

## Electronic Materials and Photonics Division Room Central Hall - Session EM-ThP

### Electronic Materials and Photonics Poster Session

#### EM-ThP-3 Electrolyte-Insulator-Semiconductor (EIS) device with Different Integrated Reference Electrodes for pH Detecting, *Rodrigo Reigota, J Diniz*, University of Campinas (UNICAMP), Brazil

In this work Electrolyte-Insulator-Semiconductor (EIS) device has been developed for pH measurements. This device operates as a Metal-Oxide-Semiconductor capacitor but instead of having the metal contact electrode, an electrolyte solution and a reference electrode are used to apply voltage. Titanium nitride (TiN), aluminium (Al) and alumina/aluminium ( $Al_2O_3/Al$ ) were used as reference electrode integrated with EIS device. These materials were deposited by DC sputtering. As dielectric material and sensitive membrane was chosen titanium dioxide ( $TiO_2$ ). This film was obtained by DC sputtering, and was structurally characterized by Atomic Force Microscopy, Raman and Ellipsometry. The structural characterization of  $TiO_2$  thin film shows the presence of rutile and anatase crystal structure, physical thickness of 50 nm, refractive index of 2.44 and roughness of 0.4 nm. Was developed MOS capacitors to make the electrical characterization of  $TiO_2$  thin films in order to determine the annealing time that leads to the best thin film properties, defined by high dielectric constant value (high-k), lower charge density ( $Q_0/q$ ) and flat-band voltage ( $V_{FB}$ ) around -0.9V. The electrical characterization done by Capacitance x Voltage (CxV) curves revealed that with 15 min annealing the films exhibit the best dielectric constant equals to 133 which is higher than reported in literature. The  $V_{FB}$  was -0.6V and  $Q_0/q$  in the order of  $-10^{12}/cm^2$ . The Current x Voltage (IxV) curve shows that the current through the dielectric is approximately  $1 \times 10^{-9}A$ . With dielectric characterized it was possible to develop the EIS device. From electrical characterization it was possible to test the integrity of the electrodes and determined the sensitivity of the device. For electrical measurement of EIS was used Normalized Capacitance x Voltage curve (CxV curve) using different pH (4, 7 and 10) solutions. From the flat band voltage ( $V_{FB}$ ) of the Normalized CxV curves was possible to determine the sensitivity of the device. The Al and  $Al_2O_3/Al$  reference electrodes showed a low acid resistance. After measurement with pH 4 the electrodes were corroded. The TiN reference electrode showed to be a very resistant material. This electrode supported the electrical measurements with the three solutions. However, the EIS with the TiN reference electrode showed a low sensitivity of 20mV/pH.

#### EM-ThP-4 Optical and Magneto-optical Properties of $Zn_{1-x}Co_xO$ / ZnO Hollow Nanospheres, *Da-Ren Liu, C Weng*, Instrument Technology Research Center, National Applied Research Laboratories

Diluted magnetic semiconductors (DMS) have attracted considerable attention due to their potential applications for spintronic devices, such as spin-valve transistors, nonvolatile memory, and magneto-optical switches. ZnCoO is one of the most promising DMS materials due to its predicted above room temperature ferromagnetism. In this study, ZnO layer was conformally deposited on the surface of polystyrene (PS) nanospheres with different diameter (100nm~800nm) by atomic layer deposition (ALD). Then the  $Zn_{1-x}Co_xO$  ( $0.01 < x < 0.1$ ) coatings were grown on ZnO hollow nanospheres by pulsed laser deposition (PLD). According to the results of high-resolution x-ray diffraction, Co-doping does not change the wurtzite structure of ZnO and the  $Zn_{1-x}Co_xO/ZnO$  hollow nanospheres are polycrystalline. Photoluminescence spectra and transmittance show an increase of the band gap with increasing Co ion concentration. The temperature-dependent magnetization (M-T) curves of the  $Zn_{1-x}Co_xO/ZnO$  hollow nanospheres were measured by a superconducting quantum interference device (SQUID) magnetometer and the magneto-optical properties were measured by micro-MOKE spectroscopy. The results show the magneto-optical properties of the  $Zn_{1-x}Co_xO/ZnO$  hollow nanospheres depend on the Co composition fraction and the size of nanospheres.

#### EM-ThP-5 Low-k Cryo-etching: Comparison of Four Different High Boiling Point Organic (HBPO), *Romain Chanson*, IMEC, Belgium; *P Lefaucheux, R Dussart, T Tillocher*, GREMI, France; *P Shen, K Urabe, C Dussarat*, Air Liquide, Japan; *K Maekawa*, TEL Technology Center, America, LLC; *K Yatsuda*, Tokyo Electron Limited, Japan; *S Tahara*, Tokyo Electron Miyagi Limited, Japan; *J de Marneffe*, IMEC, Belgium

Low temperature plasma processing is investigated for low damage etching of porous organo-silicate glass ultra-low-k (p-OSG) dielectrics. For additional film protection, in-situ micro capillary condensation is used. This

effect allows condensation of a gas precursor into the porous structure. The condensate densifies the porous structure and avoids the plasma by-products to react with the Si-CH<sub>3</sub> terminating bonds. In this work, high boiling point organic (HBPO) molecules are studied as reagents for pore filling, enabling for the different gas condensation from -20°C to -50°C. The micro-capillary condensation properties of selected molecules in p-OSG will be compared as well as their desorption kinetic and stability when exposed to a pure SF<sub>6</sub> plasma. Using the most promising reagent, patterning tests using a 45nm ½ pitch vehicle and k=2.2 periodic mesoporous oxide low-k dielectric allows to generate vertical trench profiles with good mask selectivity (TiN). A slow kinetic of desorption and a large "Working Window" are critical points for optimal low-k protection.

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#### EM-ThP-6 Carrier Ion Exchange of $Na_2O-Fe_2O_3-P_2O_5-SiO_2$ Glass-Ceramics, *Yoshikazu Kaji, N Yoshida, T Okura*, Kogakuin University, Japan

Our group has developed Na<sup>+</sup>-superionic conductive Narpisio (typically represented as a general formula of  $Na_3RP_3Si_3O_{12}$ , R=rare earth) glass-ceramics, as analogues of  $Na_3RSi_4O_{12}$  (N5)-type Na<sup>+</sup>-superionic conductors, and it was revealed that these showed excellent ionic conductivity up to  $\sim 10^{-1} S/cm$ , which is comparable to those of the conventional ceramic Na<sup>+</sup>-conductor such as b- and b<sup>2</sup>-aluminas and NASICONs. Recently we achieved two important replacements, that is, R with Fe, and carrier Na<sup>+</sup> with H<sup>+</sup>. The replacement of R with cheap and rich Fe is important in terms of cost and amounts of resources. The carrier ion exchange of Na<sup>+</sup> with H<sup>+</sup> will spread its applications, such as a fuel cell.

In this study,  $Na_{4.9}FeP_{0.1}Si_{3.9}O_{12}$  glass-ceramics of N5 phase was prepared at first, and then, exchange of carrier Na<sup>+</sup> ion with H<sup>+</sup> was tried in several conditions.

$Na_{4.9}FeP_{0.1}Si_{3.9}O_{12}$  glass-ceramics of N5 phase was prepared by melt-quenching and glass-crystallization method. Ion exchange experiment was carried out as follows; while monitoring with pH meter, prepared glass-ceramics was immersed into HCl aq. with/without NaCl at room temperature. The obtained samples were characterized by X-ray diffraction analyses (XRD), thermogravimetry-differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC).

XRD measurement indicated that glass-ceramic  $Na_{4.9}FeP_{0.1}Si_{3.9}O_{12}$  of N5 phase was successfully prepared. After ion exchange without addition of NaCl, unknown phase was appeared in XRD pattern, and this change could not be suppressed by changing concentration of HCl aq. A possible explanation against this change is due to dissolution of bonding Na<sup>+</sup> in addition to carrier Na<sup>+</sup>. After ion exchange with addition of NaCl, unknown phase was disappeared, although slight decrease in crystallinity was observed.

Glass-ceramic  $Na_{4.9}FeP_{0.1}Si_{3.9}O_{12}$  of N5 phase was successfully prepared and replaced carrier Na<sup>+</sup> ion with H<sup>+</sup> without significant changes in crystallinity under the conditions of ion exchange with addition of NaCl. Detail of experiments and thermodynamic data will be discussed in the presentation.

#### EM-ThP-7 Defect Doping ZnO Thin-Films with $\gamma$ - Radiation, *Seth King, K Slezak*, University of Wisconsin - La Crosse; *S Chamberlin*, Lawrence University; *S Lantvit*, University of Wisconsin - La Crosse

Sputter deposited ZnO thin films have been exposed to prolonged high energy gamma radiation in a 400 Ci <sup>137</sup>Cs irradiator to examine the impact of such exposure on the optical, structural, and electronic properties of this technologically important wide-bandgap semiconductor. While many studies have shown that ZnO is radiation hard to proton and electron damage [1,2], only one has investigated the effects of exposure to high-energy photons, and not in an iterative manner [3].

UV-Vis spectrometry and spectroscopic ellipsometry show little variation in the over-all transmittance, optical constants, or optical bandgap of the irradiated films. Continued exposure shows a decrease in the films' resistivity, which, along with supporting x-ray photoelectron spectroscopy data, suggests that induced O-vacancies are acting as donors to dope the irradiated films.

References:

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**EM-ThP-8 Design and Synthesis of Precursors for Photoassisted Chemical Vapor Deposition**, *Christopher Brewer*, *O Hawkins*, University of Florida; *B Salazar*, *A Walker*, University of Texas at Dallas; *L McElwee-White*, University of Florida

Chemical vapor deposition (CVD) is a potentially attractive technique for the metallization of organic thin films. However, thermal CVD processes often require high temperatures which are incompatible with organic substrates. Photochemistry provides an alternative means of initiating precursor decomposition without heating the substrate. Readily available Ru precursors, including ( $\eta^3$ -allyl)Ru(CO)<sub>3</sub>X and CpRu(CO)<sub>2</sub>X (X = Cl, Br, I), have been used to deposit Ru on functionalized self-assembled monolayers (SAMs) by means of photochemical CVD as a model system for deposition of metal on a thermally sensitive substrate. Carboxylic acid-, hydroxyl- and methyl-terminated SAMs were used to explore the effects of surface functionality on deposition and the presence of Ru on the SAMs was confirmed by HR TOF SIMS. Preliminary experiments have shown that an attractive precursor for photoassisted CVD will be volatile, have an acid sensitive functionality and have a reasonable quantum yield for ligand loss. Synthesis of the precursors, determination of the quantum yields and deposition of Ru onto the functionalized SAMs will be discussed.

**EM-ThP-9 Electrical and Mechanical Improvements with a Non-Thermal Curing Process for Porous SiCOH using Combined Ultraviolet and Vacuum-Ultraviolet Radiation**, *Sang-heum Kim*, *J Blatz*, *W Li*, *H Zhang*, *D Pei*, *T Guo*, *X Zhou*, University of Wisconsin-Madison; *Y Lin*, *H Fung*, *C Chen*, National Synchrotron Radiation Research Center, Taiwan, Republic of China; *S King*, Intel Corporation; *Y Nishi*, Stanford University; *J Shohet*, University of Wisconsin-Madison

Porous SiCOH films are rapidly emerging as preferred interplay dielectric materials in semiconductor fabrication because of their ultra-low dielectric-constant properties. Ultraviolet (UV) light on organosilicate thin films in post-deposition treatments initiates photo-chemical process by nano pores generators (porogens) and form a network to improve mechanical properties of the dielectrics. A simple and cost-saving method of improving not only the mechanical property but also electrical property was found by combined with two different UV exposure energies called UV/Vacuum Ultraviolet (VUV) photons curing without the need for heating the dielectric [1] The goal of this work is to choose the best combined UV/VUV photon energies and to investigate beneficial effects that lower the dielectric constant, minimize damage, and increase the elastic modulus of low-k dielectrics as a function of the fluence of the UV/VUV curing photons. The following measurements were made. (1) We exposed SiCOH films samples with UV/VUV photon energies ranging from 4.5 to 8.9 eV from a beamline at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. (2) Using both nanoindentation and Time-Dependent Dielectric Breakdown (TDDB) measurement, we found the most beneficial energies (usually 2) for improving both electrical and mechanical properties could be found from VUV spectroscopic measurements. (3) We exposed the same SiCOH films at the same beamline using two combined photon energies with four different fluences from  $5 \times 10^{14}$  photons/cm<sup>2</sup> and  $10^{16}$  photons/cm<sup>2</sup>. (4) We measured TDDB and the nanoindentation after exposure. We show that this method can be applied to different porous SiCOH films, so that we can overcome drawbacks of UV curing and improve the properties of these dielectrics at room temperature.

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[1] H. Zheng, *et al. Applied Physics Letters*, **108** 242906. (2016)

**EM-ThP-10 The Effects of Cesium Ion Implantation on the Mechanical and Electrical Properties of Porous SiCOH Low-k Dielectrics**, *Weiyi Li*, *D Benjamin*, *J Chang*, University of Wisconsin - Madison; *Q Lin*, IBM Research Division, T.J. Watson Research Center; *S King*, Intel Corporation; *J Shohet*, University of Wisconsin - Madison

In this work, we investigate the effects of cesium (Cs) ion implantation on both porogen-embedded and UV-cured (porous) SiCOH films. It has been shown in past work that Cs doping has benefits for either spin-on low-k dielectrics[1] or PECVD deposited non-porous SiCOH low-k dielectrics.[2] For porogen-embedded SiCOH, it was found that Cs ion implantation can greatly improve the elastic modulus up to twice its original value. It can

also increase the time-zero dielectric breakdown (TZDB) strength. It also leads to an increase in the k-value for medium and high Cs doses, but for low Cs doses the k-value decreases compared with its pristine counterpart. These effects can be understood by examining the changes in Si-CH<sub>3</sub> bonds and Si-O bonds. For UV-cured SiCOH, it was found that Cs ion implantation does not modify the elastic modulus. This also leads to lower TZDB field strength and much higher k-values than its pristine counterpart. This treatment is shown to have a potential to help solve the problem between the demand for lower k-values and the concomitant weak mechanical strength of SiCOH.

This work was supported by the Semiconductor Research Corporation under contract 2012-KJ-2359.

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**EM-ThP-11 The Effect of Proton Radiation on ALD HfO<sub>2</sub> Films and HfO<sub>2</sub> base RRAM**, *Panpan Xue*, University of Wisconsin-Madison; *Z Wang*, Stanford University; *T Chang*, University of Wisconsin-Madison; *Y Nishi*, Stanford University; *J Shohet*, University of Wisconsin-Madison

Hafnium oxide(HfO<sub>2</sub>) is one of the most popular dielectric materials for RRAM. Changes of the defect concentrations of HfO<sub>2</sub> may affect the resistive-switching mechanism of RRAM. In this work, in order to investigate the effects of proton radiation, (1) atomic-layer-deposited (ALD) HfO<sub>2</sub> blanket films deposited on a Si substrate and (2) HfO<sub>2</sub> base RRAM were exposed to proton. After exposure, electron spin resonance and FTIR measurements were made on the HfO<sub>2</sub> blanket film, forming voltage and I-V characteristics were measured on the RRAM cell. The samples were exposed to proton radiation with a range of energies from 10 to 300keV. H ion implantation was used as the proton source. ESR measurements showed that after 300keV proton exposure, the defect concentration of Si dangling bond increased. Besides, all of the fresh pristine RRAM cells need to be formed, the forming voltage is approximately 3.4 ~ 3.65V. However, a number of the low-energy proton-exposed samples are set after exposure: about 50% of the 10keV proton exposed RRAM samples are set to the "on" state after irradiation. The 300keV proton-exposed RRAM samples were not formed or set after proton exposure, but the needed forming voltage decreased and breakdown occurred at a lower voltage. This is consistent to a TRIM simulation result, after low energy exposure, some of the H ions are seen to stay in the HfO<sub>2</sub> films and generate conductive filaments that set the dielectric film to the low resistance state. However, 300keV protons have just enough energy to pass through the dielectric film. In addition, the high-resistance state (HRS) current of just-formed 300keV exposed RRAM is about 100 times higher than that for pristine RRAM. We conclude low-energy protons have a significant effect on the forming process of RRAM. However, higher-energy protons change the resistance of the HRS instead.

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**EM-ThP-12 Measurement of the Depth of Plasma Damage caused by VUV Photons and Oxygen Radicals using X-ray Reflectivity**, *Ha Nguyen*, *F Choudhury*, University of Wisconsin-Madison; *C Lee*, National Tsing Hua University, Taiwan, Republic of China; *Y Lin*, *H Fung*, *C Chen*, National Synchrotron Radiation Research Center, Taiwan, Republic of China; *J Blatz*, *D Benjamin*, *W Li*, *J Shohet*, University of Wisconsin-Madison

During plasma processing, dielectric films used in the semiconductor technology are often exposed to large doses of vacuum ultraviolet (VUV) radiation and free radicals that can damage the dielectric material. In this work, we utilize specular x-ray reflectivity to measure the depth of damage of dielectric films as a function of energy of VUV photons and various doses of oxygen radicals. First, we examine the VUV-absorption spectrum of low-k organosilicate glass (OSG) using specular X-ray reflectivity (XRR). Low-k SiCOH films were exposed to synchrotron VUV radiation with energies ranging from 7 to 25 eV and the density depth profile of the VUV-irradiated films were extracted from the fitting of the XRR experimental data. The results show that the depth of the VUV-induced damage layer is a function of photon energy. Between 7 and 11 eV, the depth of the damaged layer decreases sharply from 110 nm to 60 nm and then gradually increases to 85 nm at 21 eV. The maximum VUV absorption in the OSG films occurs between 11 and 15 eV. Next, SiO<sub>2</sub> dielectric films were exposed to oxygen plasma in an electron cyclotron resonance plasma reactor and XRR measurements were made in order to determine the depth of damage as a

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function of oxygen-radical dose. It was found that the depth of damage increases as a function of plasma exposure time and eventually saturates to ~ 66 nm after about 30 minutes of oxygen-plasma exposure. This work shows that XRR damage depth profiling can be a very effective, non-destructive tool to determine the penetration depth of VUV photons and other plasma reactive species in dielectric films [1].

This work was supported by the Semiconductor Research Corporation under contract 2012-KJ-2359.

[1] Faraz A. Choudhury *et al.* "Oxygen radical transmission through and damage to freestanding single and multilayer dielectric films" AVS 64<sup>th</sup> International Symposium & Exhibition, Tampa, Florida (2017).

**EM-ThP-13 Oxygen Radical Transmission through and Damage to Freestanding Single and Multilayer Dielectric Films, Faraz Choudhury, G Sabat, M Sussman, University of Wisconsin-Madison; Y Nishi, Stanford University; J Shohet, University of Wisconsin-Madison**

During plasma processing, dielectric films are exposed to a high concentration of free radicals that can affect the processing conditions and the properties of materials exposed to the plasma. Measuring the absorption lengths and penetration depths of free radicals is critical in order to determine their effects on the dielectric materials. Using radical-sensitive fluorescent dyes and free-standing films, the transmission of oxygen radicals through silicon nitride and silicon dioxide dielectric films is measured. The absorption length of the oxygen radicals is determined by measuring the number of transmitted radicals as a function of the thickness of the freestanding films. For silicon nitride films, the absorption length was found to be 33 nm for 15-minute oxygen plasma exposure. The absorption lengths increased to 37 and 40 nm for 30 minute and 45-minute plasma exposures, respectively. FTIR measurements showed a decrease in Si-N bond concentration after plasma exposure and a subsequent appearance of Si-O-Si bonds. In addition, the density vs. depth profiles of the pristine and plasma exposed films were obtained from specular x-ray reflectivity (XRR) measurements which showed that the plasma exposure forms a silicon oxynitride-like layer on the surface of the film which has a lower density than silicon nitride. The increase in absorption length with plasma-exposure time is attributed to the formation of the surface layer. In silicon dioxide films, the absorption length of oxygen radicals was found to be ~70 nm after 20 minutes of plasma exposure. After 30 minutes of plasma exposure under the same conditions, the absorption length was reduced to ~66 nm. XRR and FTIR measurements both reveal that the oxygen plasma exposure leads to further oxidation of the silicon dioxide film and the formation of a denser surface layer which restricts the transmission of the radicals through the film.

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**EM-ThP-15 Effect of Proton Irradiation on Device Characteristics of Bottom Gate ZnO Thin Film Transistors with Sol-Gel Derived Channel Layers, Kosala Yapabandara, V Mirkhani, S Wang, M Khanal, S Uprety, Auburn University; M Sk, Qatar University, Qatar; A Ahyi, T Isaacs-Smith, M Hamilton, M Park, Auburn University**

ZnO has been widely studied due to its promising material properties as a wide energy bandgap semiconductor, optical transparency, and high carrier mobility for thin film transistor (TFT) technology. Solution-based ZnO can easily be deposited on large areas of substrates at low temperatures, which makes this material a good candidate for commercial device manufacturing. Moreover, ZnO exhibits a higher radiation hardness compared to semiconductors such as Si, GaAs, and GaN. However, it is not entirely understood why ZnO shows superior radiation hardness over GaN.

In this work, we report the device performance analysis of solution derived ZnO TFTs upon irradiation of 100 keV proton with  $10^{14}$  cm<sup>-2</sup> fluence. A comprehensive analysis of unirradiated and irradiated samples was performed to elucidate the proton irradiation effect on ZnO TFTs. The room temperature photoluminescence analysis showed a slight reduction in intensities of near-band-edge UV peak and visible luminescence band while the peak positions and the full-width half maximum (FWHM) are unchanged upon irradiation. This implies that negligible damage has occurred in the ZnO channel layer due to the proton irradiation. From transfer characteristics analysis, it was observed that the reduction in the drain current ( $I_D$ ) at high drain-source voltages ( $V_{GS}$ ) regime is less than an order of magnitude, which also suggests minimal irradiation damage to the ZnO lattice. However, the shift in  $V_{ON}$  and an enhancement in subthreshold swing (SS) after the proton irradiation were observed, which is believed to be produced by radiation-induced electron-hole pair production in the SiO<sub>2</sub> layer. Multiple peaks in incremental mobility ( $\mu_{inc}$ ) variation with  $V_{GS}$  and a

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plateau in low-frequency C-V curve were observed in unirradiated samples. A model was proposed to explain these abnormalities. It is reasonable to think that a significant number of defects is introduced into sol-gel derived ZnO channel during the deposition process. Since our deposition process requires more than one spin coating run, ZnO-ZnO interlayer interfaces will be formed. It was hypothesized that the depletion regions are created by oxygen-related trap centers at the ZnO-ZnO interlayer interfaces. It was conjectured that the disappearance of multiple peaks in  $\mu_{inc}$  and the plateau in low-frequency C-V curve upon proton irradiation might be the result of the reduction of the depletion layer in the proximity of ZnO-ZnO interlayer interface.

**EM-ThP-16 Characterization of the Buried MgO/Al Interfaces in Multilayer Heterostructures used as Photocathodes with Hard X-ray Photoelectron Spectroscopy, Jeff Terry, Illinois Institute of Technology**

Early research and development of photocathode material was based on characterizing compounds with low work function and high quantum efficiency. Recent theoretical and experimental work has shown that the metal-insulator junctions can give rise to changes in the band structure at the interface, which in turn leads to a change in work function and quantum efficiency.

In addition to concerns about work function and quantum efficiency, many modern photoinjector designs also require low beam emittance. Beam emittance is an intrinsic property of the photocathode, therefore it is important to be able control the growth and quantify the factors that lead to such growth. Nemeth [Phys. Rev. Lett. 104, 046801 (2010)] used DFT to model metal-insulator multilayer junction. The model indicate that it is possible to reduce the emittance of the photoemitted beam. Velazquez et al [Appl. Surf. Sci. 360, 762 (2016)] has demonstrated that the work function of lab grown thin film multilayers had trends that match the theory. However the model predicted an exponential decrease of work function, but data suggests a linear decrease.

It has been suggested that the surface roughness of the lab grown thin film multilayers might be the main cause of the deviation from the theory. Thin films are synthesized with a custom build dual laser PLD system, and the surface roughness is systematically altered by growing at different substrate temperature. We utilized a Hard X-ray Photoelectron Spectroscopy (HAXPES) system on the MRCAT undulator beamline at the Advanced Photon Source to characterize the MgO/Ag multilayers to better understand the chemistry at the interface. Understanding the reactivity, can help us better understand how the growth transitions from uniform to rough with increasing layer number.

**EM-ThP-17 Gamma-Ray Irradiation Effects on HfO<sub>2</sub> RRAM Studied via EDMR, Duane McCrory, P Lenahan, Penn State University; D Nminibapiel, D Veksler, J Ryan, J Campbell, National Institute of Standards and Technology**

Resistive Random Access Memory (RRAM) is a leading candidate for future non-volatile memory applications. These devices may be extremely useful for space applications. However, at the present time there is virtually no direct experimental evidence identifying the atomic scale defects involved in RRAM radiation damage or the underlying atomic scale conduction mechanisms. One of the most promising systems for RRAM is HfO<sub>2</sub> metal-insulator-metal based devices. In these devices, it is believed that the switching mechanism is derived from filamentary conduction paths within the oxide. One widely accepted mechanism involves the migration of oxygen vacancies within the transition-metal-oxide insulator, forming the conducting filament [1]. However, to the best of our knowledge, no direct experimental evidence establishes this transport mechanism.

By far the most powerful analytical tool available for identifying atomic scale defects is electron paramagnetic resonance (EPR). Using conventional EPR, Ryan et. al. have identified two atomic scale defects directly involved in gamma-irradiation damage; an O<sup>2-</sup> coupled to a hafnium ion, and an oxygen vacancy center [2]. However, conventional EPR is not sensitive enough to observe defects within the RRAM. We must look elsewhere to identify the defects and transport mechanisms. The most sensitive technique for identifying these defects is electrically detected magnetic resonance (EDMR) [3].

In this study we have subjected the TiN/Ti/HfO<sub>2</sub>/TiN RRAM devices to 1 MRAD of <sup>60</sup>Co gamma irradiation. These 100x100 nm devices are cross-point type RRAM with 5nm thick HfO<sub>2</sub>. We have made EDMR measurements before and after gamma irradiation. We observe the radiation induced generation of two strong spectra that appear in both the in-phase and quadrature. We believe that this response is due to two different trap assisted tunneling mechanisms within the oxide. Both spectra appear to be reasonably consistent with the earlier observations of

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Ryan et. al. [2]. A DFT study by Muñoz et. al. linked this defect earlier observed for the Ryan et. al. as an oxygen vacancy [4]. DFT calculations by Bradley et. al. have linked two di-vacancy sites near the middle of the  $\text{HfO}_2$  bandgap that may contribute to transport in  $\text{HfO}_2$  [5]. Our results provide strong evidence linking electronic transport and radiation damage mechanisms to transport through oxygen vacancy related centers.

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## EM-ThP-19 Defect Dependent Luminescence Dead Layers in CdS and CdSe, Richard Rosenberg, Argonne National Laboratory

CdS and CdSe are often used in optoelectronic devices whose effectiveness may be dictated by defects in the near surface region. Luminescence is one of the main tools for studying such defects. The energy dependence of the X-ray excited optical luminescence (XEOL) spectra of these materials enables the extraction of the depth-dependence of the defect distribution. [1] Normal and time-gated XEOL spectra were obtained from these materials in the X-ray energy range 600 to 1500 eV. The individual components of each spectrum were extracted using curve fitting techniques. Each component's energy-dependent intensity was fit to a "dead layer" model. [2] We find that the results can best be understood in terms of a luminescence dead layer whose width depends on the position of the defect level in the band gap.

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## EM-ThP-20 High Breakdown Voltage (-201) $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky Rectifiers, Jiancheng Yang, S Ahn, F Ren, S Pearton, University of Florida

A reverse breakdown voltage of 1600 V was demonstrated for Schottky diodes without edge termination fabricated on 10  $\mu\text{m}$  epitaxial  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> grown bulk conductive substrate. Ga<sub>2</sub>O<sub>3</sub> has a theoretical Baliga figure of merit (defined as  $V_B^2/R_{ON}$ , where  $V_B$  is the reverse breakdown voltage and  $R_{ON}$  is the on-state resistance) significantly higher than more familiar wide bandgap semiconductors, due mainly to its larger bandgap (~4.5-4.8 eV) compared to that of 4H or 6H-SiC and GaN (~3.0-3.4 eV). The theoretical breakdown electric field is ~8 MV/cm, with experimental demonstrations as high as 3.8 MV/cm and this is already higher than the bulk critical field strengths of both GaN and SiC. In this work, the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky barrier diodes were fabricated in a vertical geometry structure consisting of Ni/Au rectifying contacts without edge termination on Si-doped epitaxial layers (10  $\mu\text{m}$ ,  $n \sim 4 \times 10^{15} \text{ cm}^{-3}$ ) grown on Sn-doped bulk Ga<sub>2</sub>O<sub>3</sub> substrates with full area Ti/Au back Ohmic contacts. The reverse breakdown voltage,  $V_{BR}$ , was a function of rectifying contact area, ranging from 1600V at  $3.1 \times 10^{-6} \text{ cm}^2$  (20  $\mu\text{m}$  diameter) to ~250V at  $2.2 \times 10^{-3} \text{ cm}^2$  (0.53 mm diameter). The current density near breakdown was not strongly dependent on contact circumference but did scale with contact area, indicating the bulk current contribution was dominant. The lowest on-state resistance,  $R_{ON}$ , was 1.6 m $\Omega$ -cm<sup>2</sup> for the largest diode and 25 m $\Omega$ -cm<sup>2</sup> for the 1600V rectifier, leading to a Baliga figure-of-merit ( $V_{BR}^2/R_{ON}$ ) for the latter of approximately 102.4 MW-cm<sup>-2</sup>. The on-off ratio was measured at a forward voltage of 1.3V and ranged from  $3 \times 10^7$  to  $2.5 \times 10^6$  for reverse biases from -5 to -40 V and showed only a small dependence on temperature in the range 25-100°C. The Schottky barrier height decreased from 1.1 at 25°C to 0.94 eV at 100°C, while the ideality factor increased from 1.08 to 1.28 over the same range. The reverse recovery time was 26 ns for switching from +5V to -5V. These results represent another impressive advance in the quality of bulk and epitaxial  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>.

## EM-ThP-21 Inelastic Electron Tunneling Spectroscopy and Electron Conduction Mechanisms of Porphyrin Molecular Junctions, Teresa Esposito, P Dinolfo, V Meunier, K Lewis, Rensselaer Polytechnic Institute

In order to achieve nanoscale electronic devices beyond the 10 nm limit predicted by Moore's Law, molecular electronic devices are being studied as alternatives to circuit elements such as diodes, switches, and transistors. Porphyrin molecules are of interest because they have been shown to exhibit switching and diode behavior. In addition, shorter porphyrins (2-3

nm) can be used as interconnects because their low attenuation factors ( $\beta < 0.01 \text{ nm}^{-1}$ ) allow for long range electron conduction. Our work investigates three types of short porphyrins: a free base porphyrin, and porphyrins with either a zinc or an iron atom ligated to the porphyrin ring. Nanostructures are formed by depositing porphyrins into a 3-5 nm gap created by electromigration of a 30x50 nm gold nanowire to create a molecular junction (MJ). In order to determine the mechanism for electron conduction through these porphyrin MJs, temperature dependent current-voltage (I/V) studies have been performed and compared to existing models of electron transport, and are shown to be direct tunneling. Inelastic electron tunneling spectroscopy (IETS), which is the second derivative of I/V, is measured simultaneously at temperatures from 4.2 to 300 K. IETS is used to verify the presence of a molecule in the gap. Peaks in the spectra indicate the excitation of a vibrational mode, which are compared to Fourier transform infrared spectroscopy, surface enhanced Raman spectroscopy, and theoretical density functional theory calculations.

## EM-ThP-22 Welding of Metal Nanowire Networks Using Eddy Current Method, JiSoo Oh, D Sung, D Kim, K Kim, G Yeom, Sungkyunkwan University, Republic of Korea

Silver nanowire (AgNW) network is one of the most promising candidates to replace indium tin oxide (ITO) as transparent conductors among several candidates such as carbon nanotubes, graphene, metal grid, conducting polymer, etc. AgNW has lots of advantages, for example, AgNW not only has inherent high electrical conductivity and high transparency but also can be easily fabricated by using various methods on the flexible substrates. Despite these advantages, AgNW has its limitations due to high surface roughness and low adhesion problem. Especially, a high contact resistance between AgNW from the coating of polyvinylpyrrolidone (PVP) due to the loose contact between individual AgNWs is a critical issue to be resolved.

In order to overcome these problems, we constructed an inductive coil system that generates eddy current and welded nanowires with different operating frequencies. This method welds only the junction between the nanowires without heating the substrate due to higher resistance at the junction. Using this method, the various metal nanowires such as Ag and Cu nanowires were successfully welded by reducing the sheet resistance about 67% without changing the optical transmittance, and it was confirmed that it can be applicable to various flexible dielectric substrates such as PET substrates. Due to the local melting at the junction, the decrease of surface roughness could be also confirmed by surface image measurement. In addition, no significant change in resistance by bending test and adhesive test was observed due to the successful welding of the junction part of the nanowire, thereby improving the properties of the nanowire networks. This welding method is believed to be applicable to all kinds of metal nanowires without heating or touching of the substrate and on a large area at short process time and at low-cost.

## EM-ThP-23 Deep Ultraviolet Light Source with Carbon Nanotube based Electron Beam Pumping, KyuChang Park, S Yoo, Kyung Hee University, Republic of Korea

Deep ultraviolet (UVC) light sources were fabricated with carbon nanotube based electron beam pumping technique. Anode materials for UVC generation made by home-made fabrication process with Zn & Si mixture and irradiated with the carbon nanotube based cold cathode electron beam (C-beam). The C-beam fabricated with triode structure with metal mesh gate electrode and CNT cold cathode. The C-beam shows more than 90% electron transmittance through gate electrode and more than 10 mA anode current in DC operation.

For UVC light generation, anode semiconducting layer formation process is very important and should be optimized with electron beam irradiation current density. The UVC light intensity strongly related on the annealing conditions of anode layer and optimized to 1,000 degree celcius and nitrogen ambient. To reduce the power consumption, C-beam irradiated with DC pulse driving.

UVC light source with novel anode and C-beam irradiation technique shows emission peak at 208 nm, 226 nm, and 245 nm. The emission peak depend on the anode fabrication process and C-beam irradiation conditions. More detail on the UVC light fabrication with C-beam irradiation will be presented

# Thursday Evening Poster Sessions, November 2, 2017

**EM-ThP-24 An Unexpected Trend between Metal Work Function and Contact Resistance to Germanium Telluride, Kayla Cooley, H Simchi, H Aldosari, J O'Neil, S Yu, A Molina, S Mahney,** The Pennsylvania State University

Germanium telluride is an emerging phase change material (PCM) that has shown exceptional promise for radio frequency (RF) switch technology. When an appropriate heating schedule is applied, this material quickly transitions between crystalline (conductive ON state) and amorphous (highly resistive OFF state). Currently, the contact resistance ( $R_c$ ) contributes 20-50% of the ON-state resistance of the switch and significantly degrades RF circuit performance. Low-resistance Ohmic contacts that are able to withstand the thermal cycling necessary for changing the phase of GeTe are therefore necessary for successful implementation of GeTe-based RF switches.

We investigated selected contact metals (Ti, Sn, Cr, Mo, Ni, Au, and Pt), resulting in  $R_c$  from 0.004 to 0.036  $\Omega$ -mm (specific contact resistances of  $5 \times 10^{-9}$  to  $4 \times 10^{-7}$   $\Omega$ -cm<sup>2</sup>). We also characterized surfaces and interfaces using X-ray photoelectron spectroscopy and transmission electron microscopy with energy dispersive spectroscopy. The lowest  $R_c$  values ( $0.004 \pm 0.001$   $\Omega$ -mm) were achieved using Sn and Mo-based contacts, with  $R_c$  ranked according to the first metal deposited as follows: Mo or Sn < Cr < Ti < Au < Ni < Pt. This trend is surprising, as high work function metals, like Au and Pt, would be expected to provide lower  $R_c$  values to p+ GeTe.

In the case of Sn-based contacts, low  $R_c$  can be attributed to a beneficial interfacial reaction that formed SnTe upon deposition at the contact interface; however, for Mo-based contacts, no such interfacial reaction was observed. Chemical reactions at the interface were not always favorable. In the case of Pt and Ni, the formation of metal tellurides resulted in very high  $R_c$ . Thermal stability of all contact metals was also investigated up to 200 °C for 30 min. While Sn and Mo-based contacts performed just as well after annealing,  $R_c$  of most other contacts increased. Te sublimation was a common source of thermal instability, with Te crystallites forming on the sides of contacts and within the gap.

**EM-ThP-25 RF Loss Improvement of GaN-HEMTs Grown on Silicon by Reduction of The Inversion Channel at Si Interface, TienTung Luong, Y Chen, J You, S Chang, Y Ho, Y Lin,** National Chiao Tung University, Taiwan, Taiwan, Republic of China; **J Woo,** University of California, Los Angeles; **E Chang,** National Chiao Tung University, Taiwan, Taiwan, Republic of China

Regarding the unique characteristics (high breakdown field, high power density, high efficiency, and broadband) GaN are now broadly recognized as a key technology for many applications. In particular, GaN-based HEMTs are able to operate at high power, high frequencies, and high temperatures, exhibiting various excellent characteristics superior to those of conventional Si-based semiconductors. GaN-HEMTs on Si technology is expected to drastically reduce the fabrication cost. However, one of the main issues is the parasitic loss that can adversely impact the RF device performances. A free-electron inversion channel, which is caused by the positive piezoelectric charge at the AlN/Si interface induced by the piezoelectric field in the tensile AlN grown on Si, plays a critical role in the RF losses. An adoption of a low-temperature AlN near Si interface induces an unintentionally carbon-doped layer acting as a negatively fixed charge layer that is able to compensate for positive piezoelectric charge resulting in the improvements of both the RF losses and the leakage.

**EM-ThP-26 The Photoelastic Coefficient  $P_{12}$  of H<sup>+</sup> Implanted GaAs as a Function of Defect Density, Andrey Baydin, H Krzyzanowska, R Gatamov, N Tolk,** Vanderbilt University

The photoelastic phenomenon has been widely investigated as a fundamental elasto-optical property of solids. This effect has been applied extensively to study stress distribution in lattice-mismatched semiconductor heterostructures. GaAs based optoelectronic devices (e.g. solar cells, modulators, detectors, and diodes) widely used in space probes are subject to damage arising from energetic proton H<sup>+</sup> irradiation. For that reason, the effect of proton irradiation on photoelastic coefficients of GaAs is of primary importance to space applied optoelectronics. However, there yet remains a lack of systematic studies of energetic proton induced changes in the photoelastic properties of bulk GaAs. In this work, the H<sup>+</sup> energy and fluence chosen for GaAs implantation are similar to that of protons originating from the radiation belts and solar flares. We present the depth-dependent photoelastic coefficient  $P_{12}$  profile in non-annealed H<sup>+</sup> implanted GaAs obtained from the analysis of the time-domain Brillouin scattering spectra. The depth-dependent profiles are found to be broader than the defect distribution profiles predicted by Monte Carlo simulations. This fact indicates that the changes in photoelastic coefficient  $P_{12}$  depend

nonlinearly on the defect concentrations created by the hydrogen implantation. These studies provide insight into the spatial extent to which defects influence photoelastic properties of GaAs.

**EM-ThP-27 Manipulation of Elliptical Polarization and Modulation of Optical Activity using Terahertz Stereo-metamaterial Reflectors, Elizabeth Philip, S Pal, S Stephens, P Kung, S Kim,** The University of Alabama

Metamaterials (MMs) are playing a vital role in the development of the field of photonics. These are artificial materials made by repeated arrays of meta-atoms of subwavelength size, and can be controlled to manipulate the electromagnetic (EM) waves interacting with them. With appropriate designing of these meta-atoms, it is possible to achieve unique EM properties such as perfect absorption, negative permittivity, negative permeability, electromechanically induced transparency, etc. Recently, in terahertz (THz) frequency regime, MMs are being employed to replace conventional polarization converters. Conventional polarizers, retarders, rotators, etc. are usually made using dichroic crystals and optical gratings that are bulky, less efficient and operate in narrow bandwidths. Whereas with MMs they can be made thin, compact, easily combinable and even flexible. Much of the current THz polarization converters made of MMs function only in the transmission mode [1]. Though there are a few that function in the reflection mode, these are mostly linear polarization converters [2]. Evidently, there is a lack of linear to elliptical or circular reflective polarizers in the THz regime. In this work, we take advantage of an interesting category of MMs called stereo-metamaterials (SMMs) to develop a linear to elliptical polarization converter. SMMs utilize the same meta-atom, but are arranged at different spatial positions. They are analogous to stereo-isomers, which are molecules constituting of the same atoms but have different spatial arrangements. Six separate devices with varying spatial arrangements are first optimized through simulations with finite element method using Comsol. By tailoring the spatial arrangement of the meta-atom, we manipulate the polarization of the reflected light to become elliptically polarized, achieving a maximum ellipticity angle of 20.5° at 0.240 THz. Furthermore, we modulate the optical activity of the device, and a pure optical rotation of 37.0° at 0.246 THz is attained from the simulation results. The devices are fabricated using standard photolithography techniques and their linear to elliptical polarization conversion and optical activity is successfully verified through THz ellipsometry measurements. The device sensitivity to incident polarization modulation and its corresponding reflective phase retardation response is also analyzed. Lastly, the influence of the dipole coupling and current distribution is studied in order to explain the microscopic origin for the manipulation of the reflected light. Such SMM with linear to elliptical polarization conversion and optical activity modulation properties in the reflection mode has promising applications in THz sensing and communication devices. [1] J.W. He, Z.W. Xie, S. Wang, X.K. Wang, Q. Kan, Y. Zhang, *Journal of Optics*. 2015;17(10):8. [2] N.K. Grady, J.E. Heyes, D.R. Chowdhury, Y. Zeng, M.T. Reiten, A.K. Azad, et al. *Science*. 2013;340(6138):1304-7.

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