Electronic Materials and Photonics Division
Room On Demand - Session EM-Contributed On Demand
Electronic Materials and Photonics Contributed On Demand Session

Due to significant copper (Cu) resistivity size-effects and limitations in scaling the thickness of the associated high resistivity tantalum- Ta) based diffusion barrier, there has been significant interest in identifying alternative metallization schemes with lower overall effective resistivities. To help identify potential metals with improved resistivity dimensional scaling properties relative to Cu, the product of electron mean free path (λ) and bulk metal resistivity (ρ) has been recently proposed as a potential figure of merit (FOM) based on the semi-classical Mayadas-Shatzkes and Fuchs-Sondheimer equations describing surface and grain boundary electron scattering in metals. Based on this FOM, over a dozen metals have been predicted to have the potential to outperform Cu at reduced geometries. However, there have been relatively few experimental investigations for some of the most promising metals identified (i.e. Ir, Rh, and Os) due to their prohibitive expense.

In this presentation, we address the limited information on platinum group metal resistivity scaling as well as the costs impeding their investigation and application. For the former, we have performed an expansive thin film resistivity literature search on all the low-λρ FOM candidate metals to robustly establish the resistivity scaling performance of rare platinum group metals (PGMs). For the latter, we have examined the supply chain for PGMs from earth to usable form in semiconductor manufacturing (i.e. sputter target, organometallic precursor, …) to assess factors that influence pricing as well as search for opportunities to drive future cost reductions. Through the combined examination of a broader thin film resistivity dataset and associated supply chain considerations, we identify and suggest metals that may merit greater consideration as well as methods to potentially improving their economics for use in the semiconductor industry.

EM-Contributed On Demand-4 Designing Transition Metal Doped Lithium Fluoride Composite Cathode Materials For Li-Ion Batteries, Clifford Denize, S. Danquah, J. Strimaitis, Center for Materials Research Norfolk State University; C. Bonner, Chemistry Department Norfolk State University and Center for Materials Research Norfolk State University; S. Pradhan, M. Behera, Center for Materials Research Norfolk State University; M. Bahoura, Engineering Department Norfolk State University and Center for Materials Research Norfolk State University
Lithium-ion batteries are ever-present in our everyday lives in cell phones and laptops. Improving cathode materials is one of the ways to satisfy the need for a better energy storage solution. Developing new types of positive electrode materials to increase the cell voltage and capacity with improved stability is the best way towards the development of next-generation Li-ion rechargeable batteries. To achieve this goal, understanding the principles of the materials and recognizing the problems confronting the state-of-the-art cathode materials are essential prerequisites. Fluoride-based conversion high-energy cathode materials can be used to build next-generation lithium-ion batteries. FeF3 and CuF2 show a theoretical specific capacity value of 713 mAh/g and 527.17 mAh/g, respectively. Similarly, LiFeF3 and Li-CuF2 show a higher theoretical energy density of 900 Wh/kg. The insulating nature of LiF and limited splitting of LiF during charging are some of the challenges for lithiated fluorides. Lithiated fluorides also show some issues due to the lack of a presence of built-in Li source, poor capacity retention, and poor rate performance. To overcome these issues, we incorporate Fe, a transition metal with higher electrical conductivity, into LiF to form a composite material. A highly conformal and smooth surface area of transition metal lithiated fluoride composite thin film sample was achieved using pulsed laser deposition, both with and without annealing. To establish a baseline of performance, coin cells of slurry metal lithium thin films grown were between a pair of AC voltage-biased copper electrodes at a temperature of 400 °C. The electrodes with the carbon film were finally fabricated into the carbon thin film field-effect transistor (CFET), where the carbon thin film between the electrodes functioned as the channel of the transistor. The carbon thin film was analyzed with high-resolution tunneling electron micrograph (HRTEM), showing wiggling nanostructures in it. The electrical property of the fabricated CFET was measured before and after subject to an electrical breakdown, demonstrating much better electrical current (I)-voltage (V) curves and transfer characteristics with on/off current ratios of over 200 after the electrical breakdown process. The growth of nanostructured carbon film is novel, and the fabrication of CFET is compatible with the silicon-based semiconductor fabrication and can be wafer-scale.
On Demand available October 25-November 30, 2021

EM-Contributed On Demand-13 Laser Induced Thermal Emission from Nickel Nanowires, Ana Silva, Celfitec, Physics Department, FCT, Universidade Nova de Lisboa, Portugal; K. Pedersen, Aalborg University, Denmark

Over the past two decades, there has been considerable progress in engineering the spectrum, directionality, polarization and temporal response of thermally emitted light using nanostructured materials [1]. Laser induced emission from self-assembled nickel wires, between 125-200 nm in diameter and tens of micrometers long, prepared by electrochemical deposition, emits strong infrared light when excited with a cw Ar+ ion laser at 488 nm or a pulsed femtosecond Ti: Sapphire laser at 800 nm. The emission spectra from aggregates of Ni nanowires (NWs) heated by the absorption of laser light are investigated as a function of the power of the excitation laser. The emitted intensity increases exponentially with laser power which is taken as an indication of a thermal process. Through time response of the emission to a time varying laser excitation, the local temperature variation of the nanowires is determined. The radiation from the nanowires is described by the classical Planck law modified by finite-size effects in nanoparticle emissivity. Similar emission spectra are observed for the two types of lasers. Theoretical modelling based on Mie’s theory[2] and Planck’s radiation law, using nanowires and nanocrystals of different sizes, is developed to fit the emission spectra.

The emission grows exponentially with pump power and over time the emission decays. The results point to thermal radiation process, modulated by size-effects, and strongly influenced by local plasmon modes (hot spots) that may lead to very large electric fields enhancements.


Acknowledgments

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EM-Contributed On Demand-16 Wake up and Endurance of Ferroelectric Hf0.5Zr0.5O2 on NbN and Nb, David Henry, Sandia National Laboratories; F. Fields, University of Virginia; S. Smith, P. Davids, Sandia National Laboratories; J. Ihlefeld, University of Virginia

This work investigates the wake up and endurance of ferroelectric behavior of atomic layer deposited (ALD) hafnium zirconium oxide (HZO) using reactiveley sputtered niobium nitride and niobium electrodes. With ferroelectricity in doped HfO2 now advancing into CMOS based devices, perturbations of the dopants has expanded from silicon into mixtures utilizing yttrium and zirconium and with electrodes ranging from platinum to tungsten and nitrates such as titanium nitride and tantalum nitride. New to the field of materials able, in part, stabilize the orthorhombic phase are other superconducting electrodes such as NbN and, in this work, Nb which we use to demonstrate stable ferroelectric behavior of Hf0.5Zr0.5O2. With the atomic similarities between Ta and Nb, a natural extension the orthorhombic phase grown semiconductors on matched substrates and then transferred to the host substrate at a device scale, circuit scale, chip scale, or wafer scale. Although the devices made using these approaches are of excellent quality, this approach is usually limited by cost, time, limited materials, and scalability perspectives. Monolithic integration approaches attempt to directly grow materials on the host substrate, but device performance is usually poor from solution-based or vapor-phase grown semiconductors on non-epitaxial substrates which give submicron-scale grain polycrystalline films. Here we show results from a liquid-vapor-phase growth approach, referred to as Low Temperature Templated Liquid Phase (LT-LTP) growth. Templates of group III materials capped with SiO2 are first realized on the non-epitaxial substrate by lithography, evaporation, and liftoff methods. The templates are then heated (≈0.5 kW/kg) and the interconnects are annealed in a growth temperature between 200 to 400 °C, and group V precursor is introduced in the gas phase as pre-cracked V-hydride. The flux of the group V precursor is controlled to ensure single nucleation in each template, which grows with time to yield single crystal III-V in each template, confirmed by

Understanding the wake up and endurance of ferroelectric HZo on superconducting electrodes play into the exciting field of integration of ferroelectric thin films with superconducting films.


Atomicsy thin transition metal dichalcogenides (TMDs) show promise for flexible devices such as sensors, energy harvesters and nanoelectronics [1-3], because they can detect factors important for environmental sensing such as temperature, humidity, gas, pressure and light [1, 2]. Furthermore, nanoscale TMD field-effect transistors (FETs) enable low-power processing of sensor data and wireless communication like radio-frequency identification [3]. We recently developed a novel transfer process for TMDs, enabling high-performance flexible nanoscale FETs [4]. In this work, we employ this transfer process to demonstrate monolayer MoS2 temperature sensors and multilayer WS2 solar cells.

We have previously found that gated monolayer MoS2 exhibits a high temperature coefficient of resistance (TCR) of +0.27 %/K compared to ultrathin metal films [5], and could enable sensors with low thermal mass due to their three-atom thinness. Here we fabricate flexible two-terminal (un gated) monolayer MoS2 temperature sensors and obtain even larger (in absolute value) but negative TCR of -1.8 %/K between 30°C and 80°C. Preliminary analysis indicates that here space-charge limited current with shallow traps leads to the negative TCR, rather than phonon scattering causing a positive TCR in gated MoS2. Furthermore, the sensors reveal a rapid real-time response of at least 150°C/min (limited by our heater stage) and reversibility.

In addition, the excellent optical absorption properties of TMDs and their near-ideal band gaps for single-junction and tandem solar cells (with Si) make this technology attractive for powering internet-of-Things sensors at an ultralow specific power (<50 kW/kg), especially in wearables and environmental sensing systems [2, 6, 7]. We fabricated flexible WS2 solar cells with graphene top electrodes and MoO3, doping/passivation layer, where the whole active material is embedded within the flexible substrate, enabling a vertical cell architecture. We achieve a record-high power conversion efficiency of ~5%, while stable under mechanical bending to a radius of 4 mm. Concluding, this work provides important ingredients for flexible electronic systems where all active components benefit from the unique properties of atomically thin TMDs.


EM-Contributed On Demand-22 2020 AVS Graduate Research Award Talk: Monolithic Integration of Crystalline III-Vs on Amorphous Substrates using a Combination of Epitaxial and Non-epitaxial Methods, Debarghya Sarkar, R. Kapadia, University of Southern California

A primary challenge for 3D integration and flexible electronics is the ability to integrate high performance devices at temperatures limited by the thermal budget of the substrate or pre-existing device layers. Present approaches mostly involve hybrid bonding techniques where epitaxial films are first grown on lattice-matched substrates and then transferred to the host substrate at a device scale, circuit scale, chip scale, or wafer scale. Although the devices made using these approaches are of excellent quality, this approach is usually limited by cost, time, limited materials, and scalability perspectives. Monolithic integration approaches attempt to directly grow materials on the host substrate, but device performance is usually poor from solution-based or vapor-phase grown semiconductors on non-epitaxial substrates which give submicron-scale grain polycrystalline films. Here we show results from a liquid-vapor-phase growth approach, referred to as Low Temperature Templated Liquid Phase (LT-LTP) growth. Templates of group III materials capped with SiO2 are first realized on the non-epitaxial substrate by lithography, evaporation, and liftoff methods. Then the templates are heated (≈0.5 kW/kg) and the interconnects are annealed in a growth temperature between 200° to 400°C, and group V precursor is introduced in the gas phase as pre-cracked V-hydride. The flux of the group V precursor is controlled to ensure single nucleation in each template, which grows with time to yield single crystal III-V in each template, confirmed by

1 AVS 2020 Graduate Student Awardee
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electron backscatter diffraction (EBSD) imaging. Photoluminescence measurements for different growth temperatures give an optimal growth window of 280-320 °C, where optoelectronic quality is found to be comparable to single crystal commercial wafer. InAs grown at 300 °C shows room temperature mobility of ~6000 cm²/V-s. Comparing the highest electron mobilities reported from different material families grown directly on amorphous dielectric surfaces, it is seen that TLP III-Vs have the best mobility with LT-TLP InAs being about 2 orders of magnitude higher than the majority. These low temperature growths have been performed on rigid dielectric substrates like SiO₂ and HfO₂, as well as on flexible polyimide. Further, these high quality single crystalline mesas have been used as growth seeds for epitaxial films by MOCVD. Growth parameter variations are studied to obtain the best MOCVD InP-on-TLP InP morphology and optoelectronic properties. This potentially opens up a scalable and cost-effective method of integrating high quality III-V materials and devices on inexpensive amorphous dielectric surfaces for 3D integration.


Atomic Layer Deposition (ALD) of ternary TiSiN leads to nanocomposites of metallic TiN atomically mixed with insulating SiN. Formulating TiSiN films with various Ti:Si ratios lead to the emergence of a temperature regime where resistivity is independent of this drift, denoted as the temperature coefficient of resistivity (nz-TCR). Further, the ease with which nanocomposites of TiSiN can be deposited using ALD offer precise tunability in TiN thickness, mass density, crystallinity and electrical properties.

Recently, our group explored TiSiN films deposited using a Eugenes® 300 mm commercial QXP mini-batch system by modulating the ratio of Ti and Si precursors with NH₃ as a co-reactant. Si-content was varied from 0 at % (pure TiN) to 24.2 at % Si while maintaining thickness ~ 140 nm. The X-ray reflectivity and grazing incidence X-ray diffraction measurements showed a reduction in film density and transition from nano-crystalline to pure amorphous phase with increase in Si-fraction. Spectroscopic ellipsometry revealed the optical constants, composition, and electrical resistivities and were supported by X-ray photoelectron spectroscopy and electrical measurements. Room-temperature resistivity measurements show an increase in film resistivity with increasing at % Si. Temperature-dependent Van der Pauw measurements found a nz-TCR of -23 ppm K⁻¹ in the temperature range of 298 K – 398 K and at 3.4 at % Si content.

We have now discovered that an at % Si = 3.0% induces a nz-TCR of ~5.7 ppm K⁻¹ from 80 K – 420 K – one of the best reported nz-TCR values for ALD thin films. Fine tuning the at % Si in TiSiN films, possible only via ALD, significantly elongated the temperature window of nz-TCR behavior. Mapping the local conductivity of individual grains through conductive atomic force microscopy (c-AFM) indicated higher resistance at the grain boundaries. The local composition at the grain boundaries may play a major role in determining the nz-TCR behavior of TiSiN films. In addition, variable temperature Hall effect measurements were performed to provide deeper insights into the nz-TCR mechanism, decoupling carrier concentration from carrier mobility effects while determining film resistivity.

Compared to other nz-TCR films, which are deposited using physical vapor deposition techniques, ALD based nz-TCR films present a unique synthesis platform for interconnect technology in topologically complex, 3D devices, circuits and sensors that undergo large temperature variation during operation but need to maintain stability in their electrical characteristics.

EM-Contributed On Demand-28 Berry Curvature Memory Through Stacking Transitions in Topological Semimetals, Jun Xiao, A. Gupta, North Carolina State University; Y. Wang, UC Berkeley; H. Wang, Texas A&M University; C. Pemmaraju, SLAC National Accelerator Laboratory; S. Wong, UC Berkeley; P. Muscher, E. Sie, C. Nyby, T. Devereaux, Stanford University; K. Qian, Texas A&M University; Y. Yao, Carnegie Mellon University; A. Lindenberg, Stanford University

Quantum materials with novel phases of matter are the key building blocks of energy-efficient quantum electronics and powerful quantum computer. Exploiting control of those materials is fascinating to achieve new functionalities and information algorithms in future quantum devices. Quantum nanomaterials like layered materials have revealed many exotic properties such as extremely large magnetoresistance (MR), type-II Weyl electron transport, and diverging Berry curvature. On the other hand, the nature of layered materials leads to ultra-large tunability of physical properties via external stimuli.

Here we report the manipulation of quantum geometrical properties in a ferroelectric semimetal (WTe₂) belonging to layered Weyl materials (Fig. 1). With such control and various characterization means, we observed substantial modulation in optical and electrical responses associated with the unique stacking orders in such exotic ferroelectric semimetal. Further nonlinear Hall transport measurements show the observed transitions are locked with the variation of topological and geometrical property (Fig. 2). Our findings demonstrate a new low-energy cost, electrically controlled topological memory in the atomically thin limit.


EM-Contributed On Demand-31 Metal-Semiconductor Contacts to β-GaO₃: Dependence on Metal Work Function and Crystallographic Surface Plane, Y. Yao, K. Jiang, E. Favela, Y. Yao, Carnegie Mellon University, USA; K. Das, North Carolina State University; Z. Galazka, A. Popp, Leibniz Institute for Crystal Growth, Germany; L. Porter, Carnegie Mellon University, USA

Because of its ultra-wide bandgap (~4.8 eV), full range of n-type doping, and availability as single-crystal substrates produced from melt-growth methods, β-GaO₃ is being intensively pursued for electronic devices that could substantially increase device operating limits for voltage and power. The successful device development of any semiconductor technology requires the ability to produce suitable ohmic and rectifying (Schottky) contacts. In the case of β-GaO₃, most metals tend to naturally form Schottky contacts, whereas few metals have been established as ohmic contacts to this semiconductor. Our investigations of numerous metal contacts have also shown significant differences for different GaO₃ surfaces. For example, Schottky barrier heights of metals on (-210) GaO₃ showed little to no dependence on the metal work functions, suggesting significant Fermi level pinning. In contrast, Schottky barrier heights for metals on (100) GaO₃ showed a strong correlation with the metal work functions: e.g., the slope S was 0.96 and 0.61 for the I-V and C-V determined Schottky barrier heights, respectively. For ohmic contacts to GaO₃, we found that the metal work function is not a dominant predictive factor; whereas interface reactions and contact morphology play important roles in ohmic contact formation. Results and analyses from electrical measurements of many different metals that formed ohmic or Schottky contacts to (-201) and (100) β-GaO₃ will be presented and discussed.


BiFeO₃ (BFO), the most extensively studied room temperature multiferroic material with Néel temperature Tₘ ~ 640K and Curie temperature Tᵥ ~ 1100K, shows strong coupling between antiferromagnetic and ferroelectric order parameters. BFO could be a potential candidate to be used in magnetoelectric logic and memory devices due to the presence of this strong coupling. However, overcoming high leakage current, high switching voltage and low remnant magnetization are the biggest challenges for its device applications. Materials with lower coercive voltages Vᵥ are desired to reduce the operating voltage for lower power consumption as well as to avoid thermal decomposition of the material in thin film form. With Fe-site substitution by magnetic element Co, the spin structure of BFO is indeed modified and a canted collinear phase with weak ferromagnetic moment at room temperature is stabilized. Also, doping with Co can lead to changes in the crystal structure that possibly affect its ferro/piezoelectric properties. Bi₁₋₀₅CoₓFe₂O₃ (xBFCO) with different x values could be a suitable material with enhanced magneto-electric properties for device application.

Epitaxial films of multiferroic Bi₁₋₀₅CoₓFe₂O₃ (0 ≤ x ≤ 0.35) are grown on SrTiO₃
(001) and SrRuO$_3$ buffered SrTiO$_3$ (001) using pulsed laser deposition technique. The effect of Co substitution on the crystal structure, magnetic properties and piezo/ferro electric properties are investigated. The XRD analysis indicates that the phase-pure xBFCO has been synthesized for (0 ≤ x ≤ 0.35) without any secondary impurity phases. As the Co concentration increases, the films are stabilized as tetragonal phase BiCoO$_3$-like structure. The semi-empirical Kay-Dunham scaling law of coercive voltage (V) with thickness (t) (V = $t^{-0.5}$) for different concentrations of cobalt are studied using piezo force microscopy (PFM) technique. Here we demonstrate that within the rhombohedral structure, systematic reduction of the coercive voltage can be achieved by increasing substitution of Fe by cobalt on BFO. These results suggest a possible pathway to realize BFO-based non volatile magneto-electric memory devices with relatively lower operating voltages. Moreover, to understand the effect of Co doping on the structural, magnetic and the electronic properties, we have performed theoretical calculations using density functional theory (DFT). The results indicate that a reduction in unit cell volume, enhancement in net magnetization and reduction in the band gap can be achieved by Co doping of BFO.

EM-Contributed On Demand-37 High-Quality Molybdenum Nitride Schottky Diodes to n-Type Gallium Nitride, Alex Molina, I. Campbell, T. Walter, A. Aygapong, S. Mohney, Pennsylvania State University

Although silicon (Si) currently dominates the semiconductor industry, its small band gap (1.1 eV) limits its maximum operating temperature, restricting its use in high-temperature, high-power devices. Gallium nitride (GaN) is an attractive semiconductor with its wide bandgap (3.4 eV), high electron mobility, large critical breakdown field, and thermal stability. While the semiconductor itself can endure harsh operating conditions, the reliability of the metal/semiconductor contacts can be a limiting factor for its use. Schottky contacts should provide a high barrier height and low reverse leakage current, and they must be electrically stable over the lifetime of the device.

The MoN$_x$/n-GaN Schottky diode was chosen for study because of the reported high work function of MoN, (5.33 eV) and its conductive and refractory nature. It is also reported to be in thermodynamic equilibrium with GaN$^2$. Films were deposited by plasma atomic layer deposition and were examined by x-ray photoelectron spectroscopy (XPS), grazing incidence x-ray diffraction (GIXD), and transmission electron microscopy (TEM) with energy dispersive spectroscopy (EDS) to determine their composition and structure. TEM reveals an abrupt interface between MoN$_x$ and n-GaN with a cubic phase that is further confirmed with GIXD and EDS. XPS show a significant amount of carbon within the cubic phase. The barrier heights were investigated using current-voltage (I-V) and capacitance-voltage (C-V) measurements. Both techniques demonstrated that the barrier height increased after an anneal at 600°C for 5 min, yielding a barrier height of 0.87 eV with an ideality factor of 1.02 by I-V measurements, while the C-V measurements revealed a barrier height of 0.94 eV. Rectifying behavior was maintained upon annealing in N$_2$ at 700°C. Future work will involve stress testing followed by materials characterization to provide more information on stable metallizations for high-power GaN devices. This work was funded by the Office of Naval Research under Grant N000141812360, distribution A, approved for public release, distribution is unlimited (DCNR 43-8038-21).


EM-Contributed On Demand-40 Area-Selective Deposition/Patterning of Boron Carbide Layers with Atomic Layer Deposition, Roja Sekhar Bale, R. Thapa, L. Dorsett, S. Wagner, A. Caruso, Department of Physics and Astronomy, University of Missouri- Kansas City; J. Bielefeld, S. King, Intel Corporation; M. Paquette, Department of Physics and Astronomy, University of Missouri- Kansas City

The semiconductor industry is pushing its boundaries in device scaling technology by way of novel processing methods and increasingly complex patterning schemes. This requires a variety of functional and patterning-assist materials as well as advanced deposition techniques. For years, Si-based materials have been used to meet these needs; however, these alone cannot fulfill the range of material requirements moving forward. Boron carbide has shown promise due to compelling dielectric, thermal, mechanical, chemical, and etch properties. Toward applying this material to next-generation integration schemes, we have been exploring the potential of going beyond traditional growth processes (e.g., plasma-enhanced chemical vapor deposition) and investigating innovative area selective atomic layer deposition (AS-ALD) strategies. Herein we explore...
The accompanying SEM images before and after the application of pressure show improved contact at the interface between the compact TiO$_2$ and the fluorine-doped tin oxide. In subsequent layer-by-layer deposition, the interface roughnesses were in the range of 10 to 40 nm RMS as measured by AFM. Initial results from energy dispersive spectroscopy demonstrate significant interlayer diffusion and cracking in pressurized solar cells, particularly of iodine, lead, and tin, but limited diffusion and much lower incidence of cracking in unpressurized devices. The devices with higher diffusion and cracking had lower power-conversion efficiencies and lower stability. 

**2** Diffusion was also studied as a function of annealing time and temperature. We will discuss the competition between improved contact and diffusion/cracking in pressurized PSCs and their implications for the improvement of long-term power conversion efficiency.


**EM-Contributed On Demand-52 Enhanced Luminescence of SiO$_x$/SiO$_2$ Multilayers Structures Obtained by Sputtering Technique, Alma Lizet Valdez, K. Monfil, Research Center of Semiconductor Devices, Mexico; A. Morales, bNstitution of Astrophysics, Optics and Electronics, Mexico; F. Morales, Center investigated of optics A.C., Mexico; F. Uribe, J. Luna, Z. Hernández, Research Center of Semiconductor Devices, Mexico; A. Muñoz, Electronics Faculty. Meritorious University Autonomous of Puebla, Mexico

In particular, the non-stoichiometric silicon oxide (SiO$_x$) has been proposed as a cheap and effective alternative to develop ultraviolet absorbers or light emitters. SiO$_x$ films can be deposited by several deposition techniques but they can be obtained at Room Temperature by Sputtering deposition technique. New devices based on SiO$_x$ films include different structures of stacked films like multilayers or superlattices. This work presents a study of the optical, structural and electrical properties of non-stoichiometric silicon oxide on silicon oxide (SiO$_x$/SiO$_2$) multilayers obtained by sputtering deposition technique. Non-stoichiometric silicon oxide films were deposited using a combination of Silicon and quartz (SiO$_2$) targets. Therefore, the study of the optical and structural properties of non-stoichiometric silicon oxide films by using silicon and silicon oxide targets is an interesting route for the design of optoelectronic devices based on Silicon technology. The SiO$_x$/SiO$_2$ multilayer structure was formed by five stacked bilayers with the different power application on target silicon. All samples were deposited on silicon substrates with low resistivity.

One of the main achievements to produce SiO$_x$/SiO$_2$ multilayers structures with different silicon excess, was to control the variation of the power on the Silicon target and keeping constant the power on silicon oxide target. In this case, electroluminescence devices were developed with multilayers structures involving silicon nanocrystals, to reduce the energy barrier for conduction between the silicon oxide layers and silicon nanocrystals. According to our results, the threshold voltages to obtain a visible electroluminescence were reduced in comparison with previous reports. Therefore, it could be better to use a multilayer that uses SiO$_x$ / SiO$_2$ mixture layers with high photoluminescence to reduce the energy barrier for conduction between nanocrystals and consequently lower voltages would be required for carriers’ injection.

**EM-Contributed On Demand-55 Optimized Deposition Conditions of Silicon Rich Nitride Obtained by Lpcvd to Achieve Down-Conversion Effect as Uv Absorption Coating on Solar Cells, Francisco Uribe-González, K. Monfil, M. Domínguez, Research Center of Semiconductor Devices, Meritorious University Autonomous of Puebla, Mexico; M. Moreno, National Institute of Astrophysics, Optics and Electronics, Mexico; A. Muñoz, Electronics Faculty. Meritorious University Autonomous of Puebla, Mexico; J. Hernández, A. Salazar, Research Center of Semiconductor Devices, Meritorious University Autonomous of Puebla, Mexico

The research trend on new materials and alternatives to improve energy generation devices, includes the synthesis and development of absorbent coatings. In particular, silicon solar cells can be optimized with coatings capable of capturing more or less energetic wavelengths than silicon can assimilate, this could be possible through silicon rich nitride (SRN). Silicon nitride has been used in many industry sectors as a protective coating, but the SRN also has convenient optical characteristics to achieve an improvement on efficiency of silicon solar cells keeping in mind the best cost-efficiency. This can be achieved by the down conversion effect. In this work, we propose an optimization on the deposition conditions of SRN films obtained by LPCVD to achieve the down-conversion effect. SRN films were obtained using NH$_3$ mixed with SiH$_4$ as precursor gases with a ratio of R$_{o}$ between 4 and 80, the temperature was varied from 600°C to 720°C and thermal annealing was applied to some samples to compare with as-deposited films. Ellipsometry showed that the refractive index can be well controlled by the gases ratio and deposition temperature. Fourier transform infrared (FTIR) spectra showed characteristic peaks of Si-N matrix and N-H vibration modes. The images of AFM showed that surface roughness morphology can be also affected by the deposition temperature. Energy dispersive spectroscopy measurements were obtained to estimate the SRN films composition, the results showed a silicon enrichment dependence on temperature. SRN films showed a clear photoluminescence (PL) at room temperature (RT), the main band was located between 380 to 650 nm. PL emission was related to donor acceptor decays between traps promoted by defects.

The optical, structural and morphological characteristics SRN films showed a clear dependence on the deposition time, the ratio of the precursor gases and the deposition temperature. Suitable refractive index, surface roughness and PL emission were obtained with a flow ratio of 4 and deposition temperature of 700 °C. These deposition conditions assure convenient optical characteristics of SRN films to achieve down conversion effect and they suppose a low influence on diffusion of PN junctions when SRN is used as UV absorption coating.

**Keywords:** Silicon rich nitride, LPCVD, Photoluminescence

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Novel computation challenges including neuromorphic networks, memory-centric computation, machine learning, or steep-slope transistors require to go beyond traditional MOSFET architecture and instead explore high-k thin films for ferroelectric or resistive random access memory (RRAM) technology. Typically, such ferroelectric or RRAM thin films are deposited on Si substrates, which still is the standard material within electronics industry. However, III-V semiconductors such as InAs or InGaAs offer a much higher charge carrier mobility and more flexibility for low-power applications. We are investigating HfO$_2$ RRAM and Hf$_2$ZrO$_2$ (HZO) ferroelectric thin films on InAs and InGaAs substrates and gate-all-around nanowire structures, the latter for reaching ultimate electrostatic control. In order to obtain state-of-the-art device performance and outperform silicon technology, we need to thoroughly understand and optimize the materials properties of the III-V/high-k interface.

Previously, we performed various synchrotron X-ray photoemission (XPS) studies of InAs/HfO$_2$ and InAs/Al$_2$O$_3$ interfaces of MOSFET devices, where we analyzed the role of different As sub-oxides and defect states, obtained As-oxide and In-oxide interface depth profiles, and also looked at interfacial thermal processes. It turned out that the device performance is matched with less interfacial oxide as possible. By implementing atomic layer deposition of HfO$_2$ at an ambient-pressure XPS synchrotron beamline, we could even reach perfect self-cleaning and reveal new insights on the surface chemistry involved in the self-cleaning mechanism.

Here, we will present systematic XPS and X-ray absorption spectroscopy (XAS) results together with electrical device data of ferroelectric HZO and RRAM HfO$_2$ films on InAs and InGaAs. In contrast to the MOSFET applications, we observe that a certain thickness and composition of interfacial oxide is required in order to obtain RRAM or ferroelectric functionality. In the case of RRAM nanowires, we find a critical dependence on the type of oxide deposition method and parameters, since these determine the amount of oxygen vacancies that influence the conductive filament formation. Furthermore, we obtain an inhomogeneous depth profile of the interfacial oxide. For ferroelectric HZO films with a thickness of down to nm, oxygen vacancies and defects at the interfaces both to the top metal electrode and to the InAs substrate turn out to be critical for device performance and polarization endurance. A combined and interactive materials science and electrical device processing approach is needed to optimize these complex interface structures.
An understanding of time-dependent dielectric breakdown (TDBD) in SiO₂ gate dielectrics has long been of great interest. Several models have been proposed involving the generation of oxide traps which eventually form a percolative leakage path through the dielectric. However, little direct experimental evidence about the traps exists. Electrically detected magnetic resonance (EDMR), and near-zero-field magnetoresistance (NZFMR) can provide this atomic scale information in real devices. We present EDMR and NZFMR studies of defects generated during the high-field gate stressing of Si/SiO₂ MOSFET arrays. Our studies substantially extend earlier resonance studies which were only able to identify one interface defect [1,2]. We subject our devices to gate stressing conditions and periodically interrupt the stress to measure interface recombination current, and spin-dependent interface recombination (SDR) current via EDMR and NZFMR. A nearly perfect correspondence between recombination current and SDR response is found at all stressing conditions. Interface state buildup occurs more rapidly early in the device lifetime, and more slowly as time goes on. By performing EDMR at multiple magnetic field orientations, we identify the stress-induced interface defects as PₓOᵧ and Pₓ centers, dangling bond centers at the Si/SiO₂ interface. In addition, we observe a weaker SDR response in lower temperature (200K) measurements due to traps created within the oxide, likely oxide silicon dangling bonds known as E’ centers. Of particular interest, we find that the NZFMR response exhibits subtle changes in lineshape after different durations of gate stress, which we attribute to changes in the population of hydrogen in the vicinity of the Si/SiO₂ interface.


Sandia National Laboratories is a minimization laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and commentary. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

EM-Contributed On Demand-64 Ultrafast Switching of FeRh Memristors, Nicholas A. Blumenschein, G. Stephen, Laboratory for Physical Sciences; C. Cress, S. LaGasse, United States Naval Research Laboratory - Electronics Science and Technology Division; A. Hambicki, Laboratory for Physical Sciences; S. Bennett, United States Naval Research Laboratory - Materials Science and Technology Division; A. Friedman, Laboratory for Physical Sciences

FeRh is widely studied because of its novel temperature-dependent antiferromagnetic (AFM) to ferromagnetic (FM) phase transition. This AFM-FM phase transition, which is accompanied by a significant change in resistivity, occurs at a critical temperature that can be fine-tuned over a wide range through substitutional doping, strain, and patterning [1,2]. Because the transition is temperature-dependent, the state can be manipulated via Joule heating. Recent reports show the AFM-FM transition occurs on a sub-picosecond timescale, a range appropriate for switching applications where operating speeds should be in excess of GHz frequency. In this work we demonstrate ultrafast memristive FeRh wires. The thermally-induced AFM-FM transition was evaluated using two-terminal devices consisting of an FeRh wire and metal contacts. By using FeRh wires of varying dimensions, we were able to identify geometrical dependencies and found the AFM-FM transition temperature scaled with both current density and wire length. Pulsed I-V measurements were used to investigate the dynamic Joule heating effects, including the device switching speed and resulting power switching losses accompanying the AFM-FM transition. The upper bound of our device switching speeds, measured to be near 300 nanoseconds, was limited by measurement equipment limitations, not the material system. The performance of this rudimentary device is comparable to other phase change memory technologies with more intricate device architectures. FeRh could be the basis for a very fast, phase-change approach to future computing.

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EM-Contributed On Demand-67 Innovative Approach and Study of Transparent Conducting Oxide as Channel Materials for the Fabrication of Thin Film Transistors, Kelsea Yarbrough, S. Pradhan, M. Bahoura, Norfolk State University

Photolithography has been the most widely used technique for semiconductor fabrication and large-scale mass production of silicon-based devices. By 2025, the photolithography equipment will have a market worth of $18 billion. Commercial, thin film transistors are developed using the process of photolithography. One technique we plan to introduce to fabrication TFT is 3D printing mask technique. 3D printed technology, commonly referred to as additive manufacturing, is a process used to reduce cost of various deposition techniques. 3D printed mask technology was used to deposit the active layer and the dielectric layer of our devices. The indium-free oxide-based channel material such as aluminum-doped zinc oxide (AZO) is the active material and can be fabricated on glass substrate or silicon for TFT application. High quality AZO thin film grown by radio frequency (RF) sputtering technique and pulsed laser deposition on p-type silicon and glass for characterization purposes. The effect of Al content on zinc oxide crystal lattice were investigated by Atomic Force Microscopy (AFM), X-ray diffraction, Raman Spectroscopy, Ultra-violet visible spectroscopy, and Keithley 4200 Semiconductor Characterization System (SCS). AFM provided details information about the roughness, grain size, and surface morphology of thin films. FE-SEM measurement was performed to show cross sectional view of the fully developed thin film transistor. Raman Spectroscopy provided vibrational frequencies and a fingerprint of thin film used for the device fabrication. Finally electrical transistor characteristics were carried out using Keithley 4200 SCS provided including on/off ratio, mobility, and threshold voltage. The present work will provide valuable scientific input of AZO based active materials TFTs for the improvement of devices performance.

EM-Contributed On Demand-70 Epitaxial Growth of Donor and Acceptor Doped β-Ga₂O₃ by Magnetron Sputter Deposition, Adedayo Adedeji, Elizabeth City State University; J. Lawson, A. Reed, S. Paceley, J. Merritt, Air Force Research Lab

High quality β-Ga₂O₃ films were deposited on various single crystal β-Ga₂O₃ substrates by magnetron sputtering. Deposition of the epilayers was achieved by co-sputtering a pure Ga₂O₃ target and Si, Sn, or Fe Si targets. The substrate temperature was 570°C during a 2-hour deposition in Ar/O₂ gas mixtures (5% O₂ by flow rate). Substrate orientations used were (010) or (1-201) and were either Sn-doped, unintentionally doped (Si doped in 10⁴ cm⁻² range), or semi-insulating Fe-doped. Radio frequency power was applied to the Ga₂O₃ target while the dopant targets were sputtered with RF or DC power. A Si-doped sample was deposited using DC sputtering on a pure Si target. The sample thickness measured by ellipsometry was 187.2 nm. At the corners of 5 mm x 5 mm samples, Ti/Al/Al contact metals were deposited by electron beam evaporation. The contacts were annealed in argon flow at 650°C. Hall-Effect measurements indicated donor concentration of about 3 x 10¹⁷ cm⁻³. The average sheet resistance, resistivity, and carrier mobility were 652 Ω/sq, 1.23 x 10⁴ Ω·m, and 19.1 cm²/V·s respectively. Additional samples were produced with either no dopant, Fe, Sn, or Si targets. Fe-doped films were found to be non-conducting. High resolution x-ray diffraction (XRD) 2θ-ω, 2θ and rocking curve measurements were performed to determine the film crystallinity. Differences in crystallinity were observed based on Ga₂O₃ film doping and substrate choice. A small secondary (2-201) Ga₂O₃ diffraction peak on 2θ-ω XRD scan for the undoped Ga₂O₃ on (2-201) Sn-doped Ga₂O₃, combined with minimal diffraction peaks on the 2θ scan and a secondary peak on the rocking curve scan, suggest predominately epitaxial growth. The XRD analysis for the Sn-doped Ga₂O₃ on the unintentionally-doped Ga₂O₃ substrate were inconclusive. Further analysis will be done to determine whether the film is amorphous or homoepitaxial.
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EM-Contributed On Demand-73 The Synthesis of NbSe₂ by Molecular Beam Epitaxy for Thermomagnetic Energy Conversion, Peter Litwin, S. Akhanda, M. Zebbarjadi, S. McDonnell, University of Virginia

The synthesis of high-quality NbSe₂ thin films is of significant interest for potential applications in thermomagnetic energy conversion. Molecular beam epitaxy (MBE) is a promising route towards this aim as it provides fine control over growth conditions. For thermomagnetic energy conversion, the metallic 2H phase of NbSe₂ is desired. However, a number of competing phases are found to form during synthesis by MBE and likely include metastable phases, such as semiconducting 1T-NbSe₂. It has been previously reported in literature that metastable 1T-NbSe₂ forms at higher temperatures than the 2H phase. Conversely, higher growth temperatures are potentially beneficial for growing high-quality 2H-NbSe₂ because of improved adatom mobility that results in better crystalline quality. We will report on an investigation of the competing effects of crystal quality versus mixed phase growth with a goal of optimizing growth conditions for thermomagnetic energy conversion. In-situ X-ray photoelectron spectroscopy (XPS) and reflection high energy electron diffraction (RHEED) will be performed to analyze the intrinsic chemical composition and growth mode of the synthesized material prior to atmospheric processing exposure. Ex-situ Raman spectroscopy will aid in phase identification. In order to obtain the Nernst coefficient, which quantifies the material’s ability to generate thermomagnetic power, ex-situ measurements will be carried out on NbSe₂ films grown on insulating muscovite.

EM-Contributed On Demand-76 Scaling of Atomic Layer Deposited Dielectrics on UV-O³ Functionalized WSe₂, Maria Gabriela Sales, University of Virginia; S. Najmaei, Army Research Laboratory; S. McDonnell, University of Virginia

WSe₂ offers fundamentally unique charge carrier and transport properties compared to other transition metal dichalcogenides (TMDs), such as its propensity for p-type doping and its enhanced spin-orbit coupling. These qualities make WSe₂ a promising channel candidate for a multitude of different applications, including field effect transistors (FETs) and low power memory devices. For integration in an electronic device, TMDs such as WSe₂ are typically capped in the gate region with a high-quality dielectric layer, where ultrathin (sub-5 nm) dielectric thicknesses are desired in order to achieve sufficient gate to channel electrostatic coupling. Atomic layer deposition (ALD) is the conventionally used technique for dielectric deposition, but it has been previously shown in various reports that typical ALD on TMDs results in clusters formed on the surface rather than a uniform film, primarily because of the lack of surface dangling bonds on TMDs. Ultraviolet-ozone (UV-O³) functionalization of TMDs has been found to be an effective route to producing more uniform ALD oxide films on TMDs because it induces adsorbed oxygen on the surface (i.e., Se-O₆⁻⁻) which serve as reaction sites for the ALD precursors on the otherwise unreactive surface. This functionalization for ALD has been well-replicated for MoS₂, but is less trivial for other TMDs such as WSe₂. The main goal of this current work is to benchmark UV-O³ functionalization of WSe₂ as a promising route towards achieving directly integrated sub-5 nm gate dielectrics. Various UV-O³ exposure times will be tested on germanium WSe₂ crystals. XPS will be performed after each UV-O³ exposure to check for oxygen adsorption on the surface and/or oxidation of the WSe₂ constituents. To investigate how effective the surface functionalization is for ALD, AFM will be performed post-ALD of HfO₂ to study the morphology of the resultant layer. Using the best UV-O³ processing parameters, various thicknesses (between 2-10 nm) of HfO₂ and Al₂O₃ will be deposited on functionalized WSe₂ substrates. Subsequent AFM characterization will be performed to analyze the resulting film morphology and uniformity. The downscaling thickness limit will be determined as the thinnest pinhole-free film produced. XPS will be performed on the HfO₂/WSe₂ and Al₂O₃/WSe₂ heterostructures to analyze their interface chemistry and band alignment.

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Electronic Materials and Photonics Invited On Demand Session

EM-Invited On Demand-1 Light Management Strategies for Photovoltaics: Luminescent Concentrators and Passive Cooling for Modules, Vivian Ferry, University of Minnesota, USA

On Demand available October 25-November 30, 2021

The solar spectrum is a broad and diffuse light source, but solar panels operate most efficiently at wavelengths near the semiconductor bandgap and over a limited range of incident angles. This talk will discuss different strategies to manage the solar spectrum in photovoltaics: the first part will discuss luminescent solar concentrators that harvest diffuse, high energy sunlight and are integrated into architectural panels, where we use nanostructured luminescent materials and photonic surfaces to enhance performance. The second part will discuss optical strategies to reduce the operating temperature of photovoltaic modules.

Our work on luminescent solar concentrators uses two different nanocrystal luminophores, CdSe/CdS core-shell nanocrystals and Si nanocrystals, embedded into a polymer matrix. These light-emitting nanocrystals offer several advantages over dye molecules, but also exhibit detrimental scattering when aggregated. I will discuss the preparation of nanocrystal-polymer composites with high optical clarity for these applications. The CdSe/CdS nanocrystals are embedded into an alternative polymer, PC, and coated into very thin films on glass. The Si nanocrystals are incorporated into PMMA and deposited in thin films via blade coating, and we show that this method results in higher loading fractions than bulk composites. We then apply photonic structures to these luminophore-polymer composites that reduce optical losses and assist in guiding light efficiently toward the edge of the concentrator and onto a small-area solar cell.

The second part will discuss photonic structures for light management in photovoltaic modules. These structures are designed to provide both optical and thermal benefit: they act as broadband and omnidirectional antireflective coatings to increase the absorption of sunlight to the module, while simultaneously reflecting near-infrared light to keep the solar cell operating temperature low. We have developed models that predict energy yield improvement for particular locations, based on typical meteorological year data, and agree with experimental measurements on test modules. We use this model to predict and contrast the performance of mirrors on the outer glass, the surface of the cell, and the rear contact, showing that the mirrors on the glass offer the most temperature reduction. Mirrors on the cell surface, while attractive for reduced weathering, are limited by the textured surface of crystalline Si as well as the optical losses of the encapsulant. To circumvent the multiple reflections at the cell surface, we examine an alternative design consisting of idealized scatterers at the cell interface, and compare the performance of these nanostructures to idealized mirrors.

EM-Invited On Demand-7 Epitaxial Quantum Dots for Quantum Science and Technology, Sam Carter, J. Grimm, A. Brakke, M. Yakes, M. Zalalutdinov, C. Kim, US Naval Research Laboratory; M. Kim, KeyW Corporation; D. Gammon, US Naval Research Laboratory

Self-assembled indium arsenide quantum dots are a promising platform for applications in quantum computing and technology. This system has the advantages of a robust solid state host, strong optical transitions, mature device fabrication, tunable properties, and a scalable, monolithic architecture. Of particular importance for many applications is the ability to charge the dots with a single electron or hole in order to make use of a spin memory. We have integrated electrical diode structures within various optical cavities and mechanical resonators that allow charging of dots and control over spin. In photonic crystal cavities, this has enabled demonstrations of fast, optical spin rotations, cavity-stimulated Raman emission, and strong coupling [1,2]. In mechanical resonators this has enabled the demonstration of large spin-mechanical coupling with both hole and singlet-triplet system in pairs of dots [3,4]. Quite recently we have also made significant progress in solving two important long-standing challenges with quantum dots. The first challenge is to combine in one system the ability to have both fast, optical control of spin and strong spin readout, which we have addressed by using a set of higher energy optical transitions with one hole in an excited orbital. These transitions provide fast optical control while the lowest energy transitions give efficient spin readout. The second challenge is inhomogeneity of quantum dot emission energies, which we have addressed using a localized strain tuning technique that allows multiple dots within the same optical waveguide to be tuned into resonance. Using this technique we have demonstrated superradiance of three quantum dots embedded in a nanophotonic waveguide [5].

First, we show that the onset of electrochemical and photoelectrochemical reactions on a graphene surface can be modified with a semiconductor-insulator-graphene (SIG) device due to injection of hot-electrons from the silicon to the graphene. We observe that the device functions similar to a catalyst, but modifies electrochemical behavior through purely electronic signals. Unlike a material catalyst, such as platinum, which reduces the overpotential at a given current by modifying the transition state energy, the electronic catalyst explored here tunes the onset potential of the reaction by modifying the energy of photoelectrons with respect to the electrochemical reduction energy levels. As a model systems, the hydrogen evolution reaction on graphene is shown to be modified in an n-Si/Al₂O₃/graphene electrochemical device, and a p-Si/Al₂O₃/graphene photoelectrochemical device. Uniquely, it is shown that for every volt of bias applied across the silicon-insulator-graphene junction, the onset of hydrogen reduction on the graphene surface is modified by 1.45 V with a saturation photocurrent density of ~40 mA/cm² indicating nearly ideal minority carrier collection despite the insulator layer.

Next, we show how hot-electron processes can dramatically reduce the optical power densities required for photoemission. In metallic emitters, single-photon, multi-photon, or strong-field emission processes are the three mechanisms via which photoemission takes place. Photons with energy lower than the material workfunction can only drive photoemission through the multi-photon, or strong-field processes, both of which require large optical powers, limiting the integration of photomitters with photonic integrated circuits. Here, we show that a waveguide integrated graphene electron emitter excited with 3.06 eV photons from a continuous wave (CW) laser exhibits two hot-electron processes that drive photoemission at peak powers >5 orders of magnitude lower than previously reported multi-photon and strong-field metallic photoemitters. Optical power dependent studies combined with modeling illustrate that the observed behavior can be explained by considering direct emission of excited electrons. These processes are dramatically enhanced in graphene due to the relatively weak electron-phonon coupling and the single layer structure. These results show that hot electron devices still offer a rich area of exploration.
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