs) have the potential to perform as the active component in energyefficient lighting and electromagnetic energy harvesting applications. However, the implementation of these engineered QDs demands that their optical and environmental stability be improved, especially with regards to inhibiting failure mechanisms related to the formation of a surface oxide layer. This reaction, accelerated by optical excitation, is called photooxidation. The overarching goal of the work presented here is to explore the chemical and physical mechanisms of photooxidation CdSe core QDs surfaces coated with oleic acid or lauric acid ligands. Understanding photooxidation mechanisms on the surfaces of QDs will allow researchers to mitigate pathways for the photooxidation reaction.

Three integrated analysis techniques were used to measure changes in QD surface chemistry, optical behavior of individual QDs, and QD morphology. Using high-resolution X-ray Photoelectron Spectroscopy (XPS) combined with unique exposure capabilities available at Carnegie Mellon University and the Argonne National Lab Advanced Photon Source, the surface chemistry and bonding of QD oxide layers were examined. QDs with oleic acid ligands or lauric acid ligands were exposed to photooxidizing conditions in an external reaction chamber and transferred to the XPS chamber for analysis. Results have shown that predominantly Se-based oxide compounds formed within the first 18 hours of exposure to  $O_2$  and light as shown in example Figure 1. The reduction of the Se:Cd ratio suggests that Se-O compounds were lost to the chamber vacuum.

Changes in photoluminescence (PL) behavior of single QDs were observed with *in situ* single-molecule fluorescence microscopy experiments. The QDs were enclosed in an environmental chamber of pure  $O_2$  or an inert gas with water vapor and excited with a 488 nm light source during image acquisitions. QD emission intensities were measured with respect to the length of exposure to atmosphere and light. Series of images and statistical analysis will be presented. Results indicated that water vapor played a significant role in PL loss during the early stages of the photooxidation process. Under dry conditions, a strong PL increase was seen as shown in the example Figure 2.

An aberration-corrected STEM/TEM was used to observe morphological changes in individual QDs exposed to  $O_2$  or inert gas and light. A systematic set of exposure lengths and conditions shows oxide growth and structural changes throughout the photooxidation process. Results showed that a thin amorphous layer forms on the QDs very quickly, but non-uniform oxide growth continues slowly for up to 38 hours as seen in example Figure 3. Series of digital images and EDX data are presented.

The systematic studies presented above complement one another by directly comparing surface chemistry results with observed changes in optical behavior and QD morphology during photooxidation. This is the first CdSe QD study to utilize these three analysis methods to describe mechanisms of photooxidation. These results will enhance the scientific understanding of the relationship between nanoparticle surfaces and engineered properties, and the engineer more stable QD structures and compositions.

# The application of zinc oxide nanosheets in dye-sensitized solar cells

#### Daniel R. Jones, James D. McGettrick, Daniel T.J. Bryant, Afshin Tarat, Thierry G.G. Maffeis

Herein we report a systematic investigation into the use of zinc oxide nanosheets in both liquid and solid-state dye-sensitized solar cells. The nanosheets were fabricated through thermal decomposition of layered basic zinc acetate at temperatures between 400°C and 600°C, and were subsequently used to support a ruthenium-based dye in a typical dye-sensitized solar cell configuration. Iodine solution was used as the electrolyte in the liquid cells, and a hole conducting polymer was utilised in the solid-state cells. An average efficiency of around 0.7% was achieved for liquid cells using nanosheets annealed at 400°C, with an average open circuit voltage of 0.66V, short circuit current density of 1.9mAcm<sup>-2</sup> and fill factor of 44%. A substantial decrease in the efficiency and short circuit current density was observed when the nanosheets were annealed at higher temperatures, although the open circuit voltage and fill factor remained fairly constant. The decreases were attributed to problems with the adhesion of the nanosheets to the substrate during the heating process. Not only are the achieved efficiencies comparable to zinc oxide nanowirebased dye-sensitized solar cells reported in the literature, but the nanosheet production process is far simpler and less time-consuming than a typical nanowire growth procedure. We propose that unlike nanowire growth, the manufacture of the layered basic zinc acetate is easily scalable and so offers the exciting possibility of future commercialisation of zinc oxide nanosheet-based solar cells.

#### Enhancing Solar Cell Performance Through the Use of Plasmon Generating Nanocomposite Materials

David Joyce<sup>\*</sup>, Srinivas Saranu, and Victoria Broadley

Mantis Deposition Ltd Unit 2 at Thame 40, Jane Morbey Rd, Thame, Oxfordshire, OX9 3RR, UK

Over the last ten years Mantis Deposition has developed an ultra-high vacuum compatible nanoparticle source capable of producing a wide range of nanoparticle structures with exquisite control over their composition and size. In collaboration with our customers we have demonstrated the capability of this technology in several sectors including energy, surface science, catalysis, biotechnology, and information technology. In this presentation we will describe how the properties of particles on the nanometer scale are being harnessed to enhance the performance of solar cells. We will show how plasmon generating nanocomposite materials can be tuned to optimise the absorption wavelength by controlling the diameter of silver nanoparticles in various thin film structures. We will also outline some of the outstanding challenges and potential strategies on the road to exploitation of this technique.

#### We0925

#### Narrowing of band gap in thin films and linear arrays of ordered TiO<sub>2</sub> nanoparticles

*Yu Liu*, <sup>1,2</sup> James Taing, <sup>1,3</sup> Cheng-Chien Chen, <sup>4,5</sup> Adam P. Sorini, <sup>4</sup> Ming H. Cheng, <sup>1,3</sup> Alexandria M. Margarella, <sup>1,3</sup> Hendrik Bluhm, <sup>6</sup> Thomas P. Devereaux, <sup>4</sup> and John C. Hemminger<sup>1,3</sup>

Utilizing ambient pressure and synchrotron x-ray spectroscopies, we report the properties of thin films and linear arrays of ordered TiO<sub>2</sub> nanoparticles under *in situ* water vapor exposure and heating. X-ray absorption and its linear dichroism spectra provide information on the valence electron configuration of the Ti atom and its ligand crystal field environment, helping to determine the phases of the TiO<sub>2</sub> particles. Our nondestructive depth profiles indicate an enhancement of the density of states (DOS) near the Fermi level due to surface  $Ti^{3+}$  states and oxygen vacancies caused by heating isolated  $TiO_2$ nanoparticles. In contrast, introducing water on the  $TiO_2$  interface eliminates oxygen vacancies and increase  $Ti^{4+}$  configurations, thereby suppressing the DOS enhancement. Our results suggest that the  $TiO_2$  band gap can be tuned reversibly under water exposure and heating, and isolated  $TiO_2$ nanoparticles can potentially enhance solar absorption efficiency and the life time of electron-hole pairs for photocatalysis.

#### Yu Liu will present this work

**Status**: 5<sup>th</sup> year graduate student in Department of Physics and Astronomy at the University of California, Irvine entered in Fall 2009, and employed as Graduate Student Researcher (GSR) with Dr. John C. Hemminger, Vice Chancellor of Research and Chemistry professor.

E-mail: <u>liuy2@uci.edu</u> Phone: 949-742-4335 FAX: 949-824-2738 Address: University of California, Irvine, Department of Physics & Astronomy, 4129 Frederick Reines Hall, Irvine, CA 92697-4575

<sup>1</sup>Center for Solar Energy, University of California Irvine, Irvine, California 92697, USA;
<sup>2</sup>Department of Physics and Astronomy, University of California Irvine, Irvine, California 92697, USA;
<sup>3</sup>Department of Chemistry, University of California Irvine, Irvine, California 92697, USA;
<sup>4</sup>Stanford Institute for Materials and Energy Science, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA;
<sup>5</sup>Advanced Photon Source, Argonne National Laboratory, Lemont, Illinois 60439, USA;
<sup>6</sup>Chemical Sciences Division, Lawrence Berkeley National Laboratory, Mail Stop 6R2100, One Cyclotron Road, Berkeley, California 94720, USA

#### MICRODIFFRACTION AND STRUCTURAL CHARACTERIZATION OF NANOCRYSTALLINE Cu<sub>2</sub>ZnSnSe<sub>4</sub> THIN FILMS: IDENTIFICATION PHASE FORMATION Cu<sub>1.8</sub>Se

A. Dussan<sup>a\*</sup>, Heiddy P. Quiroz<sup>a</sup>, N. J. Seña<sup>a</sup> <sup>a</sup> Group Nano-structured Materials, Department of Physics, Universidad Nacional de Colombia, Bogotá, Colombia \*<u>adussanc@unal.edu.co</u>

#### ABSTRACT

This work presents a study the structural characterization and microdiffraction patterns of Cu<sub>2</sub>ZnSnSe<sub>4</sub> (CZTSe) thin films by X-ray diffraction (XRD) and microdiffraction (XRMD) measurements. Samples were deposited varying both mass (M<sub>X</sub>) and substrate temperature  $(T_s)$  at which the Cu and ZnSe composites were evaporated. CZTSe samples were deposited by co-evaporation method in three stages. From X-ray diffraction (XRD) measurements, it was possible to establish, with increased T<sub>s</sub>, the presence of binary phases associated to the quaternary composite during the material's growth process. From diffraction spectra were found crystalline structural, characteristic phases and sizes of the crystallites. A stannite-type structure in Cu<sub>2</sub>ZnSnSe<sub>4</sub> thin films and sizes of the crystallites varying between 30 and 40 nm, were obtained. X-ray microdiffraction was used to investigate interface orientations and strain distributions when were varied deposition parameters. It was found that around the main peak,  $2\Theta = 27.1^{\circ}$ , the Cu<sub>1.8</sub>Se and ZnSe binary phases predominate, which are formed during the subsequent material selenization stage. A Raman spectroscopy study revealed Raman shifts associated to the binary composites observed via XRD. This case is the first report of the identification of the Cu<sub>1.8</sub>Se and ZnSe binary phases as part of the CZTSe stannite structure.



**Figure 1.** Diffraction pattern of nanocrystalline  $Cu_2ZnSnSe_4$  quaternary composite sample. The figure inset shows crystallographic structure in reference to the atomic location of the composite's atoms.

Key words: Nanocrystalline, Semiconductor, Structural properties.
#### New Measurement Technique for the Separation of Recombination and Trapping Parameters in Semiconductors.

R. K. Ahrenkiel, S. W. Johnston, and D. Kuciauskas National Renewable Energy Laboratory, Golden, CO

A key issue in semiconductor material assessment is the interpretation of minority-carrier lifetime data and the relationship to growth parameters. The minority-carrier lifetime measurement of materials is a powerful technique for material evaluation. In addition, measuring the lifetime of the material prior to device fabrication expedites the research and development. There are several artifacts that occur in the measurement techniques that produce conflicts in data interpretation. Our work addresses the discrepancy between transient photoconductive decay and transient photoluminescence decay as a major source of conflict. Photoconductive decay senses the motion of all excess carriers, whereas photoluminescence decay senses only electron-hole recombination via photon emission. Thus, when a minority carrier is captured by a shallow trap, the instantaneous photoluminescence signal is terminated. However, the associated majority carrier, created by the incident photon, continues to provide a photocurrent. The interaction between recombination and shallow traps often leads to issues of data misinterpretation. Here, we have combined the two techniques into a single instrument that provides measurement of PCD and TRPL simultaneously. The current practice is to measure the sample PCD and TRPL separately and compare the results. The PCD measurements will be performed by the newly developed transmissionmodulated photoconductive decay (TMPCD)<sup>1</sup> method. This technique has been shown to provide a very high speed time response. Therefore, trapped minority carriers contribute to the PC signal whereas photon emission is terminated. The combined technique provides a very unique signature that allows separation of the two transport effects. There are always questions of common injection levels and other variables of the measurement. Our technique bypasses the uncertainty concerning injection level dependence that occurs when separate measurements are made of PCD and TRPL. The measurement data bypasses those issues and eliminates the uncertainty related to injection level and other variables. Our technique leads to a unique separation of trapping and recombination effects. Data will be shown on materials ranging from single crystal to multicrystalline materials that display and range of trapping and recombination effects. These data will illustrate the distinct differences in the behavior of trapping and recombination effects. Details of the new measurement system will also be presented.

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# Semiconductors II, Epitaxy, and Surface Microscopy

#### Electrical and Microstructure Characterization of Low-resistance Palladium/Molybdenum based Ohmic Contacts to n-GaSb on GaAs

Nassim Rahimi<sup>1</sup>, Andrew A. Aragon<sup>1</sup>, Orlando S. Romero<sup>1</sup>, Darryl M. Shima<sup>1</sup>, Tom J. Rotter<sup>1</sup>, Ganesh Balakrishnan<sup>1</sup>, Sayan D. Mukherjee<sup>1</sup>, Luke F. Lester<sup>2</sup>

- (1) Center for High Technology Materials, University of New Mexico, Albuquerque, NM, 87106
- (2) Virginia Polytechnic Institute and State University, 910 Drillfield Drive, Blacksburg, VA 24061

Tel: (415)-637-2704, Fax: (505)-846-2290, email: nrahimi@unm.edu

GaSb is an excellent platform for multi-junction solar cells due to the large range of bandgaps that can be realized on this substrate. GaSb itself has a bandgap of ~0.73 eV and it can be lattice matched with various ternary and quaternary III-V compounds covering bandgaps from 0.3 eV to 1.58eV. Furthermore GaSb and related alloys can also be realized metamorphically on a variety of substrates including GaAs and Silicon allowing for multi-junction metamorphic solar cells as well<sup>1</sup>.

To extract carriers from the semiconductor devices to the external circuit, high quality contacts with low electrical resistances are needed. In the case of solar cells and thermophotovoltaic (TPV) cells, the series resistances of the cells are often dominated by ohmic contacts. Therefore low resistance contacts are essential in such devices<sup>2</sup>.

This work presents improved ohmic contacts with ultra-low resistances on molecular beam epitaxial (MBE) grown n-GaSb on GaAs. Different doping concentrations and thicknesses of n-GaSb have been investigated to understand the tunneling transport mechanism between the metal contacts and the semiconductor. Different contact metallization and process windows for annealing time and temperature have been studied to minimize ohmic contact resistances and to achieve optimal penetration depth of Au in GaSb for low resistances. Molybdenum/Palladium (90/10 ratio) is used as a diffusion barrier in this metallization scheme. The reasons for selecting Mo as the diffusion barrier material is as follows. First, Mo is a refractory metal and has low atomic diffusion and then has good diffusion barrier properties. Second, compared with other refractory metals such as Pt, Ni, Cr, W, its work function is smaller. This is important because for the metal with high work function, contact barrier height increases and it is disadvantageous to the formation of Ohmic contacts. In addition, Mo is relatively cheap and easy to implement in industrial production and has potential commercial value.

Furthermore, the fabrication, electrical characterization and microstructure analysis of the metalsemiconductor interfaces created during ohmic contact formation are discussed. The characterization techniques include cross-sectional Transmission Electron Microscopy and Energy Dispersive Spectroscopy. Specific transfer resistances down to 0.1  $\Omega$ -mm and specific contact resistances of  $3 \times 10^{-6}$  $\Omega$ -cm<sup>2</sup> have been observed.

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<sup>&</sup>lt;sup>2</sup> A. Vogt, H.L. Hartnagel, G. Miehe, H. Fuess, J. Schmitz, J. Vac. Sci. Technol. B 14, 3514–3519 (1996).

#### Formation and characterization of an In/Pb binary surface alloy on Ge(111): LEED, STM, ARPES and core level studies

Hafiz M. Sohail and R. I. G. Uhrberg

Department of Physics, Chemistry and Biology, Linköping University, S-581 83 Linköping, Sweden

Metals adsorbed on semiconductor surfaces are important since they provide well-ordered one or two dimensional structures useful for the study of various physical phenomena. Most of such studies have been restricted to a single metallic species, while the combination of two metals has not been given similar attention. In a few studies, a tiny amount (0.1 - 0.2 monolayers (ML)) of a second metal has been added onto a well-defined monolayer formed by the initial metal. In some cases this results in new reconstructions due to periodic positions of the added metal atoms. This kind of surfaces is, however, not considered to be a binary surface alloy. In an effort to form such surface alloys, i.e., a new class of 2D material for low-dimensional physics, we have investigated several combinations of metals on elemental semiconductor surfaces, of which the combination of Sn and Ag has been reported.<sup>1,2</sup> Another combination, In and Pb, also forms ordered binary surface alloys. The In/Pb/Ge(111) surface alloy presented here was formed by evaporating 1.33 ML of Pb onto a Ge(111)c(2×8) surface, which after annealing to  $\approx 200$  °C exhibited a  $\sqrt{3} \times \sqrt{3}$  periodicity. Further addition of 0.85 ML of In onto this surface and annealing at a temperature of  $\approx 200$  °C, resulted in a well-defined In/Pb surface alloy with 3×3 periodicity, as verified by both low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). We have performed detailed investigations of the atomic and electronic structures of this surface alloy. STM images obtained at 50 K reveal atomic sized features with a local hexagonal arrangement. Each 3×3 unit cell contains nine such features indicating a structure with 9 atoms per  $3\times3$  cell. Angle resolved photoelectron spectroscopy (ARPES) was used to obtain 2D band dispersions in the high symmetry directions of the  $3\times 3$  surface Brillouin zone (SBZ). We have identified five surface bands within the bulk band gap. Four of them cross the Fermi level leading to a metallic character of the surface. Fermi contours of the metallic bands, mapped in 2D k-space, show interesting features. In particular, two differently rotated hexagon like contours show a degeneracy of two metallic bands along the  $\overline{\Gamma} - \overline{M}$  and  $\overline{\Gamma} - \overline{K}$  directions. Similarly, rotated constant energy contours provided key information on the atomic structure of the Sn/Ag/Si(111)2×2 surface alloy.<sup>2</sup> Core level spectra of Pb 5d and In 4d show sharp core levels with no obvious shifted components indicating a well-ordered environment for the In and Pb atoms. Among the large number of possible binary combinations of atomic species, it is likely that several well-ordered surface alloys will be discovered. Of these some may exhibit exotic properties, which acts as an inspiration for this kind of studies.

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#### Polarization doping in graded III-nitride heterostructures

Morgan Ware

Arkansas Institute for Nanoscience and Engineering, University of Arkansas, Fayetteville, AR 72701, USA

The fixed polarization field which is intrinsic to nitride based III-V semiconductors in the wurtzite crystal phase can be manipulated during growth by varying the alloy composition. Recent experiments have demonstrated the effect of gradually changing this spontaneous polarization in a nitride structure by grading the composition from GaN to  $Al_xGa_{1-x}N$  while maintaining a metal polar growth. The results indicate that a three dimensional space charge region is created that results in an accumulation of a very high (n ~ 10<sup>18</sup> cm<sup>-3</sup>) concentration of electrons without the need for dopant atoms. These bulk-like layers have realized relatively high electron mobilities which approach that of nitride based 2DEG high electron mobility transistor structures [1]. Meanwhile, other groups using similar grading techniques have also demonstrated a significant enhancement in the doping effectiveness of Mg atoms for creating p-type material [2].

Here, the results of merging these two techniques to make devices based entirely on three dimensional "polarization doping" will be discussed. The space charge field which results from the changing internal polarization field of graded AlGaN films is used to form a simple p-n junction device. Our devices are fabricated from films which are graded from GaN to AlGaN then reverse graded back to GaN without the intentional addition of impurity dopants. Structural characterization of the films is reported through X-Ray diffraction rocking curves and reciprocal space maps, and the rectifying behavior of the device is demonstrated through temperature dependent I-V measurements.

The present results demonstrate that without intentional doping, compositionally graded nitride samples grown by plasma assisted molecular beam epitaxy can have a very high carrier concentration, up to  $n_{2D} > \sim 10^{14} \text{ cm}^{-2}$  for electrons at room temperature for a 100 nm thin film. Notably, these samples do not exhibit carrier freeze out and maintain their high sheet density down to cryogenic temperatures.

In addition, measurements on sawtooth graded samples demonstrate rectifying properties, i.e., forward bias passing and reverse bias blocking with large breakdown voltages [3]. Electrical and structural characterizations which support the potential of this technique of "polarization doping" for constructing useful devices will be presented.

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#### Effects of Plasma Treatment on Evolution of Surface Step-Terrace Structure of

#### Critically Cleaned C-Plane Sapphire Substrates: An AFM Study

Dan Zhang Yang Gan<sup>\*</sup>

School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin, 150001, China.

#### \*Email: <u>ygan@hit.edu.cn</u>

Evolution of step-terrace (vicinal or stepped) structure of cleaned c-plane sapphire substrates irradiated with low-pressure air plasma was studied with atomic force microscopy (AFM). Depending on plasma irradiation time and post-annealing treatment, original structure with uniform terrace width and sharp steps undergoes distinct morphology changes. For the first time to our knowledge, with longer plasma irradiation up to 30 min, we observed pairing of neighboring terraces into alternating wider and narrower terraces, steps roughening and terrace etching, and "step-terrace free" morphology with etched pits which are stable against annealing. These phenomena are discussed in terms of surface diffusion, epitaxial and chamber temperature effects. The findings reported here will have important implications for plasma modification, epitaxial growth and contamination control of sapphire substrates.



AFM height images of c-plane sapphire substrates. (a) Cleaned with the modified RCA method, (b-d) Plasma irradiated for 10 min, 20 min and 30 min. (e-f) Vaccum annealed at 1000 °C for 1 hr.
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## Structural, morphological and optoelectrical characterization of Bi<sub>2</sub>S<sub>3</sub> thin films grown by co-evaporation

F. Mesa<sup>a,b,\*</sup>, C.A. Arredondo<sup>b</sup>, W. Vallejo<sup>c</sup>

<sup>a</sup>Departamento de Ciencias Básicas, Universidad Libre, Cra. 70 Nº 53-40 Fax: +57-1-4232720, Bogotá, Colombia

<sup>b</sup>Departamento de Física, Universidad Nacional de Colombia, Cra. 30 Nº 45-03 Fax: +57-1-3165135, Bogotá, Colombia

<sup>c</sup>Grupo de fotoquímica y fotobiología, programa de Química, Facultad de Ciencias Básicas, Universidad del Atlántico, Barranquilla, Colombia

\*Corresponding author email: fgmesar@unal.edu.co

#### Abstract

This work presents results about of synthesis and characterization of polycrystalline ntype Bi<sub>2</sub>S<sub>3</sub> thin films. The films were grown by a chemical reaction from co-evaporation of their precursor elements on a soda-lime glass substrate. The effect of the experimental conditions on the optical, morphological structural properties, the growth rate and the electrical conductivity ( $\sigma$ ) was studied through spectral transmittance, Xray diffraction (XRD), atomic force microscopy (AFM) and  $\sigma$  versus T measurements, respectively. The results showed that, the films grow only in the orthorhombic Bi<sub>2</sub>S<sub>3</sub> bismuthinite phase. It was also found that the Bi<sub>2</sub>S<sub>3</sub> films present an energy band gap (E<sub>g</sub>) of about 1.38 eV, regardless of the thickness of the samples. In addition to these results, the electrical conductivity of the Bi<sub>2</sub>S<sub>3</sub> films was affected by both the transport of free carriers in extended states of the conduction band and for variable range hopping transport mechanisms, each one predominating in a different temperature range.

Keywords: Bi<sub>2</sub>S<sub>3</sub>, buffer layer, solar cells

## Cationic two-dimensional surface states at epitaxial InAs(111)A surface characterized using low-temperature scanning tunneling microscopy

Kiyoshi Kanisawa\* and Hiroyuki Tamura

NTT Basic Research Laboratories, NTT Corporation 3-1, Morinosato Wakamiya, Atsugi, Kanagawa, 243-0198, Japan

TEL : +81 46 240 3567, FAX : +81 46 240 4727 \*kanisawa.kiyoshi@lab.ntt.co.jp

Surface reconstruction structures are known to have two-dimensional (2D) electronic states. A periodic  $(2\times2)$  arrangement of atoms known as the vacancy-buckling structure [1] is a unique one stably formed on the InAs(111)A surface [2]. The unit cell of the top most atomic layer of this structure consists of three In atoms. The atomic arrangement is equivalent to that of a Kagomé lattice [3]. In this work, the local density of states (LDOS) of this cationic 2D lattice was characterized at 5 K using low-temperature scanning tunneling microscopy (LT-STM).

Scanning tunneling spectroscopy (STS) of the clean InAs surface epitaxially grown on the InAs(111)A substrate by molecular beam epitaxy revealed a broad energy spectrum peak above the Fermi level ( $E_{\rm F}$ ) in the energy region of the projected bulk band gap at the  $\Gamma$  point along the (111)A surface [4]. Around the positively charged In antisite ( $In_{As}$ ) defect beneath the surface, downward band bending by the Coulomb potential locally makes the LDOS at higher energy move to the lower energy. If the moved state has a higher (lower) LDOS, the LDOS measured at a constant bias voltage appears higher (lower) around In<sub>As</sub>. In the modified area, the higher (lower) energy part of the spectrum peak shows a lower (higher) LDOS. The energy dependence of the extent of the modified area near In<sub>As</sub> indicates that the electron wave function obeys the periodic boundary condition of the lattice; that is, there are free electronic Bloch states of the energy band. According to electron scattering theory, a plane wave (quantum number  $m_1$ of orbital angular momentum and wavelength  $\lambda$ ) does not get closer than  $m_1 \cdot \lambda/2\pi$  to the scattering center due to centrifugal barrier potential term of the 2D Schrödinger equation. This suggests that a larger diameter of the modified area means a longer  $\lambda$  of the unmodified state at the corresponding energy. At the higher energy part of the spectrum peak, higher energy shows longer  $\lambda$  (electron effective mass  $m^* < 0$ ). At the lower energy part of the peak, higher energy shows shorter  $\lambda$  (m<sup>\*</sup> > 0). Since the energy spectrum is found above  $E_F$  and empty, the free electronic evidence originates from the 2D cation lattice at the surface. The broad spectrum width is comparable to that of the tight-binding Kagomé lattice band as expected.

All STS results excellently trace the LDOS spectrum signatures of dispersive bands of the Kagomé lattice. Therefore, the  $(2\times2)$  reconstruction at the (111)A surface provides a useful basis to study the characteristics of massless Dirac fermions as well as flat band ferromagnetism [3], which are distinctive properties of the Kagomé band.

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#### Cold Tip SPM

A new generation of variable temperature SPM for spectroscopy

B. Uder, J. Koeble, C. Troeppner

#### Oxford Instruments Omicron NanoScience, 65232 Taunusstein, Germany

We will present the design and first results of a new generation of variable temperature scanning probe microscope that has been developed to enhance the performance in tunneling spectroscopy at lower temperatures. The new SPM is based on a novel design which uses a new flow cryostat compatible for cooling with liquid nitrogen or helium. In contrast to earlier established designs of variable temperature SPM's where only the sample is cooled, this new SPM also cools the scanner and tip. This is realized by a newly developed compact and stable SPM stage with thermal shields and a dedicated cooling management system. With this design we achieve lower temperatures and improve drift by more than an order of magnitude compared to previous variable temperature stages. Sample temperatures down to 10 K (with helium) and 95 K (with nitrogen) have been achieved. The temperature stability is better than 5 mK/min and the measured thermal drift is below 1 pm/s. During cooling the mechanical z stability is better than 3 pm. These conditions offer enhanced spectroscopy measurement capability with a cold tip. "Loop off" times of up to 10 s per single spectroscopy curve have been measured. The new flow cryostat also allows for changing between nitrogen cooling and helium cooling in less than 90 min during a running experiment. Pre-cooling with nitrogen during the starting phase of an experiment also reduces running costs for liquid helium. This new SPM is configured for imaging in STM as well as AFM with a non-optical sensor in a temperature range between 10- 400 K. Switching between the 2 modes can be accomplished without breaking vacuum.

#### **Figures:**



STM on Ag(111) at 10K showing electron standing waves



I(V) on Ag(111) at 10K, loop off for 10s during voltage ramp from -1V to 1V and back to -1V



STM on Au(111) at 95K using nitrogen z stability < 3pm



Simultaneous measured dI/dV on Ag(111) at 10K , loop off for 10s

#### Novel Applications in Surface Science – *In situ* sample analysis in extreme environments

Thomas Schulmeyer\*

SPECS Surface Nano Analysis Inc., 20 Cabot Blvd., Suite 300, Mansfield, MA 02048 (\*Thomas.Schulmeyer@specs.com)

Modern devices are often only functional in environments far away from ultrahigh vacuum, which is still considered the standard operating condition for all Surface Science techniques. Due to miniaturiziation down to the nanoscale, surfaces are increasingly important for device performance. In order to contribute to advanced material analysis in future Photoelectron spectroscopy, Scanning Probe Microscopies and related techniques must be performed in generic or near generic device environments. Such an environment would mean high, elevated or near ambient pressures of defined working gas mixtures, liquid media, potentials or magnetic fields; extremely low or high temperatures might also be necessary. Of course, all standard Surface Science Techniques did not work under these extreme environments previously. This work summarizes and presents existing solutions for present and future development routes to new instruments, and displays how material analysis methods are functional under these working conditions. The opportunities and limitations will be discussed from the perspective of suppliers of scientific instruments. And finally, application examples and results from existing In situ methods will be demonstrated. These methods include: high pressure treatment cells, complete High Pressure or Near Ambient Pressure Photoelectron Spectroscopy or Scanning Probe Microscopy Systems (NAP-PES or NAP-SPM), liquid and electrochemical cells, Liquid sample "manipulators", and concepts and status of equipment working in the highest or lowest temperatures, high magnetic fields and static or dynamic potentials.

# Graphene Analogs and Novel 2D Materials I

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#### Atomically thin MoS<sub>2</sub> crystals - a new two-dimensional semiconductor

Jie Shan Department of Physics Physics Case Western Reserve University

The transition metal dichalcogenides (TMDs) represent an interesting class of bulk crystals that are built up of van der Waals bonded layers. As such, just like graphene, they can be separated into stable units of atomic thickness by mechanical exfoliation or grown in the form of atomic monolayers by chemical vapor deposition (CVD). Although the structure of TMD monolayers, such as MoS<sub>2</sub>, is similar to that of the graphene honeycomb, the A and B sublattices, rather than both being occupied by C atoms, are occupied either by Mo atoms or by a pair of S atoms. This difference in symmetry leads to many interesting and unique properties in TMD monolayers.

In this talk, I will present our recent optical studies on mono- and few-layer samples of  $MoS_2$ . We show that quantum confinement effects lead to a crossover in  $MoS_2$  from a bulk indirect gap semiconductor to a direct gap semiconductor in the monolayer limit [1]. And the band gap energy can be continuously tuned by an in-plane elastic strain field [2]. In addition, we demonstrate that, as is common for lower-dimensional materials, many-body interactions are strong in atomically thin  $MoS_2$  due to significantly reduced Coulomb interactions. The optical properties are significantly modified: excitons and trions (bound states of two electrons and a hole) have been observed with large binding energies in monolayer  $MoS_2$ [3]. Finally, we discuss the unique valley properties of this class of materials and experimental demonstrations of the production of valley polarization by optical pumping with circularly polarized light [4].

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## Direct Measurement of the Thickness-Dependent Electronic Band Structure of MoS<sub>2</sub>

Wencan Jin,<sup>1</sup> Po-Chun Yeh,<sup>2</sup> Nader Zaki,<sup>2</sup> Datong Zhang,<sup>1</sup> Jerzy T. Sadowski,<sup>3</sup> Abdullah Al-Mahboob,<sup>3</sup>Arend M. van der Zande,<sup>4,5</sup> Daniel A. Chenet,<sup>5</sup> Jerry I. Dadap,<sup>1</sup> Irving P. Herman,<sup>1</sup>Peter Sutter,<sup>3</sup> James Hone,<sup>5</sup> and Richard M. Osgood, Jr.<sup>1,2</sup>

<sup>1</sup>Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027, USA

<sup>2</sup>Department of Electrical Engineering, Columbia University, New York, New York 10027, USA

<sup>3</sup>Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, USA

<sup>4</sup>Energy Frontier Research Center, Columbia University, New York, New York 10027, USA

<sup>5</sup>Department of Mechanical Engineering, Columbia University, New York, New York 10027, USA

Molybdenum disulfide (MoS<sub>2</sub>) is layered transition-metal dichalcogenide semiconductor that can be fabricated into an atomically thin two-dimensional (2D) material. Monolayer MoS<sub>2</sub> consists of a single layer of Mo atoms sandwiched between two layers of S atoms in a trigonal prismatic structure. This 2D system has attracted great interest because of its distinctive electronic and optical properties, such as (i) a transition from indirect-to-direct band gap in going from the multilayer to monolayer crystal due to a missing interlayer interaction in monolayer form and (ii) strong spin-orbit-coupling-induced split valence bands due to broken inversion symmetry, which makes  $MoS_2$  interesting for spin-physics exploration. Both properties have been predicted with density functional theory (DFT) calculations and indirectly demonstrated using photoluminescence and Raman spectroscopy.

Here, we first report the first direct observation of the thickness-dependent electronicband structure of MoS<sub>2</sub>. Micrometer-scale, angle-resolved photo-emission spectroscopy (micro-ARPES) of both mechanically exfoliated and chemical-vapor-deposition-grown MoS<sub>2</sub> crystals provides direct evidence for the shifting of the valence band maximum from  $\overline{\Gamma}$  (Brillouin zone center) to  $\overline{K}$  (Brillouin zone corner), for the case of MoS<sub>2</sub> crystals of greater than one layer, to the case of monolayer MoS<sub>2</sub>. The results are also compared with rigorous by DFT calculations of both the bands and the UV transitions. This evolution in band structure provides import support for indirect-to-direct bandgap transition in going from few-layer to monolayer MoS<sub>2</sub> and can be attributed to changes in quantum confinement as the number of layer decreases. One of the consequences of this evolution is a decrease in dispersion of the valence band at  $\overline{\Gamma}$  in monolayer MoS<sub>2</sub>, thus leading to a dramatic increase in the hole effective mass. Our results explains the low hole mobility of monolayer MoS<sub>2</sub> compared to thicker MoS<sub>2</sub>. An apparent valence band compression is found in both exfoliated and CVD-grown monolayer MoS<sub>2</sub> and compared with DFT calculations.

In addition, we have recently examined additional metal dicholgenides van-der-Waals crystals, from both exfoliation and CVD growth, using microARPES. These results along with other UHV probes such as LEED will be discussed in the talk.

#### Variability in exfoliated MoS<sub>2</sub> generated by defects

R. Addou, S. McDonnell, C. Buie, C. L. Hinkle and R. M. Wallace Department of Materials Science and Engineering The University of Texas at Dallas, Richardson, Texas 75080, USA

Transition metal dichalcogenides (TMDs) are two-dimensional materials that have received an increased attention since the successful exfoliation of graphene<sup>1</sup>. Unlike graphene, many TMDs have a bandgap in the range of 1-2 eV making them promising materials for future MOSFET and tunnel FET devices<sup>2</sup>. In this study we designed experiments using scanning tunneling microscopy and spectroscopy (STM and STS), X-ray photoelectron spectroscopy (XPS) and Schottky diode measurements to show that reliable interpretation of electrical data requires a consistent selection of identical areas. The targeted sample in this investigation is the most studied transition metal dichalcogenide  $(TMD)^{3,4}$ : the molybdenum disulfide, MoS<sub>2</sub>. The XPS measurements show detectable variations in the core level spectra across the  $MoS_2$ . Explicitly, a low binding energy shoulder on the Mo 3d core level is observed. Using the same sample, the I-V characteristics show that about 20 % of the regions exhibit a p-type behavior. Additional STM and STS experiments are performed to understand the origin of the observed variability. The STM images registered on the clean  $MoS_2(0001)$  surface show the presence of defects. The defect density changes across the surface generating a variation in the electronic signature measured by I(V) curves. We established a correlation in the observed  $MoS_2$  variability between I-V, STM/STS, and XPS measurements. The regions with low defect density act as expected n-type MoS<sub>2</sub> and the regions with high defect density reveal a ptype behavior concurrent with the detection of additional component in the Mo 3*d* core level. Consequently, device performance will be significantly affected by the concentration of these defects. These results suggest that natural MoS<sub>2</sub> is not of sufficient quality for reliable device studies and the synthesis of controllable and high quality TMD substrates must be developed in order to provide low-defect and large-area TMDs.

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#### Growth of single-layer MoS<sub>2</sub>, MoSe<sub>2</sub> and their alloys on flat and pre-patterned SiO<sub>2</sub>/Si

John Mann, Edwin Preciado, David Barroso, Gretel von Son, Ariana Nguyen, Dennis Pleskot, Velveth Klee, Sarah Bobek, Dezheng Sun, <u>Ludwig Bartels</u>

The electronic structure of 2D transition metal dichalcogenides (TMD) monolayers of the form  $MX_2$  (M = Mo, W; X = S, Se) differs significantly from that of graphene. While the latter is a semi-metal with a linear energy dispersion near the K point, the monolayer TMD sheets have direct bandgaps of 1-2 eV, with valence band maxima and conduction band minima at the K point. Excitons and charged excitons (trions) can be created in TMD monolayers by optical excitation, while the use of circular polarized light has been shown to produce long-lived valley polarization. Here we show the ability to tune continuously the bandgap of this distinctive class of atomically thin materials through the growth of S/Se alloys; this opens many new possibilities for basic studies and device concepts. The enormous impact of such bandgap engineering in traditional III-V semiconductors on both fundamental studies of electron transport and on applications from high performance transistors to lasers is well known. For the  $MoS_{2(1-x)}Se_{2x}$  system, the formation of both vertical heterojunctions of stacked monolayers and lateral heterostructures of abutting, or in their composition laterally varying, monolayers should be possible.

Patterning of SiO<sub>2</sub>/Si substrates prior to growth of TMDs permits distribution of the resultant single-layer crystallites in a predictive manner. Here we will show examples utilizing regular hole patterns and trenches on the substrate. We find growth of 2D, micron-scale crystallites at each substrate feature. In future technological applications, this may facilitate the growth TMD material directly at their intended area of application (e.g., in a transistor channel), without the need for the optimization efforts and thermal budget, that would be required to generate wafer-scale single-crystalline films.

The growth mode of TMDs that permits formation of triangular, single-crystalline 2D islands on the tens or even hundreds of micron scale on oxide substrates is not yet well understood. Experiments, in which through partial liftoff we can explore the substrate location right underneath the island offer novel insights that will be discussed.

#### Modification of Monolayer Molybdenum Disulfide Surfaces in UHV

Molybdenum Disulfide (MoS<sub>2</sub>) may be regarded as the semiconducting analogue of graphene. A single layer of MoS<sub>2</sub> consists of a sulfur-molybdenum-sulfur tri-layer, is stable in air and is a native semiconductor, thus it can serve as the active material in a transistor. However, the stability of MoS<sub>2</sub>, which is at the root of all these applications, can also be a challenge when it comes to modifying its properties and attaching it securely to other elements of an electronic structure. Here, we have found that bombardment of MoS<sub>2</sub> with low energy argon ions can selectively remove the top-layer sulfur atoms while keeping the overall material structure intact. This processing technique is novel for MoS<sub>2</sub> but compatible with conventional semiconductor device fabrication, which gives us an easy way to activate MoS<sub>2</sub> for the incorporation of dopant atoms or attachment of organic species.

To characterize our processing method we perform *in situ* X-ray photoelectron spectroscopy. By monitoring the intensity of the sulfur and molybdenum signatures we can determine the evolution of the film composition during processing. We find a continuous decrease in the sulfur to molybdenum ratio that is proportional to the exposure to argon ions but no overall removal of molybdenum. This indicates that under our processing conditions sulfur atoms are removed selectively. We also note that the overall spectral signature of  $MoS_2$  does not change even after removing  $\frac{1}{4}$  of the total sulfur. This finding highlights that, except for becoming sulfur-depleted, the  $MoS_2$  crystalline structure stays intact. Concurrent measurement of the photoluminescence of the  $MoS_2$  film shows a dimming of this effect with the increasing amount of sulfur removed. This effect can be explained by the sulfur vacancies quenching photogenerated excitons, if they are created by optical adsorption in their direct vicinity.

Once sulfur is removed, the  $MoS_2$  surface is active for subsequent reactions to modify its properties. Exposure to air quickly causes the sample to decompose exemplifying the reactivity of the vacancies. The vacancies can be removed by exposure to a sulfur source, which allows the photoluminescence to return. Current work addresses modification of this approach to insertion of a dopant or band gap modifying species.

#### Nanoscale Characterization Study of the Interface between a Carbon Substrate and Two-dimensional Gallium Selenide Nanoflakes

Raul D. Rodriguez<sup>†</sup>\*, Alexander Villabona<sup>†,‡</sup>, Susanne Müller<sup>†</sup>, Evgeniya Sheremet<sup>†</sup>, Jana Kalbacova<sup>†</sup>, Santos A. Lopez-Rivera<sup>‡</sup>, Dietrich R.T. Zahn<sup>†</sup>

<sup>†</sup>Semiconductor Physics Group, Technische Universität Chemnitz, Chemnitz 09107, Germany <sup>‡</sup>Universidad de Los Andes, Applied Physics Lab, Merida 05101, Venezuela

Due to their exceptional properties that can be tuned by material thickness and morphology, two-dimensional materials awakened a strong interest in the scientific and technological communities [1]. Most research on 2D materials beyond graphene has been limited to  $MoS_2$  and alike but very few groups have investigated the GaSe system. This situation offers good opportunities for the discovery of novel physical phenomena, in particular due to the highly non-linear properties of GaSe. Few layer GaSe was recently applied as an active channel in a field effect transistor and also as the active layer in high performance photodetectors [2,3]. In this latter application, an impressive quantum efficiency above 1300% was observed [4]. However, until now there was no report on the spatial heterogeneities in isolated GaSe nanoflakes. Our aim is to investigate possible spatial anisotropies at the nanoscale, visible in micro- and nano-Raman spectroscopies as well as structural modifications in GaSe induced by a crystalline carbon substrate (HOPG) studied by atomic force microscopy (AFM). We show the highly anisotropic nature of GaSe reflected in the Raman spectra with strong changes at the carbon/GaSe interface. We demonstrate the existence of highly localized Raman modes at the edges of GaSe nanoflakes. A strong electromagnetic coupling with the substrate at such edge-interface regions is observed as Raman enhancement of the G mode of the HOPG substrate. In addition, morphological studies of the nanostructure of GaSe by AFM show the mimicking of native defects in HOPG by the GaSe layers. Such defect translocation evidences the strong interaction between GaSe and the topmost graphene layers of HOPG. This result implies that the nanoscale topography of GaSe could be directly controlled at high precision by controlling the patterning of the underlying substrate opening a venue for the non-invasive nanolithography of this promising 2D nanomaterial.



*a*) Raman spectroscopy image of the G band from the HOPG substrate evidencing the enhancement at the edges of the GaSe flake. *b*) Spectrum of the G band extracted from the Raman map. *c*) Topography of the flake determined by AFM showing the mimicking by GaSe of the HOPG substrate defects.

#### Acknowledgments

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# Nanostructures for Electronics and Photonics

#### Radial growth surfaces and interfaces in MOCVD grown III-V nanowires

#### J. Wong-Leung

Email presenting author :jenny.wongleung@anu.edu.au

Research School of Physics and Engineering/ Centre for Advanced Microscopy, The Australian National University, Canberra ACT0200, Australia

Nanowires offer potential applications for the next generation of electronics and photonics devices. III-V nanowires are successfully grown using two main techniques (i) the vapour-liquid-solid (VLS) technique with catalyst particles such as Au or self-catalysis with Ga in GaAs growth or (ii) selected area epitaxy. Key challenges in nanowire growth for device application are control over phase, composition and morphology. Additional complications arise from the growth of heterostructures in both radial and axial heterostructures (a) abruptness of interface (b) vertical or kinked growth for axial hetrostructures and (c) composition variation. In this paper, we concentrate on (a) the growth of AlGaAs radial heterostructures on GaAs cores, (b) polarity driven issues in homogeneity and nanowire multishell heterostructures and (c) surfaces and interfaces in other III-V semiconductor nanowires.

We present detailed transmission electron microscopy (TEM) and scanning transmission electron microscopy studies (STEM) of both III-V nanowires and core-shell nanowires grown by metal organic chemical vapour deposition (MOCVD). In particular, we concentrate on the understanding of the radial growth of Al<sub>x</sub>Ga<sub>1-x</sub>As shells grown radially on GaAs core nanowires. The core nanowires were grown using the Au-catalysed VLS technique by the two temperature growth method previously described [1]. Time-resolved photoluminescence studies of the best core shell nanowires show significant improvement in the carrier lifetime and the effectiveness of the AlGaAs shell to minimise surface recombination [2,3]. High angle annular dark field images of cross-sections of these coreshell nanowires show the presence of a GaAs core faceted along the {110} planes with a hexagonal shape, an Al<sub>x</sub>Ga<sub>1-x</sub>As shell showing similar faceting with intriguing radial Al rich bands along the {112} directions [4]. A trigonal symmetry involving these bands is revealed and discussed with regards to the polarity of the nanowire structure. The microstructure is discussed with regards to the remarkable optical properties of these nanowires. Other examples of polarity driven issues affecting surfaces and interfaces in other III-V nanowires grown studied will also be discussed.

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# Polarization-induced UV nanowire LEDs on silicon and molybdenum films

A. T. M. G. Sarwar<sup>1</sup>, S. D. Carnevale<sup>2</sup>, T. F. Kent<sup>2</sup>, P.J. Phillips<sup>3</sup>, R.F. Klie<sup>3</sup>, R. C. Myers<sup>1,2</sup>.

<sup>1</sup>Dept. of Electrical and Computer Engineering, The Ohio State University, Columbus, <sup>2</sup>Dept. of Materials Science and Engineering, The Ohio State University, Columbus, <sup>3</sup>Dept. of Physics, University of Illinois at Chicago,

Polarization-induced nanowire light emitting diodes (PINLEDs) are formed by grading the composition along the c-axis of AlGaN nanowires using plasma-assisted molecular beam epitaxy (PAMBE)<sup>1</sup>. Majority (~90%) of the nanowires grow along N-face ([000-1]) crystallographic orientation, thus a p-down heterostructure forms<sup>2</sup>. Here we explore several methods for designing p-down oriented UV nanowire LEDs: growing p-down nanowire LEDs on p-Si substrate, incorporating an interband tunnel junction at the base of the nanowires, and directly depositing the nanowires on molybdenum films. Remarkably, UV nanowire LEDs function on both p-Si and Mo films despite a substantial valence band barrier in the p-contact. We discuss prospects for boosting the efficiency of these devices by engineering polarization charge in p-type graded region.

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#### Surface Studies of Single Heterostructure InAs and GaAs Nanowires with Wurtzite and Zincblende Segments

<u>J. Knutsson</u><sup>1\*</sup>, M. Hjort<sup>1</sup>, S. Lehmann<sup>1</sup>, R. Timm<sup>1</sup>, L. Samuelson<sup>1</sup>, K.A. Dick<sup>1</sup>, and A. Mikkelsen<sup>1</sup>

<sup>1</sup>Department of Physics, Nanometer Structure Consortium (nmC@LU), Lund University, Box 118, 221 00 Lund, Sweden

With the high surface to volume ratio of nanowires (NWs), the surface characteristics and morphology of the NW side-facets will be strongly coupled to the electronic properties of the NW. Hence, in order for NWs to be realized as future photonics and electronics devices surface studies are essential. In addition, III-V NWs provide the opportunity to study the wurtzite (Wz) crystal structure, giving access to surfaces not found in other III-V geometries. Regardless, very few atomically resolved surface studies have been published<sup>1,2</sup>

We have previously presented the first scanning tunneling microscopy/spectroscopy (STM/S) study on III-V NW surfaces<sup>1</sup>. With our current ability to engineer III-V NWs with axially alternating Wz and zincblende (Zb) crystal phases<sup>3,4</sup> our experimental toolbox is now further improved by the multitude of facets and interfaces provided by such NWs.

Here we present STM/S studies on all common low index facets in addition to interfaces and edges of well-defined Au-seeded heterostructure InAs and GaAs NWs. The NWs were grown using metal organic vapor phase epitaxy and tuning of the crystal structure was realized by varying the precursor gas flow such that NWs with axial stacking of Zb  $\{110\}$ , and  $\{111\}$ A/B, as well as Wz  $\{10-10\}$ , and  $\{11-20\}$ , type facets could be grown in a controlled manner. We have performed detailed imaging of the surface structure and morphology during different phases of wire overgrowth when a transition occurs from the initial saw-tooth  $\{111\}$  type facet morphology of Zb twin superlattice to smooth  $\{110\}$  type facets.

In addition, investigations of the non-polar NW facets revealed unreconstructed surfaces implying that STS data will correspond to the bulk electronic properties of the material without being perturbed by surface states related to reconstructions. The polar facets, {111}A/B, were however found to be reconstructed, which was not seen on analogous surfaces of wafers, suggesting that NW surfaces have very different surface energies.



**Figure 1**. STM results on InAs NWs. All images were obtained at negative sample bias. (A) STM image of interface between Zb {110} (top) and Wz {11-20} (bottom). Inset shows atomic structure of each facet. (B) STS data obtained on two neighbouring Wz and Zb facets in a single NW, depicting the local density of states.(C) Overview STM image of Zb twinned superlattice. (D) High resolution image of {111}A/B facet of NW TSL showing a highly reconstructed {111}B. Inset shows {111}A. (E) {111}A/B surfaces of wafers.

<sup>\*</sup> Corresponding author email: johan.knutsson@sljus.lu.se

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<sup>&</sup>lt;sup>4</sup> K. Dick *et al.,* J. Vac. Sci. & Technol. B **29** (2011) 04D1031

## Intrinsic electrical transport property extraction of Zinc Oxide nanowires using non-lithographic gated four probe measurements

#### Nathan A Smith, Alex M Lord, Jon Evans, S. P. Wilks

#### Centre for Nanohealth, Swansea University, Singleton Campus, Swansea, SA2 8PP, UK.

ZnO nanowires (NWs) are becoming increasingly investigated due to their many potential device applications in areas including electronics, optical and chemical sensing. Having a wide band gap of 3.37eV and exciton binding energy of 60meV, ZnO provides ideal properties for incorporation into devices.

Applications of ZnO NWs in nano-scale electronics have been demonstrated by several groups, in the formation of nanowire field effect transistors (FETs). The FETs are fabricated to use the quasi one dimensional wires as the active FET channel.

Numerous studies have shown that both the electrical and optical properties of intrinsic ZnO NWs demonstrate the presence of surface defects which could potentially deteriorate any potential device performance. However, in order to fabricate a nanowire field effect transistor (NWFET) the NWs can be subjected to an array of chemicals which provide potential contamination or passivation to any surface defects inherent to the NWs. This could occur during NW deposition, where the NWs are usually first placed in suspension in a solvent, or through the application of photoresist for use in the lithographic process for contact patterning. As a result, the majority of previous work performed could in fact not be intrinsic NW properties, but instead be exhibiting non intrinsic properties, attributed to the surface altered NWs.

In this study FET devices are not fabricated using a lithographic process, but instead are manufactured by placing four independently controlled STM tips in contact with a single NW and performing transconductance measurements. Furthermore the NWs used are not subjected to solvents, or placed in suspension, but instead are directly transferred onto pre-patterned substrates with direct frictional force. In doing this, any potential to alter the NW surface is removed, enabling the true intrinsic electrical properties of the NWs to be measured.

Several groups have reported transconductance measurements for nanomaterials, however the vast majority of these groups perform the readings in a two probe configuration. The main problem in doing this is when taking measurements on the nanometre scale, the contact resistance becomes increasingly important. This is especially significant when applying a gate voltage as the contact resistance can increase by orders of magnitude. In order to account for this, the measurements performed in this study are executed in a 4-probe configuration and therefore are contact resistance independent. In performing the measurements in this fashion, a host of intrinsic electrical properties such as, electron mobility, threshold voltage (enhancement mode/ depletion mode FETs) and carrier concentration can be calculated.

To further this study, these measurements are performed on NWs which are fabricated using both catalyst and catalyst free methods. This will enable us to determine if the intrinsic electrical properties between each type of wire are inherently different.

# Thursday

- Th0730 Registration and Continental Breakfast
- Th0830 Thursday Morning Session: Oxides on Semiconductors
- Th0925 Coffee Break and Poster Viewing
- Th1130 Poster Viewing
- Th1200 Conference Ends

# **Oxides on Semiconductors**

#### Exploiting Dimensionality and Defect Mitigation to Create Tunable Microwave Dielectrics with Record Performance

Che-Hui Lee<sup>1,2</sup>, Nathan D. Orloff<sup>3,4</sup>, Turan Birol<sup>5</sup>, Ye Zhu<sup>5</sup>, Veronica Goian<sup>6</sup>, Eduard Rocas<sup>7</sup>, Ryan Haislmaier<sup>2</sup>, Eftihia Vlahos<sup>2</sup>, Julia A. Mundy<sup>5</sup>, Lena F. Kourkoutis<sup>5,12</sup>, Yuefeng Nie<sup>5</sup>, Michael D. Biegalski<sup>7</sup>, Jingshu Zhang<sup>1</sup>, Margitta Bernhagen<sup>9</sup>, Nicole A. Benedek<sup>10</sup>, Yongsam Kim<sup>5</sup>, Joel D. Brock<sup>5</sup>, Reinhard Uecker<sup>9</sup>, X. X. Xi<sup>11</sup>, Venkatraman Gopalan<sup>2</sup>, Dmitry Nuzhnyy<sup>6</sup>, Stanislav Kamba<sup>6</sup>, David A. Muller<sup>5,12</sup>, Ichiro Takeuchi<sup>13</sup>, James C. Booth<sup>3</sup>, Craig J. Fennie<sup>5</sup>, and <u>Darrell G. Schlom<sup>1,12</sup></u>

<sup>1</sup>Department of Materials Science and Engineering, Cornell University, Ithaca, U.S.A. <sup>2</sup>Department of Materials Science and Engineering, Pennsylvania State University, University Park, U.S.A.

<sup>3</sup>National Institute of Standards and Technology, Boulder, U.S.A.

<sup>4</sup>Department of Physics, University of Maryland, College Park, U.S.A.

<sup>5</sup>School of Applied and Engineering Physics, Cornell University, Ithaca, U.S.A. <sup>6</sup>Institute of Physics ASCR, Prague, Czech Republic

<sup>7</sup>Department of Signal Theory and Communications, Universitat Politècnica de Catalunya, Barcelona, Spain

<sup>8</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, U.S.A.

<sup>9</sup>Leibniz Institute for Crystal Growth, Berlin, Germany

<sup>10</sup>Materials Science and Engineering Program, The University of Texas at Austin, Austin,

U.S.A.

<sup>11</sup>Department of Physics, Temple University, Philadelphia, U.S.A.

<sup>12</sup>Kavli Institute at Cornell for Nanoscale Science, Ithaca, U.S.A.

<sup>13</sup>Department of Materials Science and Engineering, University of Maryland, College Park,

U.S.A.

\*E-mail: <u>Schlom@Cornell.edu</u>

The miniaturization and integration of frequency-agile microwave circuits-relevant to electronically-tunable filters, antennas, resonators, phase shifters and more-with microelectronics offers tantalizing device possibilities, yet requires thin films whose dielectric constant at GHz frequencies can be tuned by applying a quasi-static electric field. Appropriate systems, e.g.,  $Ba_xSr_{1-x}TiO_3$ , have a paraelectric-to-ferroelectric transition just below ambient temperature, providing high tunability. Unfortunately such films suffer significant losses arising from defects. Recognizing that progress is stymied by dielectric loss, we start with a system with exceptionally low loss— $Sr_{n+1}Ti_nO_{3n+1}$  phases—where (SrO)<sub>2</sub> crystallographic shear planes provide an alternative to point defect formation for accommodating non-stoichiometry. We report the experimental realization of a highly tunable ground state arising from the emergence of a local ferroelectric instability in biaxially strained  $Sr_{n+1}Ti_nO_{3n+1}$  phases with  $n \ge 3$  at frequencies up to 125 GHz. In contrast to traditional methods of modifying ferroelectrics-doping or strain-in this rather unique system increasing the separation between the (SrO)<sub>2</sub> planes bolsters the local ferroelectric instability. This new control parameter, n, can be exploited to achieve a figure of merit at room temperature that surpasses all known tunable microwave dielectrics.

Spin Dependent Variable Range Hopping in Thin Dielectric Films in MOS and MIM Systems

M. Mutch<sup>1</sup>, P. M. Lenahan<sup>1</sup>, C.J. Cochrane<sup>1</sup>, S. W. King<sup>2</sup>, B. C. Bittel<sup>2</sup>, J. F. Conley, Jr.<sup>3</sup>, N. Alimardani<sup>3</sup>

<sup>1</sup>The Pennsylvania State University, <sup>2</sup>Intel Corporation, <sup>3</sup>Oregon State University

Variable range hopping mechanisms are important in metal-insulator-semiconductor (MIS) and metal-insulator-metal (MIM) systems of great technological interest. Such systems include low/high- $\kappa$  dielectrics<sup>1, 2</sup> and resistive memory materials<sup>3</sup>. We show that electrically detected magnetic resonance (EDMR) via variable range hopping may provide insight into defect structure in a number of these systems. In EDMR measurements, one observes electron paramagnetic resonance (EPR) through spin dependent transport, in our case, via changes in tunneling currents in MIS and MIM systems.

Dielectric films in our study include SiO<sub>2</sub>, SiOC:H, SiCN:H, SiC:H, GdO<sub>3</sub>, and HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. We observe strong EDMR responses in all cases but most responses are broad, disappointingly featureless Gaussian-like spectra, far from ideal for identification of defect structure. Fortunately, useful information can be gleaned from these EDMR results. Measuring EDMR as a function of voltage applied across the MIS or MIM structures and comparing band diagrams as a function of potential provides information about defect energy levels. Although many of these systems yield essentially featureless spectra, EDMR measurements at multiple frequencies convey some structural information. This is so because in an amorphous or polycrystalline material, a major contribution to EPR and thus EDMR line width is the range of values in the EPR g tensor. In the simplest EPR spectrum, the resonance condition is given by, hv  $= g\beta B$ , where h is Planck's constant, v is the frequency of electromagnetic energy, g is an orientation dependent number, typically expressed as a second rank tensor,  $\beta$  is the Bohr magneton and B is the applied magnetic field. In a polycrystalline or amorphous material, one simultaneously observes all possible orientations of the defect with respect to the applied magnetic field and thus the full range of g tensor components contribute to the spectrum. If no other factors contribute to the resonance condition, the line width is determined solely by the range of g tensor values. Other mechanisms generally do contribute to the resonance condition, with hyperfine interactions, interactions between unpaired electrons and nearby nuclear magnetic moments, usually the most important. To zero order, they provide a broadening of the spectrum which is independent of the measurement frequency. However, since  $hv = g\beta B$ , broadening due to g is proportional to frequency. Thus, a comparison of spectra at very different frequencies should provide a reasonable estimate of the range of g tensor components. The g tensor contains useful information about the chemical and structural nature of paramagnetic centers. For an isolated electron, g = 2.0023 ... Deviations from this value result from spin orbit coupling. Since spin orbit coupling depends upon both the nuclear charge and electron orbital angular momentum, a measure of g provides information about defect structure. We have made EDMR measurements at 9.5 GHz and 0.353 GHz and have conducted EDMR measurements as a function of voltage applied on all samples. In this presentation we will show, as described herein, that EDMR versus voltage provides information about defect energy level locations and that EDMR line width versus frequency gives information about defect structure.

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## Gd<sub>2</sub>O<sub>3</sub> deposited on GaAs(001): Optical anisotropies with modulated reflectance

N.A. Ulloa Castillo\*, L.F. Lastras Martínez, R.E. Balderas Navarro, A. Lastras Martínez

### Instituto de Investigación en Comunicación Óptica, Álvaro Obregón 64, 7800 San Luis Potosí, S.L.P., México.

#### ABSTRACT

Over the last few decades, rare earth oxide-based materials have been extensively studied due to their wide range of applications in various fields of technology such as optical devices, microelectronics, and magnetic devices [1,2]. Rare earth oxides materials, such as  $Gd_2O_3$  has been investigated in detail, as a result of their many promising properties (e.g. high dielectric constant, large band gap [3] and excellent thermodynamical stability [4]). However, the structural details associated to the interface formed between  $Gd_2O_3$  and the corresponding substrate have not been completely understood. Therefore, the need on developing experimental tools that would be useful to elucidate quantitative details in a noninvasive way.

In this work, we report on an optical study of  $Gd_2O_3$  thin films deposited on GaAs substrates under different surface conditions. The  $Gd_2O_3$  thin films were deposited using an e-Beam Evaporator in an ultra-high vacuum chamber. The evaporation study is focused mainly on 5 different GaAs surfaces: *n*-GaAs(001), semi-insulating GaAs(100), with c(4x4) and  $\beta(2x4)$  reconstructions; and semi-insulating GaAs(111) as well. The optical study used as optical probes are Spectroscopy Elipsometry (SE), Reflectance Difference Spectroscopy (RDS), Photoreflectance (PR) and Photoreflectance Difference Spectroscopy (PRD). RDS detected optical anisotropies in the visible-ultra violet range before and after evaporation of  $Gd_2O_3$  (Figure 1). PR and PRD measurements were done in order to investigate changes of the surface states caused by changes in the surface electric field (Figures 2 and 3). Both PR and PRD techniques were due to their well-known capability to isolate the lineal and quadratic contributions of the piezoelectric effect [5,6].

The results reported in this work show that  $Gd_2O_3$  modifies the GaAs surface causing a tensile stress which renders the quadratic electro-optic effect anisotropic, as shown in Figures 3 and 4. On the other hand, while the GaAs(111) surface is largely isotropic due to geometrical reasons, a RD response was detected at  $E'_0+D_0$  critical point, which is attributed to the stress induced by the Gd<sub>2</sub>O<sub>3</sub> film within the few layers below the surface.



Figure 1. Reflectance difference spectra of GaAs(100): before evaporation (black symbols) and after evaporation (blue symbols) of Gd<sub>2</sub>O<sub>3</sub>.

#### Th0920

On the Structure of the SiC/SiO<sub>2</sub> Boundary

M.A. Anders<sup>1</sup>, C.J. Cochrane<sup>1</sup>, P.M. Lenahan<sup>1</sup>, S.D. Arthur<sup>2</sup>, J. McMahon<sup>2</sup>, L. Yu<sup>2</sup>, X. Zhu<sup>2</sup>, A.J. Lelis<sup>3</sup>

<sup>1</sup>Penn State University <sup>2</sup>General Electric Global Research <sup>3</sup>U.S. Army Research Center

Silicon carbide (SiC) MOSFETs show great promise in high power and high temperature applications. The implementation of SiC MOSFET technology has been limited in part by electrically active defects at or very near to the SiC/SiO<sub>2</sub> interface. Previously, our group has studied the 4H SiC/SiO<sub>2</sub> interface via electrically detected magnetic resonance (EDMR) at X band (~9.5 GHz) and found a ubiquitous performance limiting defect in n-MOSFETs, the silicon vacancy [1, 2]. We have greatly extended our earlier EDMR measurements extending original room temperature X band studies to include: (a) elevated temperatures, up to 190°C and (b) various EDMR frequencies from 220 MHz to 16 GHz. We have also extended the range of devices explored from n-MOSFETs to include p-MOSFETs. Our new measurements demonstrate that multiple defects play important roles in device performance and also show that elevated temperature creates or activates new defect centers. Our results also suggest that SiC/SiO<sub>2</sub> interface disorder may be a contributor to low effective channel mobilities, at least in p-MOSFETs. Although both n- and p- MOSFET EDMR spectra are dominated by a relatively narrow isotropic line with a  $g \approx 2.0028$ , due to the silicon vacancy, we observe additional strong side peak structure in the p-MOSFETs and multiple changes in the spectra at elevated temperature. Utilizing low-frequency EDMR (350 MHz), we clearly resolve two strong isotropic side peaks separated by about 11 Gauss. We attribute these side peaks to a hydrogen-complexed E-prime defect called the 10.4 Gauss doublet; likely a hole trapped in an oxygen vacancy [3]. NO anneals, in all cases surveyed, greatly reduced the 10.4 Gauss doublet EDMR signal as well as the silicon vacancy signal. However, a reduction in their number does not coincide with an improvement in p-MOSFET mobilities. This result is very different from the case of n-MOSFETs. In n-MOSFETs, the NO anneal consistently reduces the interface-sensitive EDMR silicon vacancy and 10.4 Gauss doublet response by more than an order of magnitude. The anneal increases the n-MOSFET effective channel mobility by more than one order of magnitude. In p-MOSFETs, the NO anneal reduces the EDMR response by a factor of about 30 for both defects, but increases the mobility only by a factor of 1.1. Our variable frequency EDMR measurements may provide insight into this surprising result. One possible cause of low channel mobility in p-MOSFETs could be disorder in the SiC/SiO<sub>2</sub> interface region. The presence of disorder within a crystal will introduce a frequency dependent spectrum broadening due to the effects of the disorder on the g-tensor. We compare EDMR measurements made at X band (9.5GHz) and low-field (350MHz) and consistently observe a large change in line width, almost certainly a direct measure of disorder on the SiC side of the SiC/SiO<sub>2</sub> interface.

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<sup>[1]</sup> C.J. Cochrane, et al., Appl. Phys. Lett. 102, 193507 (2013)
# Graphene Analogs and Novel 2D Materials II

# Th1000 Invited

# PCSI 2014 Abstract

Title:

Mechanical Routes to Thermodynamic Stabilization of the Elusive Metallic Phase of Monolayer Mo- and W-Dichalcogenides

# Authors:

# Evan J. Reed, Karel-Alexander N. Duerloo Department of Materials Science and Engineering, Stanford University

The monolayer transition metal dichalcogenides (TMDs) are distinguished from their more studied graphene counterpart by the potential for multiple structural phases to exist. Multiple crystal structures of the individual layers are well known in bulk TMDs, but the crystal phases, their properties, and phase boundaries of monolayers have yet to be elucidated. Recent work indicating that some of these phases provide effective hydrogen production catalysis suggests that the understanding and engineering of these phases may have immediate and important applications. Here we discover that the energetic ordering of monolayer Mo- or W-dichalcogenide phases can be controlled through the application of strain or stress. We elucidate the appropriate thermodynamic constraints for monolayers, which can differ from bulk materials. We then utilize density-functional theory (DFT) and hybrid Hartree-Fock/DFT calculations to predict that the deformations required to yield a phase transition range from 0.5 to 15% engineering strain for this set of monolayers, falling within the experimentally demonstrated range of elastic deformations afforded by the exceptional tensile strength of TMD monolayers. The potential application space for this discovery ranges from catalysis to information storage and nanoscale electronics.

# Spin polarization of monolayer hexagonal boron nitride on Ni(111) studied by spin-polarized metastable de-excitation spectroscopy.

<u>Manabu Ohtomo</u><sup>1</sup>, Pavel V. Avramov<sup>1</sup>, Shiro Entani<sup>1</sup>, Yoshihiro Matsumoto<sup>1</sup>, Hiroshi Naramoto<sup>1</sup>, Yasushi Yamauchi<sup>2</sup>, Seiji Sakai<sup>1</sup>

 <sup>1</sup> Advanced Science Research Center, Japan Atomic Energy Agency (JAEA), 2-4 Shirakata-shirane, Tokai-mura, Ibaraki 319-1195, Japan
<sup>2</sup> National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan e-mail: ohtomo.manabu@jaea.go.jp

Hexagonal boron nitride (h-BN) is a promising material for ultra-thin tunnel barrier for graphene spintronics. In this study, we used spin-polarized metastable de-excitation spectroscopy (SPMDS) in order to study spin and electronic states of monolayer h-BN on magnetic metal surfaces.

The well-defined epitaxial monolayer of h-BN can be prepared on Ni(111) by ultra-high vacuum chemical vapor deposition (UHV-CVD). Whereas the interaction between monolayer h-BN and Ni(111) substrate surface was considered to be physisorption [1], it was also suggested that h-BN is chemisorbed on Ni(111) with orbital mixing between Ni 3*d* and h-BN  $\pi$  orbital [2].

The direct observation of  $\pi$ -d orbital mixing, however, have been challenging because of strong Ni 3*d* resonance. The conventional photoemission spectroscopy (PES) probes electronic structure deep below the surface. Since the covering h-BN have monolayer thickness, what we extract from PES measurement is superposition of small signal from monolayer h-BN on huge signal from Ni(111).

Spin-polarized metastable de-excitation spectroscopy (SPMDS), on the other hand, is an ideal technique because of its extreme surface sensitivity. In SPMDS, the probe is metastable helium atoms (He\*) with long lifetime  $(4.2 \times 10^3 \text{ s})$  and low kinetic energy (<0.1 eV), which do not penetrate into the sample. Moreover, SPMDS is a spin-resolved method by using triplet He\*  $(2^3S)$ .

The extreme surface sensitivity of SPMDS enabled us to elucidate the spin polarized states of h-BN monolayer on Ni(111) separately from strong Ni 3d resonance. It was directly confirmed that  $\pi$ -d orbital mixing of nitrogen  $\pi$  orbital and Ni 3d orbital produce in-gap states. As a consequence of empty levels formation around the Fermi level, the metastable He\* atoms mainly de-excite via resonance ionization + Auger de-excitation (RI + AN) process, which imply h-BN is metallic on Ni(111). The spin asymmetry of SPMDS spectra indicates that the in-gap states of h-BN are spin-polarized parallel to Ni majority spins.

The results demonstrated here would give us some implication for h-BN as an ultra-thin tunnel barrier for spin injection. We confirmed the occupied states below the Fermi level are spin-polarized parallel to Ni majority spins, while DFT calculation suggests that empty states above the Fermi level are anti-parallel. The device geometry and operating parameter should be designed with taking the spin-polarized in-gap states into account. [1] Journal of Physics: Condensed Matter **9** (1), 1 (1997). [2] Phys. Rev. B **70** (16), 165404 (2004).

# **COMPUTER SIMULATION OF POINT DEFECTS IN GRAPHANE**

Yadgarov I.<sup>1</sup>, Stelmakh V.<sup>1</sup>, Dzhurakhalov A.A.<sup>2</sup>

<sup>1</sup>Institute of Ion-Plasma and Laser Technologies, 33, Do'rmon yo'li Street, 100125 Tashkent, Uzbekistan, iyadgarov@mail.ru <sup>2</sup>Dept. of Mathematics and Computer Sciences, University of Antwerp, Antwerp, Belgium, dzhurakhalov@mail.ru

The ideal structure of graphane is two-dimensional hexagonal lattice of carbon atoms and hydrogen atoms. The presence of defects in such lattice leads to a disruption of this structure and to changes in physical and chemical properties of graphane. Using Metropolis Monte Carlo method, the formation of point defects and stable configurations of graphane have been studied. The interatomic interactions have been described by the Brenner's reactive empirical bond order potential which was parameterized specifically for carbon and hydrocarbon systems [1].

Graphane has been modeled by 112 carbon atoms arranged in a flat plane with the appropriate configuration for graphene and by 112 hydrogen atoms bonded with carbon atoms alternatively on both sides of carbon lattice. Moreover, to simulate a graphane the periodic conditions were superimposed on the boundary atoms of graphane along its plane. The presence of point defects has been modeled as sequence of point vacancies of carbon and hydrogen atoms located in one primitive cell of the lattice. We studied their effects on changes in the lattice structure and binding (cohesive) energy of atoms. Figure shows how the cohesive energy varies on the number of point vacancies in a point defect for graphane. In particular, it was found that carbon point defects results in decreasing the cohesive energy of studied systems.



Figure. The dependence of the cohesive energy on the number of point vacancies of hydrogen (triangles) and carbon (squares) atoms.

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# A Multi-walled Carbon Nanotube Sheet based flexible conductive film

Daewoong Jung, Ma-Eum Han and Gil S. Lee\*

Department of Electrical Engineering, The University of Texas at Dallas, Richardson, Texas, USA

# gslee@utdallas.edu

In the recent years, intense research efforts have been dedicated to developments of flexible display devices using transparent conductive film (TCF); they have become a most important commercial interest in the mobile display industry. To date, the indium tin oxide (ITO) has sufficiently high transparency and conductive properties for market demand for TCF. However, ITO films have some demerits, such as a slow thermal response, brittleness, and cost. These drawbacks in ITO films hinder their use in bendable electrical circuitry and flexible display applications [1]. Great efforts have been devoted to develop flexible conducting films that overcome these ITO disadvantages. Since the discovery of carbon nanotubes (CNT), there has been much research regarding their outstanding physical properties. Films made of CNTs are most powerful alternatives for TCF due to their high conductivity, flexibility, and the abundance of raw carbon. In particular, single-walled CNT (SWCNT) films have been investigated widely for use in TCF applications such as electrodes, actuators, sensor and transistors. Although theoretical and experimental analysis toward SWCNT films has been reported, several obstacles hinder the further development of SWCNT based TCF [2-3]. SWCNT still has some issues in their purification, separation, and dispersion in a substrate used to enhance their electrical and optical properties. It is difficult to control the density and thickness of the SWCNTs. Moreover, there is no a reliable and efficient transfer way to reproducibly fabricate SWCNT based TCF up to now.

In this paper, spin-capable multi-walled carbon nanotube (MWCNT) is proposed to fulfill the above challenges [4-5]. The TCF fabricated by MWCNT sheet, which pulled out from spin-capable MWCNT forest has large surface area and well aligned individual MWCNT. The sheet has a high transmittance and a low sheet resistance. These figures are comparable to those found for SWCNTs and ITO and provide an excellent opportunity to use them in a wide range of applications for flexible conductive films.

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- [5] Jung et al., Sens. Actuators. A 199, 176 (2013).

# A Multi-walled Carbon Nanotube Sheet based infrared thermal detector

Maeum Han, Daewoong Jung and Gil S. Lee\*

Department of Electrical Engineering, The University of Texas at Dallas, Richardson, Texas, USA

# gslee@utdallas.edu

The photo-response of carbon nanotubes (CNTs) has attracted great research attention due to their excellent electrical, physical, mechanical, chemical properties [1]. Based on their outstanding properties, numerous literatures are reports on the infrared (IR) photo-behavior in the conductivity of single-walled carbon nanotube (SWCNT) [2-3]. Although SWCNT shows promising electrical and optical properties for IR detector, several obstacles prevent the realization of actual devices [4-5]. First, an uneven dispersion of SWCNTs because of the van der Waals force can result in degraded electrical and optical properties in the SWCNT. Second, SWCNT films have poor adhesion to the substrates, affecting the device performance. Furthermore, SWCNTs show an environmentally-caused deterioration of their properties when exposed to moderate temperatures [6]. In order to solve these issues, the multi-walled carbon nanotube (MWCNT) sheet has been introduced in order to examine the possibility of alternate materials that ensure stable electrical, optical properties upon exposure to adverse environments while maintaining good adhesion to the substrate [6-7]. By analyzing theoretical with experimental results, we found that the sensitivity and response time of MWCNT IR detectors are influenced by several factors, which gives help for practical applications. We've founded that the extremely low heat capacity per unit area of MWCNT in sheet enabled a fast IR response of the MWCNT IR detectors. Experiments by acid treatment and increasing the surface area of CNT films have been carried out to improve the sensitivity and response time of the CNT film detector. We observed that the MWCNT IR sensor shows a 16 % resistance change with a fast response time of 10 ms under 10 mW/mm<sup>2</sup> of IR illumination at room temperature.

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# Tuning the Oxidation States and Crystallinity of Copper Oxide Nanofibers by Calcination

Juyun Park<sup>1</sup>, Sung-Wi Koh<sup>2</sup>, Sungyong Seo<sup>1</sup>, and Yong-Cheol Kang<sup>1, \*</sup>

<sup>1</sup> Department of Chemistry, Pukyong National University, 45, Yongso-ro, Nam-Gu, Busan, 608-737, KOREA
<sup>2</sup> Electronics and Division of Mechanical Engineering, Pukyong National University, 365, Sinseon-ro, Nam-Gu, Busan, 608-739, KOREA

e-mail: yckang@pknu.ac.kr

The Cu oxide/polyvinyl alcohol (PVA) nanofibers were synthesized by sol-gel and electrospinning process. The obtained Cu oxide/PVA nanofibers were calcined to remove the PVA compound at 673 and 873K. The ultrafine Cu oxide nanofibers were characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The Cu oxide nanofibers were successfully prepared by electrospinning and calcination and the average diameters of Cu/PVA nanofibers were 268.9±97.2 nm. After the nanofibers were calcined at higher temperature than rt, the morphologies of the nanofibers were changed. XRD results showed that the crystalline structure was changed from amorphous to monoclinic CuO through cubic Cu<sub>2</sub>O. TEM images also verified the crystal phase of Cu oxide nanofibers. XPS spectra revealed that the major oxidation state of Cu were changed with thermal oxidation process.

# P-Type Conductivity in MoS<sub>2</sub> and WS<sub>2</sub> by Nb doping

E.W. Lee II<sup>1</sup>, M.R. Laskar<sup>1</sup>, D.N. Nath<sup>1</sup>, L. Ma<sup>2</sup>, C.H. Lee<sup>1</sup>, T. Kent<sup>3</sup>, Z. Yang<sup>3</sup>, R. Mishra<sup>4</sup>, M.A. Roldan<sup>4</sup>, J.-C. Idrobo<sup>4</sup>, S.T. Pantelides<sup>4</sup>, S.J. Pennycook<sup>4</sup>, R. Myers<sup>3</sup>, Y. Wu<sup>2</sup>, S. Rajan<sup>1,3</sup>

<sup>1</sup>Department of Electrical and Computer Engineering <sup>2</sup>Department of Chemistry <sup>3</sup>Department of Material Science and Engineering The Ohio State University, Columbus, OH, 43210

We report on the first demonstration of p-type doping in large area few-layer films of (0001)-oriented chemical vapor deposited (CVD)  $MoS_2$ . Nb, which has one less electron than Mo, was used as a substitutional defect in an  $MoS_2$  thin film, and was found to behave as an acceptor with low ionization. Using this method, we achieved high hole sheet density (up to  $10^{20}$  cm<sup>-3</sup> with associated Hall mobility of up to  $10 \text{ cm}^2/Vs$ ) in large area p-type  $MoS_2$  films, in addition p-type  $WS_2$  films. Theoretical scattering rate calculations for mobility were found to match well with the measured hole mobility over a range of acceptor concentrations. This is the first report of in-situ grown substitutional p-type acceptor for thin film  $MoS_2$ , thus fulfilling a critical requirement for useful electronic and optoelectronic devices.

The reported work utilizes a previously reported method to achieve large area (0001) oriented  $MoS_2$  with good crystalline and structural qualities by chemical vapor transport on single crystal (0001) sapphire<sup>1</sup>. Such CVD-grown  $MoS_2$  overcomes limitations associated with the commonly used mechanical exfoliation approach (control of thickness and area) and is therefore viable for large-scale device fabrication.

In the present work, a metal stack of 2.5 nm Mo/0.2 nm Nb/2.5 nm Mo was deposited on (0001) sapphire templates by electron beam evaporation. The substrate was vacuum sealed in a quartz tube with 20 mg of sulfur, placed in a furnace and heated at 900°C for ten minutes. Niobium was found to act as an efficient acceptor up to relatively high density in MoS<sub>2</sub> films. For a hole density of 4 x 10<sup>20</sup> cm<sup>-3</sup> Hall mobility of 8.5 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> was determined, which matches well with the theoretically expected values. AFM and optical images show that smooth continuous films of few-layer MoS<sub>2</sub> were formed. XRD spectra show (002) and (006) peaks associated with 2H-MoS<sub>2</sub>, and Raman spectra display the characteristic in-plane (E<sup>1</sup><sub>2g</sub>) and out-of-plane (A<sub>1g</sub>) vibrational modes of MoS<sub>2</sub> at 381 and 407 cm<sup>-1</sup>, respectively. Absorption measurements showed that the doped sample had similar characteristics to high-quality undoped samples and exfoliated samples, with a clear absorption edge at 1.8 eV. These measurements suggest that the inclusion of Nb acceptors does not degrade the energy band structure or structural quality of the MoS<sub>2</sub>. This demonstration of p-type doping in large area epitaxial MoS<sub>2</sub> enable a wide variety of electrical and opto-electronic devices based on layered metal dichalcogenides.

<sup>&</sup>lt;sup>1</sup> M.R. Laskar, L. Ma, S. Kannappan, P.S. Park, S. Krishnamoorthy, D.N. Nath, W. Lu, Y. Wu, S. Rajan, *Appl. Phys. Lett.* **102**(25), 252108, (2013).

# Epitaxial Co-Deposition Growth of CaGe<sub>2</sub> Films by Molecular Beam Epitaxy for Large Area Germanane

The discovery and mechanical exfoliation of single layer graphene has led to a revolution in nanoscale materials science by enabling a plethora of new physics and chemistry in two dimensions (2D) that is not possible in conventional three-dimensional materials. Beyond graphene, there is great interest in exploring 2D materials that offer properties not found in graphene such as a native band gap, strong spin-orbit coupling, and strong exciton confinement. Of particular interest is germanane (GeH), the germanium-based analogue of graphane (CH),



**Figure 1.** Atomic structure diagram of germanane (GeH).

as shown in Figure 1. Germanane has several properties that make it extremely attractive for science and engineering. First, it has a direct band gap of ~1.5 eV and is theoretically capable of high mobility transport (~18,000 cm<sup>2</sup>/Vs), which make it favorable for optoelectronics and nanoscale digital



**Figure 2.** Cross-sectional views of CaGe<sub>2</sub> (top), and stacked germanane layers (bottom).

electronics.<sup>1</sup> Second, it is thermodynamically stable at room temperature and is resistant to oxidation, which is advantageous for exploratory physics studies as well as future device applications. Finally, the larger spin-orbit coupling associated with heavier element Ge (as compared to C in graphene) opens up new opportunities to explore spintronics in 2D such as manipulation of spin by internal spin-orbit fields, spin Hall effect, and quantum spin Hall effect.

Germanane has recently been synthesized as a bulk single-crystal and exfoliated onto insulating substrates.<sup>1</sup> This was achieved by first synthesizing bulk crystals of layered Zintl-phase CaGe<sub>2</sub>, then submerging the crystals in hydrochloric acid (HCl) to de-intercalate the Ca atoms (Fig. 2). This results in stacked layers of 2D germanane sheets, where each sheet consists of Ge atoms arranged in a buckled honeycomb lattice and sp<sub>3</sub>-hybridized due to covalent bonds to hydrogen as shown in Fig 1. To go beyond mechanical

exfoliation, one of the primary challenges is the synthesis of high quality, large area germanane films.

In this work, we report the successful co-deposition growth of  $CaGe_2$  films on Ge(111) substrates by molecular beam epitaxy and their subsequent conversion to germanane by immersion in hydrochloric acid. We find that the growth of  $CaGe_2$  occurs within an adsorption-limited growth regime, which promotes stoichiometry of the film. We utilize *in situ* reflection high energy electron diffraction (RHEED) to explore the growth temperature window and find the best RHEED patterns at 750 °C. Finally, the  $CaGe_2$  films are immersed in hydrochloric acid to convert the films to germanane. Auger electron spectroscopy of the resulting film indicates the removal of Ca and RHEED patterns indicate a single-crystal film with in-plane orientation dictated by the underlying Ge(111) substrate. These results signal a major advance for 2D semiconductors and layered van der Waals heterostructures for novel electronic, optical, and spintronic devices.

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**Figure 3.** RHEED pattern after the growth of  $CaGe_2$  on Ge(111) at 750 °C.

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Rahimi, N	Mo0935, We1040
Rajan, S	Mo0830, Tu0855, Th1120
Razak, M.B.A.	Mo1710
Redondo-Cubero, A	Tu0940
Reed, E.J	Th1000
Regan, W.	Mo1625
Reinicker, A.	We0910
Rice, W.D	Tu0900
Richardella, A	Su1620
Riss, A	Mo1625
Robinson, Z.R.	Mo1620, Mo1705
Rocas, E	Th0830
Rodriguez, C	Mo1145
Rodriguez, R.D	Tu1150, We1530
Rodyakina, E.E	Tu1150, Tu1155
Roldan, M.A	Th1120
Romero, O.S	Mo0935, We1040
Rose, V	Tu1045
Rosen, E.L	Tu1145
Rosenberg, R	We0910
Rotter, T.J	Mo0935, We1040
Rowe, M.J.E.	Mo1450
Rubio, A	Mo1625

# <u>S</u>

Sachet, E.....Mo1450 Sadowski, J.T.....We1440 Sakai, S.....Th1040 Samarth, N. .....Su1620 Samuelson, L. .....We1755 Saranu, S. .....We0920 Sarwar, A.T.M.G.....We1750 Sawvel, A.M. .....Tu1145 Schlom, D.G. .....Su1620, Th0830 Schulmeyer, T. .....We1155 Self, E.....Mo1620 Seña, N.J......We0930 Seo, S.....Th1115 Shabani, J. .....Su1645 Shan, J. .....We1400 Sheremet, E. .....Tu1150, Tu1155, We1530 Shima, D.M......We1040 Shoron, O.F.....Tu0855 Shytov, A.V......Mo1625 Smith, D.J.....Su2010 Smith, N.A. ......We1800 Sohail, H.M.....We1045 Son, G.V......We1525 Sorini, A.P. ......We0925 SpringThorpe, A. .....Mo1445 Stelmakh, V.....Th1100 Stemmer, S. .....Su1930, Tu0855, Tu0920 Stuart, S.C.....Mo1450 Sun, D. .....We1520

Sutter, P	We1440
Suzuki, A	Tu0950
Suzuki, S	Mo1610
Sveshnikova, L.L	Tu1155
Swartz, A.G	Mo1715, Mo1440

# Ţ

Tachikawa, T Tu0850	
Taing, J We0925	
Takamura, M Mo1610	
Takeuchi, I Th0830	
Talin, A.A Mo1100	
Tamura, H We1145	
Tarat, A We0915	
Thompson, J.D Tu0900	
Timm, R We1755	
Tischler, J.G Mo0915	
Troeppner, C We1150	
Tsai, HZ Mo1625	
Twigg, M.E Mo0915	

# <u>U-V</u>

Uder, B	We1150
Uecker, R	Th0830
Uhrberg, R.I.G	We1045
Ulrich, M	Mo1450
Urban, J.J	Tu1145
Uruno, A	Mo0930
Usui, A	Mo0930
Vallejo, W	We1140
van der Zande, A.M	We1440
Villabona, A	We1530
Vlahos, E	Th0830
von Son, G	We1520

# W

Wallace, R.M	We1500
Wang, C	We1525
Wang, J	Su1640
Wang, S	Mo1140
Wang, S.	Mo1610
Wang, Y	Mo1625
Ware, M.	We1050
Wen, H	Mo1715
Wheeler, V.D	Mo1620, Mo1705
Wickenberg, S	Mo1625
Wilks, S.P.	We1800
Willett-Gies, T	Mo1145
Williams, M.C.	. Tu0950
Wilson, N	.Tu1000
Witting-Larsen, E	.Tu1125
Wong, D	Mo1625
Wong-Leung, J	We1710
Wu, Y	Th1120

# <u>X,Y,Z</u>

Xi, X.X	Th0830
Xu, H	Tu1125
Xu, S.C	Mo0920
Xu, SY	Su1620
Yadgarov, I	Th1100
Yamaguchi, K	We1525

Yamauchi, Y	Fh1040
Yang, SH	Fu0920
Yang, Z	Fh1120
Yeh, PC	Ne1440
Yeryukov, N.A.	Fu1155
Yokomizo, Y	Mo1615
Yu, E.T	Mo1140
Yu, L	Fh0920
Zahn, D.R.T	Fu1150, Tu1155, We1530
Zaki, N	Ne1440
Zettl, A	Mo1625
Zhang, D	Su1620
Zhang, D	Ne1135
Zhang, D	We1440
Zhang, J	Fh0830
Zhu, JN	Mo1500
Zhu, X	Fh0920
Zhu, Y	Fh0830
Zollner, S	No0920, Mo1145