Electronic Materials and Processing
Room: 211A - Session EM+AS+SS-MoA

MIM Diodes, Functional Oxides, and TFTs
Moderator: Pat Brady, RedWave Energy, Inc., John Conley, Oregon State University

2:20pm **EM+AS+SS-MoA1 Engineered Tunnel-Barrier Terahertz Rectifiers for Optical Nantennas**, ***Ivona Mitrovic***, *N. Sedghi, A.D. Weerakkody, J.F. Ralph, S. Hall, J.S. Wrench, P.R. Chalker*, University of Liverpool, UK, *Z. Luo, S. Beeby*, University of Southampton, UK

Thin film metal-insulator-metal rectifying devices using double, triple or quadruple insulator layers are currently the focus of attention for the development of next-generation optical nantennas for infrared energy harvesting. The interest is driven by their distinctive attributes, such as nanoscale footprint, room temperature operation, zero bias voltage requirement, and ease of integration with Complementary Metal Oxide Semiconductor technology. Highly asymmetric and nonlinear current-voltage (IV) behaviour at low applied voltages is critical for this application. In this paper, we present comprehensive experimental and theoretical work on tunnel-barrier rectifiers comprising double (Ta_2O_5/Al_2O_3 and Nb_2O_5/Al_2O_3) and triple ($Ta_2O_5/Nb_2O_5/Al_2O_3$) insulator configurations engineered to enhance low voltage nonlinearity. There are two mechanisms that allow metal-insulator-insulator-metal (MIIM) rectifiers to have a high nonlinearity while keeping the resistance low: (i) resonant tunnelling, and (ii) step tunnelling. This paper focuses on the former approach. A modified multi-layer Tsu-Esaki method has been used for IV calculations from the transmission coefficient by the transmission matrix method. The theoretical work indicates that the onset of resonant tunneling in MIIM and MIIIM rectifiers can be adjusted to be close to zero volts by appropriate choice of work function difference of the metal contacts, the thickness of insulator layers, and the depth of the quantum well. The double and triple insulator rectifiers were fabricated using atomic layer deposition (ALD) and rf magnetron sputtering, while different metal contacts including Al, Ta, W, Nb, Cr and Ag were defined by photolithography or shadow mask and deposited by e-beam and thermal evaporation. The thickness, band gap, surface roughness, band offsets and work functions have been extracted from variable angle spectroscopic ellipsometry, atomic force microscopy, x-ray and inverse photoelectron spectroscopy on fabricated devices to ascertain the quality of the interfaces and to measure barriers. The key rectifier properties, asymmetry, nonlinearity and responsivity have been assessed from current voltage measurements performed in the range 293-370 K. A superior low voltage asymmetry (18 at 0.35 V) and responsivity (9 A/W at 0.2 V) has been observed for fabricated bilayer Ta_2O_5/Al_2O_3 and Nb_2O_5/Al_2O_3 MIIM devices respectively, in advance of state-of-the-art experimental values. The results demonstrate ALD and rf sputtered tunnel-barrier rectifiers which enhance low voltage nonlinearity and have the potential to be employed in optical nantennas for infrared energy harvesting.

2:40pm **EM+AS+SS-MoA2 MIM Diodes for RF Energy Harvesting**, *A.A. Khan, A. Syed, F. Ghaffar,* ***Atif Shamim***, King Abdullah University of Science and Technology

Metal Insulator Metal (MIM) diodes that work on fast mechanism of tunneling have been used in a number of very high frequency applications such as (Infra Red) IR detectors and optical Rectennas for energy harvesting. Their ability to operate under zero bias condition as well as the possibility of realizing them through additive techniques makes them attractive for (Radio Frequency) RF applications. However, two major issues namely, high surface roughness at the metal-insulator junction which effects the reliability of the diode, and very high resistance (typically in Mega Ohms) which complicates its matching with RF antenna have prevented its wide spread use in RF rectennas.

In this work, various metal deposition methods such as sputtering and electron beam evaporation are compared in pursuit of achieving low surface roughness. Amorphous metal alloy has also been investigated in terms of its low surface roughness. Zinc oxide has been studied for its suitability as a thin dielectric layer for MIM diodes. Finally, comprehensive RF characterization of MIM diodes has been performed in two ways: 1) by standard S-parameter methods, and 2) by investigating their rectification ability under zero bias operation.

It is concluded from the Atomic Force Microscopy (AFM) imaging that surface roughness as low as sub 1 nm can be achieved reliably from crystalline metals such as copper and platinum. This value is comparable to surface roughness achieved from amorphous alloys, which are non-crystalline structures and have orders of magnitude lower conductivities. Relatively lower resistances of the order of 1 Kilo Ohm with a sensitivity of 1.5 V^{-1} have been obtained through DC testing of devices with MIM diode structure of platinum/zinc oxide/ titanium. Finally, RF characterization reveals that input impedances in the range of 300 Ω to 25 Ω can be achieved in the low GHz frequencies (from 0.5-10 GHz). From the rectification measurements at zero bias, a DC voltage of 4.7 mV has been obtained from an incoming RF signal of 0.4 W at 2.45 GHz, which indicates the suitability of these diodes for RF rectenna devices without providing any bias. These preliminary results indicate that with further optimization, MIM diodes are attractive candidates for RF energy harvesting applications.

3:00pm **EM+AS+SS-MoA3 Diode Structure Based on Carbon Materials for Ultra high Frequency Driving**, ***JaeEun Jang***, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Republic of Korea

If the antenna can be designed to absorb wavelengths in the range of a few hundred THz with multi-antenna array design, it results in high conversion efficiency due to power production from various light sources between ultraviolet (UV) and infrared (IR) radiation that is often thought of as heat and exists beyond the visible range for humans. One of the problems in this idea, however, is the nature of visible or IR light to oscillate at ultra-high frequencies. Therefore, a rectifier working at such an ultra-high frequency should be developed with a highly efficient coupling between antenna and light. Because Schottky diode is limited to frequencies less than ~ THz level, nanometer size MIM diode structure has been suggested as alternative design. Two different metals have used normally to make an asymmetric characteristic of current-voltage. However the work function difference between the metals cannot produce a high asymmetry, which causes a poor rectifier performance, even though the structure can be driven in THz range. To solve this issue, we used a structural asymmetric MIM design. The planar asymmetric design using various metals or grapheme showed better asymmetric I-V characteristics than that of simple MIM structure. In addition, for the vertical aligned design, single multi-wall carbon nanotube was formed as one electrode to get high tunneling current caused by the structural effect of sharp tip. The structural asymmetry can make a different field density states to the metals, which induces a high rectify characteristics. The contrast ratio between the forward and the reverse bias is $\sim 10^4$ level. The estimated cut-off frequency is about 4.74THz. The electrical characteristics are stable up to 423K.

3:20pm **EM+AS+SS-MoA4 Optical Rectenna Arrays using Vertically Aligned Carbon Nanotubes**, ***Baratunde Cola***, Georgia Institute of Technology

The response of a multiwall carbon nanotube to visible light has been reported to be consistent with conventional radio antenna theory. Researchers have proposed that this result might be exploited to realize an optical rectification device – that is, a device that converts free-propagating electromagnetic waves at optical frequencies to localized d.c. electricity. However, an experimental demonstration of this concept requires that the multiwall carbon nanotube antenna be coupled to a diode that operates on the order of 1 petahertz (switching speed on the order of a femtosecond). Ultralow capacitance, on the order of a few attofarads, could allow a diode to operate at these frequencies; and the development of metal-insulator-metal tunnel junctions with nanoscale dimensions has emerged as a potential path to diodes with ultralow capacitance, but these structures remain extremely difficult to fabricate and couple to a nanoscale antenna reliably. Here we demonstrate optical rectification by engineering metal-insulator-metal tunnel diodes at the tips of multiwall carbon nanotubes, which act as the antenna and metallic electron emitter in the diode. This performance is achieved using diode areas based on the diameter of a single carbon nanotube (about 10 nanometers), geometric field enhancement at the carbon nanotube tips, and a low work function semi-transparent top metal contact. Using vertically-aligned arrays of the diodes, we measure d.c. open-circuit voltage and short-circuit current at visible and infrared electromagnetic frequencies that is due to a rectification process, and quantify minor contributions from thermal effects. Our devices show evidence of photon-assisted tunneling, and exhibit zero-bias diode responsivity on the order of 0.1 amps per Watt and zero-bias differential resistance as low as 100 ohms-centimeter squared under illumination. Additionally, power rectification is observed under simulated solar illumination. Numerous current-voltage scans on different devices, and between 5-77 degrees

Celsius, show no detectable change in diode performance, indicating a potential for robust operation.

3:40pm **EM+AS+SS-MoA5 World Record Tunable Microwave Dielectrics**, *C.H. Lee,* Cornell University, *N.D. Orloff,* National Institute of Standards and Technology (NIST), *T. Birol, Y. Zhu, Y. Nie,* Cornell University, *V. Goian,* Institute of Physics ASCR, *R. Haislmaier,* Pennsylvania State University, *J.A. Mundy,* Cornell University, *J. Junquera,* Universidad de Cantabria, *P. Ghosez,* Université de Liège, *R. Uecker,* Leibniz Institute for Crystal Growth, *V. Gopalan,* Pennsylvania State University, *S. Kamba,* Institute of Physics ASCR, *L.F. Kourkoutis, K.M. Shen, D.A. Muller,* Cornell University, *I. Takeuchi,* University of Maryland, College Park, *J.C. Booth,* National Institute of Standards and Technology (NIST), *C.J. Fennie,* ***Darrell Schlom***, Cornell University **INVITED**

The miniaturization and integration of frequency-agile microwave circuits—relevant to electronically tunable filters, antennas, resonators, phase shifters and more—with microelectronics offers tantalizing device possibilities, yet requires thin films whose dielectric constant at GHz frequencies can be tuned by applying a quasi-static electric field. Appropriate systems, e.g., $Ba_xSr_{1-x}TiO_3$, have a paraelectric-to-ferroelectric transition just below ambient temperature, providing high tunability. Unfortunately such films suffer significant losses arising from defects. Recognizing that progress is stymied by dielectric loss, we start with a system with exceptionally low loss—$Sr_{n+1}Ti_nO_{3n+1}$ phases—where $(SrO)_2$ crystallographic shear planes provide an alternative to point defect formation for accommodating non-stoichiometry. Guided by theoretical predictions, we biaxially strain a $Sr_{n+1}Ti_nO_{3n+1}$ phase with $n = 6$ to introduce a ferroelectric instability and create a new type of tunable microwave dielectric. This tunable dielectric exhibits a world record figure of merit at room temperature and frequencies up to 125 GHz. Our studies also reveal details about the microscopic growth mechanism of these phases, which are relevant to preparing atomically precise oxide interfaces to these and other Ruddlesden-Popper phases.

4:20pm **EM+AS+SS-MoA7 Bandgap Engineering and Application of SiZnSnO Amorphous Oxide Semiconductor**, ***Sang-Yeol Lee***, Cheongju University, Republic of Korea **INVITED**

The band gap of the amorphous SiZnSnO (SZTO) semiconductor has been controlled by bandgap engineering using Si ratio. The addition of small amount of Si in SZTO channel layer can change the position of Fermi level in band gap. By investigating the ultraviolet photoelectron spectroscopy (UPS) characteristics, it is verified that Si atoms can modify the Fermi energy level of SZTO thin films. Carrier generation originated from the oxygen vacancy could modify the Fermi level in the band gap of oxide thin films since Si could be an oxygen vacancy suppressor. This is also related with the origin of defect state which was observed to be involved with the creation of oxygen vacancies. Since it is not so easy to derive directly the change of the Fermi energy level in the energy band gap of amorphous oxide semiconductor, no report of the relation between the Fermi energy level in the energy band gap of oxide semiconductor and the device stability of oxide thin film transistors has been reported. We derive directly band gap and Fermi energy level by using the ultraviolet photoelectron spectroscopy (UPS) characteristics, Kelvin probe (KP) and electron energy loss spectroscopy (EELS). The instability mechanism of amorphous oxide thin film transistors based on the band parameter of oxide semiconductor will be discussed and applied to display applications.

5:00pm **EM+AS+SS-MoA9 Self-aligned Vertical ZnO-based Circuits by Spatial ALD**, ***Shelby Nelson***, *C.R. Ellinger, L.W. Tutt,* Eastman Kodak Company

Metal oxide thin-film transistors (TFTs) are becoming the mainstream for display backplanes. These TFTs are fabricated with traditional photolithographic techniques, typically on rigid substrates. In our lab, we explore approaches that are more “print-compatible”, with broad alignment tolerance and no small-gap mask features. We deposit zinc oxide (ZnO) semiconductors, aluminum oxide (Al_2O_3) dielectrics, and aluminum-doped zinc oxide conductors by the fast, atmospheric pressure, large-area-compatible, spatial atomic layer deposition (SALD) process. In addition to depositing good-quality thin-film transistor layers at temperatures at and below 200 °C, this process can work with a wide variety of rough and deformable substrates.

Here we describe vertical TFT and circuit architectures that unite process simplicity with high performance. The liberal design rules result from vertical transistors with self-aligned source and drain contacts that define the sub-micron channel length. Using 10-micron design rules for both the minimum line/space dimensions and for alignment tolerances, we have fabricated 9-stage ring oscillators with greater than 1 MHz oscillation frequency, at supply voltage below 6 V. Starting with a gate layer with a re-entrant profile on the edge, these devices use spatial ALD to conformally coat the Al_2O_3 gate dielectric and ZnO semiconductor, and a line-of-sight deposition process such as evaporation for the aluminum electrodes. Individual device characteristics as well as circuit performance will be discussed.

5:20pm **EM+AS+SS-MoA10 Geometrically Asymmetric Tunneling Nanostructures by Atomic Layer Deposition**, ***Jie Qi***, *X. Jiang, B.G. Willis,* University of Connecticut

Geometrically asymmetric tunneling nanostructures are of interest to make ultra-high frequency diodes for applications in detection and solar energy harvesting. Atomic layer deposition (ALD) is one of the most promising techniques for fabrication of tunneling nanostructures. In previous work, it has been demonstrated that individual metal-vacuum-metal (MVM) tunnel junctions with a gap distance of 1-2 nm can be fabricated by selective-area ALD of Cu onto Pd templates. However, optimizing nonlinearity and scaling up to large arrays of tunneling devices both introduce new challenges that include achieving precise control of nucleation and good quality conformal growth on sharply defined asymmetric nanostructures.

In this study, the fabrication of large arrays of MVM tunnel junctions is investigated using selective-area ALD. Nano-patterned Pd nanostructures with sharp asymmetric features are prepared as seed layers for planar, geometrically-asymmetric junctions on SiO_2 / silicon substrates by high-resolution electron beam lithography. Selective-area ALD applied to patterned Pd nanostructures allows tuning the size of junctions to nanometer dimensions. Microscopy and chemical analysis are used to evaluate nanostructure morphology, tunnel junction uniformity, and selective area growth characteristics. In-situ electrical measurements are used to measure DC current-voltage curves and nonlinearity. It was found that film nucleation and growth selectivity can be greatly affected by different pre-deposition sample treatments. UV/Ozone (UVO) cleaning and hydrogen annealing before ALD both enhance the nucleation of Cu thin films on Pd seed layers. In addition, UVO treatment promotes selective growth on Pd vs. SiO_2 areas while boiling samples in water to hydroxylate SiO_2 surface area contributes to a loss of selectivity. In-situ measured electrical data during ALD growth demonstrate a gradual convergence to tunneling with sub-nm control provided by the ALD method. However, control of tunneling non-linearity and geometric asymmetry is complicated by an incomplete understanding of the growth mechanism and the morphology evolution of nanostructures. There is a compromise between conditions that promote good ALD growth and those that maintain geometric asymmetry. We conclude with suggestions to promote growth, maintain sharp asymmetric features, and achieve non-linear tunneling characteristics.

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