Fundamentals and Technology of Multifunctional Materials and Devices

Room Royal Palm 4-6 - Session C2-1

Thin Films for Active Devices

Moderators: Vanya DarakchievaMarco Cremona, Pontificia Universidade Católica do Rio de Janeiro, Junichi Nomoto, Kochi University of Technology, Japan,

10:00am **C2-1-1 Application of Gallium Oxide for High-Power Electronics**, ***Masataka Higashiwaki***, *M Wong, K Konishi,* National Institute of Information and Communications Technology, Japan*; K Sasaki, K Goto,* Tamura Corporation, Japan*; H Murakami, Y Kumagai,* Tokyo University of Agriculture and Technology, Japan*; A Kuramata, S Yamakoshi,* Tamura Corporation, Japan **INVITED**

Wide bandgap semiconductor material - gallium oxide (Ga_2O_3) - has emerged as a new competitor to SiC and GaN in the race toward next-generation power devices by virtue of the excellent material properties and the relative ease of mass wafer production. In this talk, following a short introduction of material properties and features of Ga_2O_3, an overview of our recent development progress in device processing and characterization of Ga_2O_3 field-effect transistors (FETs) and Schottky barrier diodes (FP-SBDs) will be reported.

State-of-the-art Ga_2O_3 metal-oxide-semiconductor FETs (MOSFETs) were fabricated with unintentionally-doped (UID) β-Ga_2O_3 (010) epitaxial layers grown on semi-insulating Fe-doped substrates by ozone molecular beam epitaxy [1]. Selective-area Si-ion implantation doping of the UID Ga_2O_3 epilayer formed the device channel and ohmic contacts, while the high resistivity of UID Ga_2O_3 was harnessed for planar device isolation without mesa etching. SiO_2-passivated depletion-mode MOSFETs with a gate-connected field plate (FP) demonstrated a high off-state breakdown voltage (V_{br}) of 755 V, a large drain current on/off ratio of over nine orders of magnitude, DC-RF dispersion-free output characteristics, and stable high temperature operation against thermal stress at 300°C.

We also fabricated and characterized Pt/Ga_2O_3 FP-SBDs on n^--Ga_2O_3 drift layers grown on n^+-Ga_2O_3 (001) substrates [2], owing to the success of halide vapor phase epitaxy (HVPE) for high-speed growth of high-quality Ga_2O_3 thin films [3, 4]. The illustrative device with a net donor concentration of 1.8×10^{16} cm^{-3} exhibited a specific on-resistance of 5.1 $m\Omega\cdot cm^2$ and an ideality factor of 1.05 at room temperature. Successful FP engineering resulted in a high V_{br} of 1076 V. Note that this was the first demonstration of V_{br} of over 1 kV in any Ga_2O_3 power device.

In summary, we succeeded in fabricating depletion-mode Ga_2O_3 FP-MOSFETs and vertical Ga_2O_3 FP-SBDs on single-crystal β-Ga_2O_3 substrates. Despite the simple structures, both the FP-MOSFETs and FP-SBDs revealed excellent device characteristics and demonstrated great potential of Ga_2O_3 electron devices for power electronics applications.

This work was partially supported by Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), "Next-generation power electronics" (funding agency: NEDO).

[1] M. H. Wong *et al.*, IEEE Electron Device Lett **37**, 212 (2016), [2] K. Konishi *et al., 74th Device Research Conference IV-A.5, 2016*, [3] K. Nomura *et al.*, J. Cryst. Growth **405**, 19 (2014), [4] H. Murakami *et al.*, Appl. Phys. Express **8**, 015503 (2015).

10:40am **C2-1-3 Phenomenon of Oxygen Ion Migration in In_2O_3-Based Resistive Random Access Memory**, ***Cheng-Hsien Wu***, National Sun Yat-sen University, Taiwan*; T Chang, T Tsai,* National Sun Yat-Sen University, Taiwan

In this study, we demonstrate how using a positive bias or negative bias in the forming process can control whether the switching layer of a Pt/In_2O_3/TiN device is near the Pt electrode or the TiN electrode. This means that In_2O_3-based resistive random access memory (RRAM) not only can be switched at either the active or inert electrode, with resistive switching I–V curves for both electrodes exhibiting stable memory windows. Therefore, it is a bilaterally operating RRAM device. Since RRAM usually switches at the active electrode, we investigate the mechanism during operation at the inert electrode. After curve fitting, we found multi-set and multi-reset stages, both dominated by Schottky emission, as well as gradual changes in the value of the slope and the intercept. Finally, we use this result to propose a model with oxygen ions.

11:00am **C2-1-4 Vapor-Liquid-Solid Growth of SnO_2 Nanowires Utilizing Alternate Source Supply and Their Photoluminescence Properties**, ***Tomoaki Terasako***, *K Kohno,* Ehime University, Japan*; M Yagi,* National Institute of Technology, Kagawa College, Japan

An important *n*-type wide band gap semiconductor, tin dioxide (SnO_2), has various high functionalities. Especially, we pay attention to the applications of SnO_2 to the gas-sensing devices. It is expected that the use of the nanowires (NWs), nanorods and nanobelts is effective for achieving the high gas-sensing performance. Among the various techniques, vapor-liquid-solid (VLS) growth based techniques are most widely studied because of their high forming position and diameter controllability. In general, the diameters of the NWs grown through the VLS growth can be controlled by the diameters of the catalyst particles or the thickness of the catalyst film. However, the film growth on the NW's side walls by vapor-solid (VS) growth contributes to the increase in average diameter and obstructs the growth of the NWs with the well-controlled diameters [1,2]. In this paper, we will examine the possibility of suppressing the influence of the VS growth on the shapes of the NWs utilizing alternate source supply (ASS). During the VLS growth process, the catalyst particle acts not only as a crystal growth front, but also as a "storage box" of the metal atoms by forming the alloy droplet. The ASS technique utilizes the latter.

The SnO_2 NWs were grown on the Au/α-Al_2O_3(001) substrates by atmospheric-pressure CVD using Sn powder and H_2O as source materials. Both the substrate and Sn powder were heated by the horizontal furnace, whereas H_2O was vaporized in its own vaporizer. Both the vapors of Sn and H_2O were timely separated and transported onto the substrate by nitrogen carrier gaseous.

X-ray diffraction measurements and SEM observations revealed the successful growths of the SnO_2 NWs by the ASS conditions. The average diameter of the SnO_2 NWs grown under the simultaneous source supply (SSS) condition increased exponentially with increasing growth temperature (T_g), reflecting the enhancement of the contribution of the VS growth. In contrast to this, the average diameter of the NWs grown under the ASS condition was almost independent of T_g, indicating that the contribution of the VS growth is effectively suppressed using the ASS condition. PL spectra showed the increase in the intensity of the orange band emission with increasing Tg, suggesting that the increase in the O vacancies and/or Sn interstitial atoms [3]. Moreover, the NWs average diameter was found to be independent of cycle number in the cycle number range of 300-700.

This work was supported by JSPS KAKENHI Grant Number JP26390029.

[1] T. Terasako *et al.*, Thin Solid Films 528 (2013) 237.

[2] T. Terasako *et al.*, Thin Solid Films (to be published).

[3] D. Calestani *et al.*, Mater. Sci. Eng. C 25 (2005) 625.

11:20am **C2-1-5 Endurance Improvement and Resistance Stabilization of Transparent Multilayer ReRAM with Oxygen Deficient WO_x Layer and Heat Dissipating AlN Buffer Layer**, ***Yu-Hsuan Lin***, National Chiao Tung University, Taiwan*; D Huang,* Peking University, China*; T Tseng,* National Chiao Tung University, Taiwan

This paper discusses the transparent resistive random access memory (ReRAM) from ITO/WO_3/ZnO/ITO structure to multilayer ITO/WO_x(x<3)/WO_3/ZnO/AlN/ITO structure with oxygen concentration distribution and heat dissipating layer. The X-ray photoelectron spectroscopy (XPS) is used to confirm the existence of WO_x/WO_3 double layers. The transmission electron microscopy (TEM) images show the AlN layer has limited effect on the grain structure and the interface roughness of ZnO. Moreover, the transmittance of the multilayer ReRAM achieves 85.49% that is suitable for optoelectronic applications.

The bipolar ReRAM mechanism is based on filament model with the movement of oxygen vacancies. Because the oxygen ions may recombine with the vacancies and break the conductive path near the top electrode during the SET operation, the WO_x between electrode and WO_3 provides sufficient vacancies for efficient resistive changes. In the meanwhile, the WO_3 can limit the rupture and formation region of filaments. This gradient tungsten oxide stabilizes the low resistance states, decreases the operating voltages, and increases the endurance from < 10^3 cycles to 10^4 cycles. Since the electrical field and heat drive the movements of ions and vacancies, the inserted AlN with high thermal conductivity can dissipate the uncontrollable heat and remain the directional electrical field. This AlN layer prevents the ReRAM from the heat-activated ion movement and further masters the high resistance state, so the resistance levels of the multilayer ReRAM are tight and stable. Conclusively, in the

ITO/WO_x/WO_3/ZnO/AlN/ITO ReRAM, the operating voltages of SET and RESET operations are 1.9V and -1.1V, respectively, the retention stay more than 10^4s at 150°C, the endurance is 10^4 cycles with resistance ratio over 20x, and both of the low and high resistance states are extremely stable during cycling.

11:40am **C2-1-6 Mechanism of Selectivity Increased during Operation on Vanadium Oxide Based Selector**, *C Lin,* National Sun Yat-sen University, Taiwan*; T Chang, K Chang,* National Sun Yat-Sen University, Taiwan*; T Tsai, C Pan,* National Sun Yat-sen University, Taiwan*;* ***Jih-Chien Liao,*** National Tsing Hua University, Taiwan*; P Chen,* National Sun Yat-sen University, Taiwan*; C Chen,* National Sun Yat-Sen University, Taiwan*; S Sze,* National Chiao Tung University, Taiwan

Technological development for memory, logic IC, on-display devices and batteries is indispensable for advanced portable electronic products. Among all these devices, a reliable, fast-working, and energy-saving non-volatile memory is extremely important. There are several next generation memory under developed, RRAM, PCRAM, MRAM, MTJ, FeRAM. All these devices must use array to storage, but the sneak path current is still the problem that we can't integrate large amount of advanced RAM into a chip. One Selector connect to one Memory is one of the solution to sneak current, and it is the most efficient method to integrate memories into array chip.

Selector can be used in any resistance-changed memory. There are large amounts of selectors developed in recent year, one of they use transition metal oxide to achieve double side diode properties. Metal insulator transition (MIT) has been widely developed because of its volatile state switch. In this article, we use Vanadium Oxide to be our device to find two factors that influences the switch characteristic. Because MIT happens in the difference of temperature, we think the thermal and electric field will influences the devices meanwhile. By current fitting and Comsol simulation, we conclude the phenomena happens in transition layer.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Royal Palm 4-6 - Session C2-2
Thin Films for Active Devices

Moderators: Vanya DarakchievaMarco Cremona, Pontificia Universidade Católica do Rio de Janeiro, Junichi Nomoto, Kochi University of Technology, Japan,

1:30pm **C2-2-1 Ga-doped ZnO Films by Magnetron Sputtered at Ultralow Discharge Voltages: Effects of Defect Annihilation***, Yuyun Chen, M Fanping, F Ge, H Feng,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

Preparation of high quality transparent conductive oxide (TCO) films by sputter deposition involves an intricate balance of defect generation by the highly energetic negative oxygen ions (depending on the discharge voltage) and the concomitant annihilation of these defects during film growth. Ga-doped ZnO films with a low Ga content (1.7 at%) were deposited to investigate the effects of defect annihilation on the microstructure evolution as well as the optical and electrical properties. To achieve this aim, we prepared the GZO films by magnetron sputtering at ultralow discharge voltages (<80 V) to minimize the defect generation, and varied the substrate temperature (from room temperature to 673 K) to adjust the annihilation rates. The microstructure was systematically characterized by X-ray Diffraction (XRD), X-ray Reflectivity (XRR), Raman Spectroscopy, and Extended X-ray Absorption Fine Structure (EXAFS). The electrical and optical properties were obtained by a Hall-effect measurement system and Spectroscopic Ellipsometry (SE), respectively. It was found that (i) even under the condition of highly controlled defect generation, a sufficient annihilation of the defects cannot be realized without externally heating the substrate; (ii) both the structural quality and the electrical properties were improved with the increased temperature; and (iii) there existed a critical temperature, above which the generated defects were sufficiently annihilated, resulting in significantly higher Hall mobility and carrier concentration. These results reveal that the growth temperature during the GZO film deposition has played an important role in effective annihilation of the irradiation-induced structural defects.

1:50pm **C2-2-2 Reactive Sputter Deposition and Annealing of Nanometer Scale NiO Thin Films for Metal-Insulator-Metal Tunnel Junction Diodes***, **Frank Urban**, S Bhansali,* Florida International University, USA*; A Singh,* Intel, USA*; D Barton,* Retired, USA

The increased switching speed of metal-insulator-metal (MIM) tunnel diodes over existing diodes has the potential to open new applications including high frequency detectors for example. This work here analyzes the effect of the insulator layer (NiOx) properties on performance of such Ni-NiOx-Cr based junctions. The films were deposited by reactive magnetron sputtering of a Ni target in an atmosphere containing oxygen. Films ranged from 10 to 30 nm in thicknesses and were smooth as determined by atomic force microscopy. Initial ellipsometry examination showed that the as-deposited films were inhomogeneous in the growth direction and exhibited high optical absorption across the visible wavelength range (midrange k = 0.8 and up). While this is not unexpected considering what is known about nucleation and initial growth, it is undesirable for the intended use. Consequently treatment of the films was carried out by annealing in an oxygen atmosphere at 400°C for 3, 6, and 12 minutes. This resulted in both a significant decrease in the optical absorption and a dramatic improvement in film homogeneity. Examination using Secondary Ion Mass Spectroscopy did not show significant increases in film oxygen suggesting that atomic rearrangement rather than oxidation occurred during annealing. Performance of MIM junctions with the annealed films was investigated using current-voltage measurements. The results were correlated with capacitance-voltage measurements.

2:10pm **C2-2-3 HVPE GaN and AlGaN Thin vs Thick Freestanding Films for Electronic and Optoelectronic Devices***, **Tania Paskova**,* North Carolina State University, USA **INVITED**

The current nitride electronic and optoelectronic technology employs two generally different groups of approaches. The first group is focused on development of bulk GaN and AlN substrates and the intensive research efforts during the last years have led to a demonstration of high-quality material with huge application potential, including for devices with nonpolar and semipolar alignment of the active regions. HVPE technique has led the effort in quasi-substrate development and is the only one offering GaN freestanding films of all surface orientations of interest. The cost of this method, however, remains still high and several challenges have to be resolved to allow the cost to go down. The second group of research efforts is focused on thin film template development of GaN, AlGaN and AlN on sapphire, SiC and Si substrates. Most of these efforts, using lateral overgrowth approaches, have showed devices with good performance and have been commercially implemented. Each of the approaches employs different buffer layers or nucleation schemas, as well different growth recipes, and results in as-grown substrates and templates with different thickness limitations. The doping alternatives, using either silicon or oxygen for achieving n-type conductivity and iron for achieving resistivity in wide ranges, respectively, were found to successfully alter the electrical properties of the materials, while the optical quality was largely maintained until reaching the saturation level. In addition, besides the reduced dislocation density achieved, the HVPE technique was proven capable of producing material of high purity, regarding residual impurities and point defects. This in turn leads to improved thermal conductivity, allowing better thermal management and device performance.

Recent advances in the research and development of a variety of optoelectronic and electronic devices produced on HVPE templates and freestanding quasi-substrates has resulted in a significant improvement of device performance for a number of applications. This motivates the increased demand for HVPE nitrides, which should boost the material availability and will drive down the production cost. In this talk, we will present a comparative summary of the most promising approaches for HVPE growth of GaN and AlGaN materials. The focus will be on the different doping approaches and their effect on the thermal transport in low-defect-density materials. High thermal conductivity values in wide temperature region will be presented and scattering mechanisms including at elevated temperatures, highly relevant for high power electronic and optoelectronic devices, will be discussed.

2:50pm **C2-2-5 Characteristics of Non-polar ZnO Films Grown by Catalytic Reaction Assisted Chemical Vapor Deposition***, A Kato, M Ikeda, Y Adachi, R Tajima, **Kanji Yasui**,* Nagaoka University of Technology, Japan

ZnO films are usually grown on c-plane sapphire substrates, which results in the films having a <0001> orientation. These films are often used in optoelectronic devices, such as light-emitting diodes and laser diodes, operating in the ultraviolet region. However, in such <0001>-oriented ZnO films, a macroscopic electrostatic field is generated along the growth direction, and this results in spontaneous piezoelectric polarization. This induced electric field can negatively affect the device properties by, for example, causing a decrease in the overlap between the electron and hole wave functions in quantum wells, which leads to a reduction in the internal quantum efficiency. In order to eliminate such polarization effects, growth of non-polar ZnO films is required.

In the present study, non-polar ZnO films were grown on r-plane sapphire substrates through a reaction between dimethylzinc and high-temperature H_2O produced by a Pt-catalyzed reaction between H_2 and O_2 [1]. The ZnO films were evaluated using atomic force microscopy, X-ray diffraction, and photoluminescence spectroscopy. The surface morphology of the films was found to be anisotropic, consisting of arrays of nanostripes. In the X-ray diffraction profile, an intense peak was present at 2θ=56.64°, which was associated with the ZnO (11-20) planes. The photoluminescence results indicated anisotropy in the polarization between the directions parallel and perpendicular to the c-axis. The angular dependence of the linear polarization of the band-edge emission was found to be large in ZnO films grown at low temperatures. The ratio between the maximum (the electric field vector *E*: perpendicular to the c-axis) and minimum (*E*: parallel to the c-axis) emission intensity was 4 for a ZnO film grown at 500°C, while it was 2 for a ZnO film grown at 700°C. The width of the nanostripes along the a-axis for the ZnO film grown at 500°C was less than 0.1 μm, while for the ZnO film grown at 700°C it was approximately 0.5 μm. The small domain width in the film grown at the lower temperature may enhance the anisotropy of the band-edge emission. This unique polarized light emission may be exploitable in various types of polarization-sensitive optoelectronic devices in the ultraviolet wavelength region.

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Reference: [1] K. Yasui et al., MRS Symp. Proc., **1315** (2011) 21.

3:10pm **C2-2-6 Mechanism of a Number of Operation Resulted in Degradation on Multilayer Resistance Random Access Memory***, **Yi-Ting Tseng**,* National Sun Yat-sen University, Taiwan*; T Chang, K Chang, T Tsai,* National Sun Yat-Sen University, Taiwan*; C Wu,* National Sun Yat-sen University, Taiwan*; P Chen, C Lin,* National Sun Yat-Sen University, Taiwan*; S Sze,* National Chiao Tung University, Taiwan

Resistance random access memory (RRAM) is most potential to serve as the new generation nonvolatile memory (NVM). Because RRAM device has low power consumption, simple structure, fast operation and high density. Sneak path current issue is very important when RRAM is fabricated stand-alone memory array. To solve sneak path current problem, complementary resistive switching (CRS) RRAM was researched.

The Pt/ZnO/SiO_2/ZnO/TiN structure device has two electric characteristics bipolar RS and CRS behavior in previous experiment result. The reason the SiO_2 layer generated oxygen vacancies and became oxygen ion storage during the forming process. The endurance of bipolar RRAM device is over 10^7 times with pulse. But, the RRAM device was degradation that high resistive state (HRS) of value increased until its fail after operating over 10^7 times. The HRS fitting curve is Schottky emission every operated time. From Schottky emission of intercept and slope, the barrier height became large and dielectric constant became small. The SiO_2 layer of oxygen ions were been activation by joule heat generated by every a million times of operation. Therefore, a lots oxygen ions could switch resistance of RRAM and the SiO_2 layer generated a number of oxygen space resulted in degradation of RRAM device.

3:30pm **C2-2-7 An Ion Mass and Ion Energy Selected Hyperthermal Ion-Beam Assisted Deposition Setup for Nitride Nanofilm Synthesis***, **JürgenW. Gerlach**, P Schumacher, M Mensing,* Leibniz Institute of Surface Modification (IOM), Germany*; S Rauschenbach,* Max Planck Institute for Solid State Research, Germany*; B Rauschenbach,* Leibniz Institute of Surface Modification (IOM), Germany

Ion-beam assisted deposition (IBAD) is an effective physical thin film deposition technique which on the one hand offers the opportunity to investigate fundamental processes involved in ion-assisted film growth and on the other hand provides manifold possibilities to intentionally modify the properties of the prepared thin films. The technique is characterized by simultaneous irradiation of the growing thin film with energetic ions during deposition. IBAD or - at a higher level of sophistication - ion-beam assisted molecular-beam epitaxy (IBA-MBE) is mainly defined by the separability of the material fluxes, that are directed towards the sample, as well as by the accurately adjustable parameters vapor flux and ion flux, the latter generated in form of a broad ion beam. As for nitrogen ion beams however, nitrogen plasma based ion-beam sources counteract the demand to chose the ion-beam parameters as freely as possible, because the resulting ion beam consists of a blend of both molecular and atomic nitrogen ions. Particularly in the case of hyperthermal ion energies ranging from several 10 eV to a few 100 eV this creates great difficulties in assessing the dissemination of the ion energy to the growing film surface.

In the first part of this contribution, a custom setup is presented which allows to create a hyperthermal nitrogen ion beam with selectable ion mass and variable ion energy. This was realized by the unique combination of a constricted glow-discharge plasma beam source [1] with a quadrupole mass filter, equipped with entry and exit ion optics, ion-beam deflection, as well as ion-beam current monitoring. The key features of this setup are demonstrated. For the second part, as a model system for hyperthermal ion-beam assisted growth with energy and mass selected ions, thin films of gallium nitride (GaN) were deposited epitaxially on single-crystalline substrates at elevated temperatures. GaN is well known as base material for optoelectronic devices. In the present study, hyperthermal ion-beam assisted GaN film growth with either molecular or atomic nitrogen ions of well-defined energy was monitored *in situ* by reflection high energy elec-tron diffraction. The orientation relationships between substrates and films formed on them were obtained by x-ray diffraction. Scanning probe microscopy was applied to examine the topography of the obtained films. Influences of ion mass and ion energy on growth mode, topography, crystalline quality, defect structure and luminescence properties of the films are presented and the results are discussed.

[1] A. Anders and M. Kühn, *Rev. Sci. Instrum.***69**, 1340 (1998).

3:50pm **C2-2-8 Improve Switching Characteristic of Resistive Random Access Memory with Chemical Plasma Treatment on TiN electrode***, **Chih-Hung Pan**, T Chang, T Tsai,* National Sun Yat-sen University, Taiwan

In this letter, the TiN electrode was treated with CF_4 plasma to improve the switching characteristics of its random resistive access memory (RRAM). After CF_4 plasma treatment, not only did the stability of HRS increase but the distribution of SET voltages was more concentrated. Furthermore, the device can be operated without current compliance. In addition, the surface of the TiN electrode became rougher after CF_4 plasma treatment, leading to oxygen entering the TiN electrode to form a $TiNO_X$ layer on the electrode. The electrical characteristics of RRAM with $TiNO_X$ are different from that with a TiN electrode. Finally, we propose a model to explain the mechanism causing the improvement in RRAM after the CF_4 plasma treatment. This is due to the difference in TiN electrode surfaces after CF_4 plasma treatment, and was verified by electrical and material analyses.

4:10pm **C2-2-9 Critical Layer to Improve the Orientation Distribution and Carrier Transport of Direct-current Magnetron Sputtered Al-doped ZnO Polycrystalline Films using Various Al_2O_3 Contents Composite Targets***, **Junichi Nomoto**, H Makino, T Yamamoto,* Kochi University of Technology, Japan

We demonstrate a nanoscale materials design using a very-thin critical layer to achieve a high-Hall-mobility Al-doped ZnO (AZO) polycrystalline film showing a texture with a well-defined (0001) orientation. 500-nm-thick AZO films were deposited on glass substrates at a substrate temperature of 200 ºC by direct current (DC) magnetron sputtering with a DC power of 200 W using Al_2O_3 contents ranging from 0.5 to 3.0 wt.% in the composite targets. In this study, a 10-nm-thick Ga-doped ZnO films on a glass substrate deposited by ion plating with DC arc discharge having a texture with a preferential *c*-axis orientation was used a critical layer. First, we investigated the influence of various Al contents on the crystallographic orientations of critical-layer-free AZO films. The crystallographic orientations were characterized by X-ray diffraction (XRD) pole figures measurements of 0002 reflections. The peaks at *a* values of 0º (1^{st}) attributed to the (0001) orientation and of about 66º (2^{nd}) originated in a mixture of multiple orientations, such as (10-11), (20-21) and (30-32), were clearly observed. Note that with increasing Al_2O_3 contents (C_{Al2O3}) up to 3.0 wt.%, the intensity of the 2^{nd} peak corresponding to the complex orientation decreased, whereas the 1^{st} peak intensity increased. To characterize the degree of the (0001) orientation, we estimated the volume fraction of grains with the (0001) orientation, $V_{(0001)}$; the larger the value of $V_{(0001)}$, the higher the degree of the (0001) orientation. The values of $V_{(0001)}$ of AZO films with C_{Al2O3} of 0.5, 1.0, 2.0 and 3.0 wt.% were 84.6 %, 92.9 %, 96.3 % and 98.4 %, respectively. This clearly showed that an increase in C_{Al2O3} improves the orientation distribution of the AZO films. Then, we have developed a technology using the critical layer to tailor the degree of the crystallographic orientation of AZO films.

We deposited DC-magnetron-sputtered AZO films on glass substrates with critical layers. The resulting films had a 500-nm thickness. Note that the use of the critical layers improved theevolution of the orientation distribution of the AZO films, regardless of C_{Al2O3}.: all of the values of $V_{(0001)}$ of the AZO films with the critical layers turned to become of more than 99 %. We will demonstrate a relationship between the orientation distribution and carrier transport of AZO films without and with the critical layers.

4:30pm **C2-2-10 Next-Generation Electronic Materials Processing Tools Newly Developed at AFRL***, **Brandon Howe**,* Air Force Research Laboratory, USA

Next-generation warfighter electronics rely on the development of truly disruptive and robust electronic and optical materials in order to enable game-changing advancements in RF/microwave performance and frequency-agility. The community is extremely materials limited and the major scientific challenge lies in the creation of novel materials and heterostructures with exceptionally high crystalline quality in order to unlock and explore unique and interesting properties. In order to accomplish this, one must create novel processing schemes in order to access never-before-achieved synthesis space, thus unlocking the ability to grow materials with properties far beyond conventional materials. Recently, at the Materials and Manufacturing Directorate at AFRL, we have built up a state-of-the-art PVD epitaxy suite capable of quickly scanning through an enlarged processing space in order to rapidly assess and identify novel materials with enhanced physical properties towards AF application. This talk will focus on the buildup and characterization of both a fully automated UHV pulsed laser epitaxy tool for the growth of high quality ferromagnetic oxides and oxide heterostructures as well as a truly one-of-a-kind and fully automated multifunctional epitaxial growth system (MEGS) capable of applying magnetic fields during both magnetron sputter epitaxy as well as pulsed laser deposition and creating complex metal/metal nitride/oxide heterostructures never before achieve. I will show how these systems are already creating exceptionally high quality

transition metal nitride for resilient plasmonics (as TiN and ZrN mirror the properties of gold and silver) and novel magnetic oxides with record magnetic and microwave performance. The nitrides grown by sputtering demonstrate properties among the best reported as well as reveal incredibly low roughness values and evidence of step-flow growth, while our novel AlNiZnFerrite material demonstrates record high magnetostriction while mitigating prohibitively large losses (microwave damping).

4:50pm **C2-2-11 The Role of Oxidized TiN Bottom Electrode in Resistive Random Access Memory with Supercritical CO_2 Fluid Treatment***, **Yu-Ting Su**, C Pan, T Chang,* National Sun Yat-sen University, Taiwan

This letter investigates an improvement of electrical characteristics attributed to oxidized TiN bottom electrode in resistive random access memory (RRAM) devices after supercritical CO_2 ($SCCO_2$) treatment. Compared to untreated devices, more oxygen ions exist in the bottom electrode, resulting in a layer of TiON. Due to this resistive layer, self-compliance behavior during the set process appears at a small current compliance and the current conduction of low resistance state (LRS) transfers to Schottky emission. Moreover, an analysis of Schottky currents at different compliances further verifies this proposed TiON mechanism.

5:10pm **C2-2-12 Excellent Bipolar Resistive Switching Behavior in WN Thin Film for Non-volatile ReRAM Device Application***, **Ravi Prakash**, D Kaur,* Indian Institute Of Technology Roorkee, India

Resistive memory using sputtered deposited insulating WN thin film as switching layer has been developed with Cu/WN/Pt stack configuration. Excellent bipolar resistive switching (RS) properties have been observed at a low voltage of +0.9 and -1 V respectively, which favors device to reduce the power consumption. Formation/disruption of the conducting filament is verified as the main cause for exhibiting the RS properties. Ohmic behavior and trap-controlled space charge limited current (SCLC) conduction mechanisms are confirmed as dominant conduction mechanism at low resistance state (LRS) and high resistance state (HRS). High resistance ratio between HRS and LRS (10^6), good write/erase endurance (10^5) and non-volatile long retention (10^5s) are also observed. This study demonstrated that the sputtered WN thin films have a great potential for the future non-volatile resistive random access memory (ReRAM) device application.

Fundamentals and Technology of Multifunctional Materials and Devices

Room Royal Palm 4-6 - Session C1

Optical Metrology in Design, Optimization, and Production of Multifunctional Materials

Moderators: Ludvik Martinu, Polytechnique Montreal, Nikolas Podraza, University of Toledo

8:00am **C1-1 Metamaterials: from Design and Modeling to the Experimental Confirmation of their Optical Performance***, **Michel Lequime,*** Institut Fresnel, France **INVITED**

Control of the microstructure of the matter at the sub-wavelength scale offers a great flexibility for designing artificial materials with an exotic electromagnetic response at optical frequencies, like for instance, the near-zero or negative index of refraction. The optical properties of such new, artificial materials (usually called meta-materials) are derived both from the inherent properties of their constitutive elements as well as the geometrical arrangement of these elements. Their development paves the way for controlling and manipulating light through entirely new schemes (slow light, perfect lens ...).

Numerous examples of such metamaterials including fishnet structures and metasurfaces will be provided. Manufacturing techniques, such as electron-beam lithography, focused ion-beam milling or interference lithography will be described, as well as the characterization methods including refraction measurements, spectral transmittance and reflectance measurements, interferometric measurements.

Possible applications to thin-films and multilayer stacks will be analyzed in a preliminary way.

8:40am **C1-3 Use of FDTD Method for Data Analysis of Spectroscopic Ellipsometry Data of Non-periodic sub-wavelength Structures***, **Juan Antonio Zapien,*** City University of Hong Kong, Hong Kong*; Y Foo,* City University of Hong Kong, Hong Kong Special Administrative Region of China

The optical response of complex, non-planar samples have the capability to determine superb sub-wavelength imaging information based on spectroscopic ellipsometry (SE), non-imaging, measurement and full vectorial data analysis. This has played a vital role in optical critical dimension (OCD) characterisation for the semiconductor industry. Rigorous coupled-wave analysis (RCWA) sets the standard in the determination of the fine structure of 1D gratings based on polarimetric and scattering techniques [1]. The ability to reproduce that level of detail in the characterization of complex nanostructured samples, particularly 2D or plasmonic nanostructures, is yet to be demonstrated using RCWA and is also much needed for sensing, active metamaterials research, and others [2,3]. To date, the use of RCWA analysis for such complex structures is largely limited to quantitative modeling of reflectance ratios whereas phase information, crucial for enhanced sensing capabilities [3], is largely disregarded. It seems necessary to secure additional analysis tools to provide complimentary fully-vectorial SE data analysis of nano-structured 2d and plasmonic materials. The finite difference time domain (FDTD) method presents attractive advantages as generality, ability to retrieve wide frequency range from single simulations as well as non-linear effects or non-periodic morphologies [4]. Previously, we have shown that the SE response of thin films can be obtained from FDTD using far-field projections of near-field simulation based on the FDTD method [5]. In this contribution we provide new results discussing the difficulties and strategies to needed to accurately model the SE response of non-periodic samples at large AoI. We will discuss the optimization of the modeling strategies and expected applications.

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References

[1] E. Liu, F.L. Terry, *Immersion scatterometry for improved nano-scale topography measurements*, Phys. Status Solidi **205**, 784 (2008).

[2]Losurdo M, Hingerl K. Ellipsometry at the nanoscale. Springer-Verlag: Berlin Heidelberg, 2013.

[3] Johann Toudert *Spectroscopic ellipsometry for active nano- and meta-materials* Nanotechnol Rev **3**, 223 (2014).

[4] A. Taflove, S.C. Hagness, Computational *Electrodynamics: the Finite-Difference Time-Domain Method*, 3rd ed. Artech House, MA, 2005.

[5] K.T. Cheung, Y. Foo, C.H. To, J.A. Zapien, *Towards FDTD modeling of spectroscopic ellipsometry data at large angles of incidence*, Appl. Surf. Sci. **281**, 2 (2013).

9:00am **C1-4 Analysis Procedures for Multiple Sets of Ellipsometric Spectra***, **Nikolas Podraza,*** *K Ghimire, P Uprety, M Junda,* University of Toledo, USA

Ellipsometric parameters are collected as a function of photon energy, spatial position on a sample, and time during a process. Analysis provides spectroscopic complex dielectric functions, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, and structural information (layer thicknesses, surface roughness, interfaces). The particular photon energies measured can yield information pertaining to component layer intrinsic properties, with some regions of the spectrum more closely linked to particular material and electrical properties. Also, depending on material ε and the arrangement of materials in a sample, different spectral ranges are more or less sensitive to layer structure. To more fully understand the nature of materials comprising a sample, ellipsometric spectra are often measured over wide spectral ranges, using more than one instrument, and analyzed jointly. In other scenarios, multiple sets of ellipsometric spectra are collected either as functions of spatial position on a sample or time during a process to identify subtle material variations. Here we will discuss details of data analysis pertaining to four scenarios: (1) applying realistic parametric models of ε over the appropriate spectral ranges to deduce structural information, (2) simultaneous analysis of measurements collected from the millimeter (THz) to the ultraviolet spectral range using $\geq$2 ellipsometers, (3) utilizing spatially resolved mapping measurements to deduce material property variations, and (4) analysis of in situ time real time spectroscopic ellipsometry (RTSE) collected during thin film growth or post deposition modification. For (1) and (2) metal oxides will be considered, specifically aluminum doped zinc oxide (ZnO:Al) with particular attention to the analyzed spectral range dependence on resultant electrical properties. For (3), disordered nano-/polycrystalline semiconductors (Si:H, CdTe, $CuIn_{1-x}Ga_xSe_2$) for use in thin film solar cells will yield maps of thicknesses and degree of crystallinity. (4) Methylammonium lead iodide ($CH_3NH_3PbI_3$) perovskites will be monitored using RTSE during vapor deposition and post-deposition atmospheric exposure to track phase segregation into component CH_3NH_3I and PbI_2 as well as changes in the perovskite itself. The respective strengths and weaknesses of these methods are discussed.

9:20am **C1-5 High Precision Absorption Measurements in Optical Films using the TRACK Method: Comparison with the Laser-induced Deflection***, R Vernhes,* Polytechnique Montreal, Canada*; C Muhlig,* Leibniz-Institute of Photonic Technology (IPHT), Germany*; **Ludvik Martinu,*** Polytechnique Montreal, Canada

The accurate determination of optical constants of thin films is both challenging and critical for many optical applications. In this study, we focus on the methodology for the precise evaluation of the extinction coefficient (k) assessed by multi-angle spectrophotometry using the recently developed TRACK method [1]. More specifically, we present how absorption can be directly derived from transmission and reflection spectra in p polarization for complex samples showing non-idealities such as inhomogeneities, interfaces and thickness non-uniformity. As an example, we apply this method to a non-uniform inhomogeneous silicon nitride film deposited on glass and we demonstrate that the complete optical modeling of the non-idealities is not necessary to obtain k values. Finally, we compare the results determined by this method to those obtained by the highly sensitive laser induced deflection (LID) technique over a broad spectral range (400 to 1000 nm) and for various materials of interest for optical applications, such as TiO2, ZnO, silicon, etc.

1. R. Vernhes and L. Martinu, "TRACK – A new method for the evaluation of low-level extinction coefficient in optical films," Optics Express 23 (2015) 28501.

9:40am **C1-6 Durability and Wear Mechanisms of Easy-to-clean Coatings on Glass and Displays Assessed by *in situ* Tribometry***, J Qian, T Schmitt, B Baloukas, **Jolanta Ewa Klemberg-Sapieha,*** *L Martinu,* Polytechnique Montreal, Canada*; C Kosik-Williams, J Price, E Null,* Corning Incorporated, USA

Fluorine-based easy-to-clean (ETC) coatings, with contact angles higher than 110º and friction coefficients of ~0.1, are widely applied on touch-screen displays to reduce staining and to enhance abrasion resistance.

In the present work, we evaluate the durability and study the wear mechanisms of ETC coatings on glass substrates using an *in situ* tribometer (TribTik) equipped with a camera system; this allows one to image, in real

time, the contact area between the glass substrate and the abrading counterpart. Through this unique combination, the instantaneous friction coefficient and the contact area's status can be monitored and correlated *in situ,* thus offering the opportunity to abort the test at critical stages of the wear process and study its progression.

The morphology and composition of the wear tracks are further examined at different stages to understand the wear mechanisms of the ETC. We demonstrate, with the support of optical, SEM and EDX analyses that the instantaneous friction coefficient and the obtained *insitu* images correlate very well with the wear process. The progression of the wear mechanism is then defined as follows: 1) generation of unconsolidated debris, 2) formation of a layered tribofilm, 3) cracking of the tribofilm, and 4) damage to the underlying glass substrate.

10:00am **C1-7 Insitu Metrology for Surface Topography and Stress Characterization***, **Wojtek Walecki,*** Frontier Semiconductor, USA

Novel metrology tool for in-situ characterization of surfaces of coatings during deposition process. The tool measures the total integrated scatterer for smooth wafers when measuring forward, or back-reflection at very large angles of incidence. The tool is insensitive to vibrations and stray light. We discuss polarization resolved data and characterize our technique using NIST traceable standards. We discuss it's applications to semiconductor manufacturing.

The grazing angle reflection measurements were subject of radar [1], semiconductor [2], machine vision [3], space [4], traffic materials [5], and theoretical research [6]. The grazing angle forward reflection metrology was reported by us earlier [7], however, we are not aware of the fully polarization resolved grazing angle back-reflection metrology of roughness of functional coatings.

In addition we discuss recently developed polarization sensitive Raman scattering tool, and submicroradian and nanoradian beam deflection techniques for characterization of stress tensor in coatings on global and microscopic scale.

[1] Billingsley, J. Barrie. *Low-angle radar land clutter: measurements and empirical models*. IET, 2002.

[2] Stover, John C. *Optical scattering: measurement and analysis*. Vol. 2. Bellingham: SPIE optical engineering press, 1995.

[3] Ngan, Addy et al. "Experimental Analysis of BRDF Models." *Rendering Techniques* 2005.16th (2005): 2.

[4] Speicher, Andy. *Identification of geostationary satellites using polarization data from unresolved images*. Diss. UNIVERSITY OF DENVER, 2015.

[5] Belcour, Laurent, et al. "Bidirectional reflectance distribution function measurements and analysis of retroreflective materials." *JOSA A* 31.12 (2014): 2561-2572.

[6] Elfouhaily, Tanos Mikhael, et al. "A critical survey of approximate scattering wave theories from random rough surfaces." *Waves in Random Media* 14.4 (2004): R1-R40.

[7] Walecki, Wojciech, et al. "Robust diffuser and roughness metrology tool for LED manufacturing." *SPIE OPTO*. International Society for Optics and Photonics, 2015.

10:20am **C1-8 Scratch Failure vs Residual Stress: a Relationship Applied to Optical Coatings***, T Poirié, **Thomas Schmitt,*** Polytechnique Montreal, Canada*; E Bousser,* University of Manchester, UK*; L Martinu, J Klemberg-Sapieha,* Polytechnique Montreal, Canada

The display industry became an engineering-driven sector which has shifted from mainly industrial uses to consumer products such as flat-panel displays, touch screens, multimedia devices, transportation, ophthalmic lenses and many others. The use of these devices implies various mechanical solicitations that become very critical in situations when sensitive substrates, such as polymers, are applied. Specifically, optical coatings in use today involve transparent ceramic-based materials which show a strong mechanical mismatch with the substrate. In addition, their typical thickness, which ranges from several tens to several hundreds of nanometers, makes their mechanical durability very challenging. It is therefore crucial to understand the failure mechanisms occurring during mechanical loading of these coated systems, and their relationships with the intrinsic properties such as internal stress.

In this work, we systematically study the scratch resistance and the delamination behavior of thin e-beam evaporated TiO_2 films deposited on plastic substrates. The use of Ion Beam Assisted Evaporation has been used to tailor the residual stress and to produce coatings which exhibit stress levels ranging from tensile to compressive. By combining an *in situ* scratch testing technique and a new approach based on reverse scratching sequence starting from high to low load, we were able to assess specific failure mechanisms in dependence on the stress level. Moreover, this method establishing the relationship between the scratch failure and the internal stress allows one to extract the yield strength, in the present context applied to model thin TiO_2 coatings. Finally, this study and the related methodology significantly enhances the understanding of the failure mechanisms occurring during scratch testing, and it can be applied to any optical and other films.

10:40am **C1-9 Fast Characterization of nm Thin to Thick Coatings using Pulsed-Rf Glow Discharge Optical Emission Spectrometry***, **Philippe Hunault,*** *M Chausseau, K Savadkouei,* HORIBA Scientific, USA*; P Chapon, S Gaiaschi,* HORIBA Scientific, France

Glow Discharge Optical Emission Spectrometry (GD-OES) provides direct measurement of the chemical composition of materials as a function of depth and can be used to characterize various coatings, made of both thin and thick layers, conductive or non-conductive materials

It consists in a pulsed radiofrequency glow discharge plasma source that is sputtering a large area of the material of interest and real time detection by a high resolution optical spectrometer of the sputtered species excited by the same plasma. All elements from H to U can be measured using this technique.

With its capability to perform depth profiling with a nanometric resolution and to go up to 150 µm deep into the sample within few minutes, GD-OES is an ideal tool to evaluate depth profiles on materials and to study interfaces between layers, diffusion processes or to optimize coatings processes. Many elements can be analyzed simultaneously, including Oxygen, Hydrogen, Deuterium, Carbon, Fluorine, Sulfur, Lithium… GD-OES is a versatile tool to study materials that complements other techniques such as XPS and SIMS.

Results obtained on various nm thin and thick oxide coatings, nitriding, carburizing, galvanization and energy storage will be shown. Examples of GD-OES as a tool for layer thickness determination will also be presented.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Royal Palm 4-6 - Session C2-3
Thin Films for Active Devices

Moderators: Vanya DarakchievaMarco Cremona, Pontificia Universidade Católica do Rio de Janeiro, Junichi Nomoto, Kochi University of Technology, Japan,

2:30pm **C2-3-4 High Dielectric Constant of Polymer-inorganic Nanocomposites as Gate Dielectrics for Organic Thin Film Transistor Applications**, ***Cheng-Huai Yang***, *Y Yu, C Chiu,* Ming Chi University of Technology, Taiwan

Organic thin film transistors (OTFTs) based on pentacene and hydroxyl-containing polyimide-zirconium dioxide (PI-ZrO_2) hybrid films were fabricated on silicon substrate in which the PI and ZrO_2 were as the semiconductor and the gate dielectrics, respectively. Zirconium butoxide ($Zr(OBu)_4$) was used as the precursor to synthesize nano-sized ZrO_2 colloid through the hydrolysis and condensation reaction in a sol-gel process. Then, PI-ZrO_2 hybrid solution was synthesized from a condensation reaction between hydroxyl-containing ZrO_2 and polyimide, followed by a spin coating to form the PI-ZrO_2 dielectric composites. Cyclic olefin copolymer (COC) was used as a modify layer to enhance the interface property between the semiconductor and the dielectric layer. In addition, PffBT4T-2OD was replaced by pentacene as semiconductor to expect a good performance on device. The thermal, optical, surface, dielectric, and electrical properties of the PI-ZrO_2 dielectric composites were investigated and correlated to ZrO_2 content due to the dispersion and aggregation behaviors of the nanoparticles. The PI-ZrO_2 hybrid dielectrics showed the tunable insulating properties, including high dielectric constants, high capacitances, and low leakage current densities. Besides, the bottom-gate top-contact OTFTs based on the PI-ZrO_2 hybrid dielectrics PZ30% and PZ30%-COC showed the best performance with the near zero threshold voltage and the field-effect mobility (μ) about 1.12 $cm^2V^{-1}s^{-1}$ and 3.25 $cm^2V^{-1}s^{-1}$ and the current on/off ratio (I_{on}/I_{off}) about $1.2x10^4$ and $1.2x10^6$, respectively. Based on the above results, PI-ZrO_2 hybrid dielectrics were synthesized and the OTFTs based on the PI-ZrO2 hybrid dielectrics and pentacene were fabricated successfully. The best performance for OTFTs was obtained when the ZrO2 content in hybrid films was 30%.

2:50pm **C2-3-5 Different Nitridation Condition Influence NBTI in FinFETs**, ***Hsi-Wen Liu***, *T Chang,* National Sun Yat-Sen University, Taiwan

This research uses different Nitridation condition to investigate negative bias instability (NBTI) in p-channel fin field effect transistors (p-FinFETs). We find that low Nitridation temperature device suppress NBTI compare to high Nitridation temperature device. It is because that nitrogen located at Si/SiON interface more at higher temperature. Beside, we compare spike and soak post-Nitridation anneal. We find soak one can suppress NBTI effectively.

3:10pm **C2-3-6 Analysis of Abnormal Transconductance in Body-tied PD SOI n-MOSFETs**, ***Chien-Yu Lin***, *T Chang,* National Sun Yat-sen University, Taiwan

This letter investigates the mechanism of abnormal transconductance (Gm) and abnormal charge pumping current (ICP) in body-tied partially-depleted silicon-on-insulator n-channel metal-oxide-semiconductor field effect transistors. The ICP second hump region increases with channel length, yet is not affected by channel width. The cross-sectional view of the L-gate structure along the width direction demonstrates that a part of the poly gate area near the body contact is covered by a P^+ implant, inducing a parasitic channel under the P^+ poly gate. This parasitic channel leads to the abnormal Gm and ICP hump, and such mechanism is further verified by body floating devices.

3:30pm **C2-3-7 Influence of the Ammonia Hardening on the Properties of Sol-Gel Thin Film Coatings**, ***Christophe Boscher***, *J Avice, H Piombini, X Dieudonné, P Belleville, K Vallé,* CEA, France

Introduction

The Laser Megajoule is one of the most important parts of simulation program of CEA. Its purpose is to create the thermodynamic conditions of a nuclear fusion at the laboratory scale. The LMJ is made of different large aperture components (typically 40X40 cm^2) in order to amplify and transport light and then to concentrate it on a millimetric microtarget.

To minimize the parasit reflexions and to maximize the energy on the target, all the components must be treated with an antireflective thin film coating. This surface treatment is realized thanks to a sol-gel process associated with a liquid phase coating.

2. Colloïdal silica antireflective coating

The sol-gel solution used for the antireflective treatment is a colloidal suspension synthetized by sol-gel route inspired of Stöber method [1]. The synthesis results of the hydrolyze-condensation of tetraethyl orthosilicate in an alcoholic solution. Then, it is deposited on optical components by spin/dip-coating or laminar induction method.

The cohesion between particles and the adherence on the substrate are relatively weak, that ' s why the coating is little adherent mechanically.

To increase the cohesion of these colloïdal thin films, a chemical modification of the nanoparticles is achieved thanks to a post-processing using ammonia vapors, called "ammonia hardening process" [2].

This process permits a modification of the nanocontact chemical bonds from Van Der Walls to Hydrogen & Covalent bonds.

The purpose of this study is to follow these modifications during the ammonia hardening process. We use different characterization techniques as IR spectroscopy or surface tension measurements (chemical changes inside the layer or in the surface), UV/VIS spectroscopy (refractive index or thickness modifications) and an acoustic pico-second method (mechanical changes).

3. Conclusion

The precise knowledge of the ammonia hardening mechanisms has permitted to reduce the duration of the ammonia hardening step. This point is crucial in order to increase the production rate in an industrial process.

4. Bibliography

[1] ***Werner Stöber*, *Arthur Fink*, *Ernst Bohn "controlled growth* of *monodisperse silica spheres***in the***micron size range" journal***of ***colloid***and***interface science*, *volume 26*, *issue 1*, *January 1968*, *pages 62-69* **Growth of Monodisperse Silica Spheres**

[2] Philippe F. Belleville and Herve G. Floc h, "Ammonia hardening of porous silica antireflective coatings", Proc. SPIE 2288, pp25-3, (1994).

3:50pm **C2-3-8 Miniaturized Shape Memory (SMA) Bimorph Actuators with Polymer Layers**, ***Cory Knick***, *G Smith, N Jankowski, C Morris,* US Army Research Laboratory, USA

Shape-memory alloy (SMA) actuators based on nickel-titanium (NiTi, or NITINOL) are promising candidates for miniaturized sensors and actuators in MEMS applications [1]. Thermal processing constraints currently limit monolithic SMA actuator integration for example in soft body micro robotics or onto soft polymer substrates. Other electronic materials can also degrade when exposed to typical NiTi crystallization temperatures in excess of 450 °C. Historically, NiTi crystallization requires sputter or anneal temperatures of 450 °C or more so there is a desire to obtain shape memory effects at lower processing temperatures.

To motivate the mating of polymer and crystallized NiTi SMA layers, we developed and carried out the microfabrication of a simple, yet novel, shape memory (SMA) bimorph actuator, outlined in Figure 1, and based on previous deposition and micromachining processes of NiTi on platinum [2, 3]. By following crystallized 270 nm NiTi SMA with a 1 micron photosensitive polymer layer, we created a bimorph with a large coefficient of thermal expansion (CTE) mismatch (>40 ppm/°C) allowing significant yet predictable curvature upon release. An analytical strain/curvature model [4] predicted the radius of curvature to within 10% as shown in Figure 2, and resulted in a measured radius of curvature down to 50 μm for an actuator that folded flat upon actuation.

The full benefits of combining SMA materials with polymers can only be realized without the constraint of high temperature crystallization coming before polymer deposition. To this end, we carried out experiments to investigate the crystallization of amorphous NiTi using a Novacentrix pulse forge additive manufacturing tool. This tool is used to sinter metal powders on standard polymer substrates, and our goal was to assess whether the as-deposited amorphous NiTi could be crystallized using intense (>10,000 W/cm^2) microsecond bursts of light. We tested experimental stacks of sputtered, amorphous submicron thick films of NiTi on Si and on 1.2 micron films of polyimide. We developed thermal models used to predict transient temperature profiles in the NiTi film/substrate stacks, using differential scanning calorimetry (DSC) scans on substrate-released NiTi films to determine specific heat values. Using these values, models and preliminary

experiments using x-ray diffraction analysis indicate that the pulse forge method may be a novel technique to crystallize shape memory materials while limiting thermal exposure of adjacent polymer layers or other electronic materials.

4:10pm **C2-3-9 Investigating Degradation Behaviors Induced by Hot Carriers in the ESL in Amorphous InGaZnO TFTs with Different Electrode Materials and Structure***, **Chung-I Yang,*** National Chiao Tung University, Taiwan*; T Chang,* National Sun Yat-Sen University, Taiwan

We discuss the indium gallium zinc oxide (InGaZnO) thin film transistor

hot carrier effect, the etching terminating layer contact window type element because

of source pole and drain pole excess electrode leads to electron injection in drain pole

excess electricity and lower channel etch stop layer, and the injected electron will be

confined to the excess electrode position, such electronic injection state gate source

capacitance curves is due to the phenomenon of two-stage uplift. The relationship

between the thermal field emission activation energy and the work function of the

metal materials can be found by the amount of different electrode materials.

Fundamentals and Technology of Multifunctional Materials and Devices

Room Royal Palm 1-3 - Session C3-1

Thin Films for Energy-related Applications

Moderators: Jim Partridge, RMIT University, Martin Allen, University of Canterbury

9:20am **C3-1-5 Solar Photovoltaic Energy Generation in Thermal Insulation Glazing**, ***David McKenzie,*** The University of Sydney, Australia **INVITED**

There is renewed interest in combining solar photovoltaic technologies with thermally insulating glazings. Modern cities have multi storey buildings with large areas of glazed facades that represent the majority of the building envelope. These facades have large energy exchanges with the environment that must be managed efficiently in order to avoid major energy wastage. The combination of PV technologies with thermal insulating glazings is a novel approach with potential to increase the harvesting of solar energy while minimising unwanted energy exchanges. New technologies for PV such as perovskite cells have shown good efficiency while allowing for some useful residual light transmission with an options for a choice of colour. There is a synergy with double glazed insulating units, first because of the local generation of energy while minimising losses, and second because the perovskite cells are moisture sensitive. In a synergistic design the thermal insulating glazing can act as a protective encapsulation of the cells. Recent advances and the current status of available technologies in this area will be discussed in this paper .

10:00am **C3-1-7 Effects of Annealing on Thermochromic Properties of W-doped Vanadium Dioxide Thin Films Deposited by Electron Beam Evaporation**, ***Shao-En Chen,*** National Cheng Kung University, Taiwan*; H Lu,* National Chin-Yi University of Technology, Taiwan*; S Brahma, J Huang,* National Cheng Kung University, Taiwan

Thermochromic vanadium dioxide (VO_2) undergoes a fully reversible semiconductor-metal transition (SMT) at a critical temperature T_t of ~68 °C with a dramatic change in electric and optical properties, which makes it an attractive candidate for use in smart windows. Switchable VO_2 and W-doped vanadium dioxide ($W_xV_{1-x}O_2$) thin films are grown successfully over quartz substrates via electron beam evaporation technique by using VO_2 / $W_xV_{1-x}O_2$ as targets at room temperature (RT) followed by a post annealing process at different temperatures. The films were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, scanning electron microscopy (SEM) and optical transmittance measurement. The XRD analysis shows that the as-deposited films are amorphous, and that transform into (011)-preferred orientation of monoclinic VO_2 (VO_2(M)) after annealing at 500 °C under vacuum. Moreover, (011) peak of W-doped VO_2 films shifts to a lower diffraction angle as compared with un-doped VO_2 films which confirm the incorporation of W ions into the VO_2 lattice. Temperature dependent optical transmittance (T-T) measurement demonstrates the thermochromic properties, with a reduction in the phase transition temperature (T_t) as observed in W-doped VO_2 films, which is attributed to the variation of electron structure in VO_2 due to doping.

10:20am **C3-1-8 Fabrication and Characterization of Titanium Doped β-Ga_2O_3 Thin Films for Application in Oxygen Sensors**, ***Sandeep Manandhar,*** *E Rubio, R Chintalapalle,* The University of Texas at El Paso, USA

The electrical conductivity changes in metal oxides when exposed to atmosphere have attracted considerable interest in the field of gas sensing. Several candidate metal oxides (SnO_2, ZnO, TiO_2 and Ga_2O_3, WO_3) have high sensitivity to gases. Among these metal oxide, Gallium oxide (Ga_2O_3), the stable oxide of gallium, finds attractive applications in luminescent phosphors, high temperature sensors, antireflection coatings, and solar cells. Ga_2O_3 has been recognized as a deep ultraviolet transparent conducting oxide (UV–TCO), which makes the material a potential candidate for transparent electrode applications in UV optoelectronics. Ga_2O_3 thin film has proven to detect the presence of oxygen at high temperatures (>700 °C). However, recent trends and demand for reliable oxygen sensors imposed restrictions on the response time and sensitivity. In this work, we proposed and investigate to modify the properties of Ga_2O_3 by selectively doping with titanium (Ti). Ti doped β- Ga_2O_3 thin films with variable Ti content were deposited by co-sputtering of the Ga-oxide ceramic and Ti metal by varying the sputtering power to these targets. The effect of Ti on the crystal structure and electronic properties of β- Ga_2O_3 thin films is significant. The results will be presented and discussed in the context of utilizing these materials in oxygen sensor applications.

10:40am **C3-1-9 Bombardment of Tungsten Oxide Thin Layers by Low Energy of He and D Ions**, ***Hussein Hijazi,*** *Y Addab,* Aix-Marseille Université, France*; A Maan, J Duran, D Donovan,* University of Tennessee-Knoxville, USA*; C Pardanaud, M Cabié,* Aix-Marseille Université, France*; F Meyer, M Bannister,* Oak Ridge National Laboratory, USA*; R Pascal, C Martin,* Aix-Marseille Université, France

Tungsten is the plasma-facing material for next fusion reactors (e.g. ITER divertor) due to its high melting temperature, high thermal conductivity and low erosion yield. As a drawback, tungsten has a strong chemical affinity with oxygen and native oxide is naturally present on tungsten surfaces, which leads to the formation of tungsten oxide layers. In order to study the effect of oxidation on tungsten properties, the behavior of WO_{3-x} layers under deuterium/helium bombardment and thermal cycling effect in divertor-like conditions, we have produced, by thermal oxidation, thin layers of WO_{3-x} on W substrates which mimic the possible oxidation of tungsten plasma facing components. The produced tungsten oxide layers were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy and X-ray diffraction (XRD) techniques. The thickness of the colored oxide thin layer δ, measured by SEM using focused ion beam cross-section (FIB), follows a parabolic law as a function of the oxidation time. A set of those oxide tungsten thin film samples were separately exposed, at PIIM laboratory (Marseille-France) and in collaboration with the University of Tennessee UT (Knoxville-USA) and Oak Ridge National Laboratory ORNL (Oak Ridge-USA), to D and He plasma beams with energy range from 20 eV to 320 eV and total fluence ~ 4.10^{21} m^{-2} and sample temperatures RT-673 K. At RT, due to D implantation (which has high affinity to bond formation) followed by its deep diffusion [1], preliminary results show a phase transition in the WO_{3-x}, change in the layer color as well as formation of tungsten bronze (D_xWO_3) have been observed. However, the He implantation (that has high affinity to induce the creation of bubbles, holes and nanostructure morphology on W [2]) neither causes surface morphological change on the oxide of tungsten nor changes in its color. However, at 673K, an erosion effect was observed due to He implantation in the oxide layer. Deep analysis on the process of structural damage in surface/bulk and estimation of the erosion rate will be described for both exposures using the coupling of Raman spectroscopy and SEM approaches.

Fundamentals and Technology of Multifunctional Materials and Devices

Room Royal Palm 1-3 - Session C3-2

Thin Films for Energy-related Applications

Moderators: Jim Partridge, RMIT University, Martin Allen, University of Canterbury

1:30pm **C3-2-1 P-type Cu_2O Modified by NiO_x as a Photocathode for Efficient Hydrogen Production in Photoelectrochemical Water Splitting**, ***Ching Lin***, *J Ting,* National Cheng Kung University, Taiwan

First, Cu_2O/NiO_x nanoparticles were synthesized using a hydrothermal method with CuCl and NiO as precursors. Second, Cu_2O/NiO_x nanoparticles were made into a thin film by spin coating method. The NiO_x modified the surface of Cu_2O particles seem to be efficient way as a protective layer in order to enhance the efficiency of H_2 production. The core-shell structure of Cu_2O/ NiO_x nanoparticles were examined with a SEM. Due to an appropriate band energy structure, the photogenerated electrons from Cu_2O are easily transferred to the conduction band of NiO. Therefore, the possibility of the electrons and holes recombination is considerably reduced. XPS spectra revealed that the surface species of NiO_x is a mixture of NiO and $Ni(OH)_2$, which enhances charge separation in photoexcited Cu_2O. The role of NiO and $Ni(OH)_2$ is similar and both were suggested to act as a trap for photoelectrons, therefore retarding charge recombination. We demonstrate that a Cu_2O-based electrode for H_2 evolution can be prepared free of noble metals and we show its utilization in a PEC water splitting cell made solely from earth abundant elements.

1:50pm **C3-2-2 High Temperature Resistant Molybdenum Thin Film Metal Mesh Electrode as Replacement for ITO**, ***Niklas Bönninghoff***, National Taiwan University of Science and Technology, Taiwan

Indium tin oxide (ITO) films are still, despite their disadvantages, the main choice for thin film optoelectronic applications. Indium however is steadily increasing in price. One alternative to ITO is the use of a metal mesh. The most important parameters of a meshed thin film for optoelectronic devices to control are transparency, conductivity and compatibility with industrial processes (e.g. high temperature). Generally, the smaller the mesh dimensions (line width and pitch), the better the device, but the higher the costs.

Two different metal mesh patterns (line grid and hexagonal grid) have been fabricated on a glass substrate, using I-line photolithography to create a pattern on a photoresist, which was used to mask the substrate during DC magnetron sputter deposition. The material used is 5N pure Molybdenum. The deposition parameters (working pressure, DC power and substrate temperature) were chosen to gain a high conductivity film (measured by four-point probe), while still achieving acceptable adhesion (measured by scotch tape test), by usage of a bilayer. The grid pitch has been optimized for a specific device with an area of 15 mm^2.

The mesh's line thickness is 2 microns. The pitch is 300 microns for the line grid and 360 microns for the hexagonal grid, which results in a calculated transparency of 97% and 98% respectively. The transparency however decreases with increasing device size.

In conclusion, a metal mesh with good conductivity, high temperature resistance and an excellent transparency has been fabricated.

2:10pm **C3-2-3 Piezoelectric and Pyroelectric Materials and Systems for Energy Harvesting**, ***Chris Bowen***, *M Xie, Y Zhang, D Zabek, J Roscow,* University of Bath, UK **INVITED**

The continuing need for reduced power requirements for small electronic components, such as wireless sensor networks, has prompted renewed interest in recent years for energy harvesting technologies capable of capturing energy from ambient vibrations and heat. This presentation provides an overview of piezoelectric harvesting system along with the closely related sub-classes of pyroelectrics and ferroelectrics [1,2]. These properties are, in many cases, present in the same material, providing the intriguing prospect of a material that can harvest energy from multiple sources including vibration and thermal fluctuations [3-5].

Examples of modelling and experimental investigations of porous materials for harvesting are discussed including novel freeze cast and sandwich layer structures are described. Pyroelectric layers for thermal harvesting are also described with the use of patterned electrodes to enhance thermal fluctuations and the potential to use pyroelectric charge for water splitting discussed.

[1] C. R. Bowen, H. A. Kim, P. M. Weaver and S. Dunn, Piezoelectric and ferroelectric materials and structures for energy harvesting applications, Energy and Environmental Science, 7, 25-44 (2014)

[2] CR Bowen, J Taylor, E LeBoulbar, D Zabek, A Chauhan, R Vaish, Pyroelectric materials and devices for energy harvesting applications, Energy & Environmental Science 7 (12), 3836-3856 (2014)

[3] J Zhang, C Wang, C Bowen, Piezoelectric effects and electromechanical theories at the nanoscale, Nanoscale 6 (22), 13314-13327 (2014)

[4] C. R. Bowen and M. H. Arafa, Energy Harvesting Technologies for Tire Pressure Monitoring Systems, Advanced Energy Materials 5, 1401787 (2015)

[5] J. Roscow, Y.Zhang, C.R.Bowen et al., Porous ferroelectrics for energy harvesting applications, *Euro. Phys. J. Special Topics.,* 224, 2949-2966 (2015)

2:50pm **C3-2-5 Ion-assisted Growth of Compound Thin Films for Energy-related Applications**, ***Tomas Kubart***, *A Aijaz,* Uppsala University, Sweden

Energy-related applications generally require high quality thin film materials. In many cases, low growth temperatures are desired while the performance is still critical. In this contribution, low temperature ion-assisted growth of compound thin films is discussed using piezoelectric AlN and thermochromic VO_2 as examples.

Using ions instead of neutral atoms provides means for additional energy input which can be readily controlled by externally applied electric fields. We use High Power Impulse Magnetron Sputtering (HiPIMS), a sputtering technique in which a very high ionization degree of the material is achieved due to the pulsed mode operation of the discharge. Low frequency operation with a duty cycle of about 1% is typically used, which leads to two orders of magnitude higher electron densities and corresponding increase in the ionization of the deposition flux.

For piezoelectric AlN films, we have demonstrated a significant enhancement of the AlN texture by using the HiPIMS process [1]. Already at room temperature, films with good texture and low FWHM values of the rocking curve were grown directly on silicon without any seed layer. This is attributed to the high flux of low energy Al and N ions formed in HiPIMS as well as high dissociation of N_2 in the dense HiPIMS plasma. Such films are suitable for electroacoustic devices, microelectromechanical systems, or energy harvesters.

The deposition temperature is also an important factor for thermochromic materials. Vanadium dioxide thin films provide means for controlling solar energy throughput and can be used for energy-saving applications such as smart windows. At present, however, the deployment of VO_2 in thermochromic devices is limited by the high growth temperature, typically above 450°C. Using HiPIMS, we have reduced the growth temperature to 300°C [2]. We have varied the ion energy and found and optimum at 100 eV. Strategies to further reduce the deposition temperature are discussed.

References

[1] M.A. Moreira, T. Torndahl, I. Katardjiev, T. Kubart, Journal of Vacuum Science & Technology A 33 (2015) 021518.

[2] A. Aijaz, Y.-X. Ji, J. Montero, G.A. Niklasson, C.G. Granqvist, T. Kubart, Solar Energy Materials and Solar Cells 149 (2016) 137-144.

3:10pm **C3-2-6 Growth and Characterization of Thin Film $CaMnO_3$ and $CaMn_xNb_{1-x}O_3$ Thermoelectrics**, ***Erik Ekström***, *B Paul, F Eriksson, P Eklund,* Linköping University, IFM, Sweden

Thermoelectrics show great promise as waste heat harvesters in power plants, cars and other applications. This places demands on their physical and chemical properties. They should be non-toxic, have a high conversion efficiency and thermally stable.

In this work, thermoelectric thin film $CaMnO_3$ and $CaMn_xNb_{1-x}O$ perovskite oxides on Al_2O_3 (0001), (1-100) and (1-102) have been investigated. The films were deposited by magnetron sputtering followed by annealing at 800 °C in oxygen [1]. Nb was introduced by co-sputtering. The structural properties of the films were assessed using X-ray diffraction (XRD) by performing q-2q scans and by plan-view scanning electron microscopy studies.

Isothermal annealing was performed in high vacuum using an in situ XRD furnace to study the phase evolution up to 1100 °C. The annealing was done in 100 °C steps, doing a measurement for each step. The structure of the film after the 3 h post deposition heat treatment was orthorhombic

$CaMnO_3$. This structure remained stable up to 700 °C, while above 800 °C it decomposed into cubic $Ca_xMn_{1-x}O$. The cubic structure is stable at 800 °C, but at 900 °C the phase changes to orthorhombic MnO_2 and Ca rich cubic $Ca_xMn_{1-x}O$. Additionally, the structure decomposed into a multitude of phases at 1100 °C. X-ray diffraction was also recorded while cooling down, showing that the structure obtained at 1100 °C remained to room temperature.

Scanning electron microscopy revealed that by changing the Ca composition in the rangepower on the Ca magnetron changes the surface structure of the films. A low Ca content resulted in Mn-rich nano-inclusions which are also visible in the XRD. Increasing the Ca content reduces the amount of inclusions and at the ideal composition they disappear. When increasing the Ca content the grain size decreases laterally as seen in SEM and decreases vertically as indicated by an increasing peak width.

Four point probe measurements at room temperature show a decrease in resistivity for the alloyed samples compared to the un-alloyed ones and it is also observed that substrate orientation influences the resistivity. The lowest resistivity for un-alloyed films is 1.70 Ωcm, 1.80 Ωcm and 0.69 Ωcm for (0001), (1-100) and (1-102) orientation, respectively. Having an Nb content of x = 3 results in the lowest resistivity of 0.46 Ωcm, 0.06 Ωcm and 0.10 Ωcm for (0001), (1-100) and (1-102) orientation, respectively. The reduction of resistivity is due to an increase in carrier concentration which has been observed in other studies [2].

1 Paul et al Advanced Electronic Materials **1,** 1400022 (2015).

2Xu et al Solid State Ionics **171,** 147 (2004).

3:30pm **C3-2-7 3D-Painted Solid Oxide Fuel Cells: A New Approach to Functional Multi-Ceramic Construct Fabrication***, **Nicholas Geisendorfer**, A Jakus, H Wang, Z Gao, S Barnett, R Shah,* Northwestern University, USA

The fabrication and assembly of solid oxide fuel cell (SOFC) components into an integrated structure, including both support and functional layers, remains one of the primary challenges preventing the widespread adoption of SOFCs as an energy conversion technology. We present an efficient and highly scalable multi-material process for fabricating SOFCs using a combination of 3D-Painting (a room-temperature, liquid extrusion-based 3D-printing process) and dip-coating of particle-laden, liquid-based 3D-inks. 3D-printing is used to sequentially deposit anode and cathode functional layer materials, nickel oxide-yttria stabilized zirconia (NiO-YSZ) and lanthanum strontium manganite (LSM), respectively, without the need to alter printing parameters, allowing unprecedented control over gas channel geometries. Depositing layers thinner than 100 µm using 3D-printing is impractical, so these inks, designed for 3D-printing, are repurposed for the production of mechanically robust, controllably thick, multi-material films via dip-coating to be used as YSZ electrolytes and strontium lanthanum titanate (SLT)/LSM interconnect bilayers. The inks used for both 3D-printing and dip-coating are synthesized through simple, room-temperature mixing of a combination of organic solvents, a biomedical elastomer binder (~10-40 vol.%) and powders of interest (~60-90 vol.%). Vol % powder controls shrinkage and porosity during firing; tailoring the powder vol % for each ink is vital to preventing warping and cracking during cell co-firing and to ensure optimal performance of each component. Fully assembled fuel cell structures are co-fired in air at 1250°C for 4 hours. The microstructural and electrochemical characteristics of fired cells are analyzed and compared with cells produced entirely using tape-casting techniques. We demonstrate that this technique is highly scalable and useful for fabricating monolithic, planar SOFCs of various sizes without the need for cumbersome support materials.

3:50pm **C3-2-8 Nanoengineering Periodically Structured SiCu Thin Film Anodes for Rechargeable LIBs***, **Billur Deniz Polat Karahan**, B Bilici,* Istanbul Technical University, Turkey*; O Eryilmaz,* Argonne National Laboratory, USA*; K Amine,* Argonne National Laboratory, USA, United States of America*; O Keles,* Istanbul Technical University, Turkey

In the quest for a radically better lithium-ion battery, a promising direction is suggested so-called “silicon (Si) composite” anodes, in which the negative electrode contains a higher proportion of Si with another material. In the current technology, while the Si composite electrodes have the potential to have far higher energy density, long cycle life and high reversibility are still not satisfactorily provided due to intrinsic properties of Si such as low electrical conductivity and high volumetric changes upon cycling.

Therefore, in this work, to create electron conduction pathway in the electrode and to increase the ductility of the film 10%at. Cu atoms are co-deposited with Si. Then to induce homogeneously distributed interspaces in the electrode structured composite thin film has been engineered by glancing angle electron beam deposition (GLAD) method. This process enables to deposit coatings of any materials without a need of binders or any conductive additives. Plus, various structures from nanocolumns to helices might be deposited by optimizing the evaporation rate of source materials, the incident angle and the azimuthal rotation rate of the substrate.

An innovative approach involving adaptation of ion assistance to GLAD has been also proposed in this study. The well adherent composite nanostructures are expected to provide large reaction area with Li, facile stress relaxation (to prevent electrode pulverization or delamination), effective electrical contacts with the substrate and short Li diffusion distances.

To evaluate the electrochemical performances of the structured composite films, two samples have been deposited on Cu collector with different evaporation rates: quartz crystal microbalances of Cu and Si show 0.4-4 Å/s and 0.9-10 Å/s for Samples 1 and 2, respectively. The morphological analyses show that depending on the evaporation rates of sources the structure of the film changes which affects their performances in cycling.

4:10pm **C3-2-9 A Mesoporous CuAlO2 Hole Transport Layer for Perovskite Solar Cell***, **Wei-Jie Sun**, J Ting, P Chen,* National Cheng Kung University, Taiwan

Mesoporous CuAlO2 (CAO) has been investigated for use as a hole transport layer in perovskite based solar cells (PSC) having a p-i-n heterojunctions configuration. CuAlO2 nanopowders (NPs) was first synthesized using a sol-gel method with Cu(NO3)2 and Al(NO3)3 as the precursors. The obtained CuAlO2 NPs were spinning-coated onto indium-tin oxide substrate to form a hole transport layer. The obtained CuAlO2 NPs and layers were examined for the material characteristics, in particular, photoelectrical properties. Effects of the synthesis conditions of these characteristics are addressed and discussed. PSCs having a CuAlO2 transport layer were fabricated. The cell performance was evaluated to demonstrate the advantages of using CuAlO2 as a hole transport layer.

4:30pm **C3-2-10 Fabrication of Hybrid Perovskite Solar Cells based on Low Temperature Solution Process***, **Tzung-Wei Tsai**, Y Yu, C Teng,* Ming Chi University of Technology, Taiwan

Organic–inorganic perovskite solar cells have recently emerged at the forefront of photovoltaics research due to its dual electron and hole mobility. Organo-metal halide perovskites were composed of an ABX3 (e.g. $CH_3NH_3PbI_3$) structure in which A represents a cation, B a divalent metal cation (e.g. Pb^{2-}) and X a halide (e.g. F, Cl, Br, I). We used two different materials such titanium dioxide (TiO_2) as the perovskite electron transport layer of the solar cell in this study. The titanium dioxide colloid was prepared by using a ball-milling process with the 50 micrometer zirconia balls in a SiC pot for 8~10h. Then, the titanium dioxide powders were prepared after annealing. The effects of annealing temperature on the properties of perovskite thin film were also investigated. The organic–inorganic perovskite solar cells with structure ITO/TiO2/Perovskite/Spiro-OMeTAD/Ag were fabricated. The best performance of the prepared solar cells had a photo conversion efficiency of 6.4%, J_{sc} of 12.11 mA/cm^2, V_{oc} of 0.96V, and fill factor of 0.56, respectively.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Grand Exhibit Hall - Session CP
Symposium C Poster Session

CP-1 Reversible Photo-Induced Deformation of Amorphous Carbon Nitride Films and their Potential Application to Light Driven Actuators, *T Harata, M Aono, K Ishii, N Kitazawa,* ***Yoshihisa Watanabe,*** National Defense Academy, Japan

Amorphous carbon nitride (a-CNx) films are known as useful coating materials. Recently, we first observed reversible photo-induced deformation of hydrogen-free a-CNx films under visible light illumination [1]. This phenomenon suggests that the a-CNx films have potential applications to light driven actuators. In this paper, we report fundamental studies for applying a-CNx films to light driven actuators.

The hydrogen free a-CNx films were prepared by reactive radio frequency magnetron sputtering using a graphite target and pure nitrogen gas. The substrate temperature during deposition was kept at 573 K. The substrates used were silicon single crystal plate with the thickness of about 0.5 mm. The self-standing a-CNx film with the thickness of about 1 μm was obtained by peeling the deposited film from the Si substrate in pure water. The diaphragm with the diameter of 4.6 mm was prepared by sandwiching the self-standing a-CNx film between metal rings and the movement of the diaphragm was measured using a laser vibrometer under white light illumination.

The photomechanical response was measured when the light illumination is turned on and off with the interval of 15 s, and the results show that the diaphragm reiterates stably and the typical amount of the displacement was about 120 μm. These results suggest that the a-CNx films have potential for light-driven actuators with good stability.

The authors would like to thank Keyence Corporation for helping the laser vibrometer measurements. This research is supported by JSPS KAKENHI Grant Number 26790054.

[1] M. Aono, T. Harata, N. Kitazawa, Y. Watanabe, Diamond & Related Materials **41** (2014) 20-24.

CP-2 Mechanisms of Grain Growth Enhancement in Sintered-CZTS Nanoparticle Thin Films, ***Edgar Palmes,*** *S Exarhos, R Xu, L Mangolini,* University of California, Riverside, USA

An innovative and scalable synthesis approach to the formation of Cu_2ZnSnS_4 (CZTS) nanocrystals has been developed using aerosol spray pyrolysis. This quaternary-phase material is a potential replacement for currently commercialized semiconductors such as CdTe and CIGS that are currently used in photovoltaic devices. However, sustainability and environmental issues threaten long-term viability of these materials. Based upon earth abundant constituents and low chemical toxicity, CZTS, with a reported band gap of ~1.5 eV, appears to be a superior alternative to these other materials. Additional research and development is necessary to increase the efficiency of CZTS-based cells from the current record (12.6% by Wang *et al.*[1]) to the >18% necessary to be considered commercially viable. Our work stresses the controllable, cost-effective, and reproducible synthesis of high-quality CZTS nanoparticles and sintered thin films. Specifically, our goal is to demonstrate increased crystal grain growth in CZTS needed for higher efficiency rates of CZTS-based cells. Incorporating alkali dopants, specifically sodium, has been successful in enhancing grain growth in CZTS thin films [2]. However, current methods of sodium doping primarily rely on imprecise external diffusive sources such as sodium halides, sodium hydroxides, or the use of soda lime glass. Based off of work by Tiong *et al*., who experimented with controllably doping sodium into CZTS films via dipping in sodium halide solutions [3], we show further results of attempting to control sodium composition by coating the surface of CZTS nanoparticles with a controlled amount of sodium hydroxide – our group has also shown that the introduction of an oxide to the surface of CZTS nanoparticles can also enhance uniform grain growth. The coated particles are then dispersed into a CZTS nanoparticle ink, coated onto a sodium-free substrate, mechanically compacted, and annealed at 600 ºC for 1 hour in a low pressure sulfur atmosphere. The resulting material is extensively characterized to determine morphology, composition, and structure.

[1] Wang, Wei, Mark T. Winkler, *et al*. "Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency." Advanced Energy Materials 4, no. 7 (2014).

[2] Johnson, M., S. V. Baryshev, *et al*. "Alkali-Metal-Enhanced Grain Growth in Cu2ZnSnS4 Thin Films." Energy & Environmental Science 7, no. 6 (2014): 1931-38.

[3] V. Tiong, T. Hreid, *et al*. "Morphology evolution and stability of Cu_2ZnSnS_4 nanocrystals in sodium halide salt solution." Thin Solid Films, Vol. 615 (2015).

CP-3 Development of Dual Coating Process for Effective Combination of Sand Mold Process and 3D Printing Technique, ***Hyun-Hee Choi,*** *H Park, E Tumenbayar, G Cho, E Kim, Y Jung,* Changwon National University, Republic of Korea*; J Zhang,* Purdue University, USA

In a conventional sand casting, the mold is prepared by mixing silica-based starting powders with resin-based organic binders. Therefore, the mold collapses easily by the degradation of the organic binders during casting. Nevertheless, the sand mold has been widely used in the manufacturing industry due to its simplicity and low production cost. In this work, a dual coating process is developed to combine the sand mold process and 3D printing technique. Two types of polyvinyl alcohol (PVA) with the different boiling points were applied. In the dual coating process, the starting powder was coated with PVA with the lower boiling point, and then re-coated with PVA with the higher boiling point, followed by 3D printing process. The sample was heat-treated at 250C for 4h in order to burn out the PVA with the lower boiling point. The heat-treated sample was dipped into an inorganic binder slurry, composed of tetraethyl orthosilicate (TEOS) and sodium methoxide (NaOMe), which are the silica (SiO_2) and sodium oxide (Na_2O) precursors, respectively. After dried at 80C for 1h, the final heat-treatment was conducted at 1000C for 1h for organic-inorganic conversion. The green and firing strengths were much enhanced compared with the conventional converting process, which are due to the increased amount of inorganic precursor causing a sol-gel reaction for the green strength, and the glass phase converted by the inorganic precursor filled in the spaces of the evaporated PVA and coated on the surfaces of particles for the firing strength. Relationship between the coating process and the strength was extensively discussed, including applicability of dual coating process into 3D printing technique.

CP-4 New Converting Process for Fabrication of Ceramic Core through 3D Printing Technique, ***Hye-Yeong Park,*** *H Choi, E Tumenbayar, G Cho, E Kim, Y Jung,* Changwon National University, Republic of Korea*; J Zhang,* Purdue University, USA

In a conventional converting process, the core green body prepared with starting powder and organic binder, generally called as resin, is directly dipped in the inorganic binder precursor. However, the process reduces the content of inorganic precursor by the organic binder filled on the interface between the starting particles, resulting in reduced mechanical properties of the core. In this work, a new converting process combined with 3D printing technique has been developed to fabricate core samples. The new process allows to provide sufficient amount of inorganic binder on the particle surface and at the interface between particles. Two types of poly vinyl alcohol (PVA), which have the same molecular structure with a large difference in the boiling point, were used as an organic binder. Green body with the two kinds of PVA was 3D printed, and then heat-treated at 250℃ to evaporate the PVA with the lower boiling point. The heat-treated core samples were dipped into the inorganic precursor, and dried and heat-treated at 1000℃ for organic-inorganic converting process. T his series of new processes could enhance the fracture strength of core owing to the increase of the inorganic precursor infiltrated in spaces/sites of the evaporated PVA. In the new converting process, the formability of core sample was induced through the organic compounds remained and inorganic binder penetrated between particles and/or coated on the particle surfaces, and the firing strength is attributed from the glass phase generated by the inorganic precursor. Therefore, the formability and firing strength of core prepared through the new process were favorably improved. This means it would be readily applied to the production of core using 3D printing techniques, without further shrinkage in heat treatment at high temperature.

CP-7 Bias-photo Stability of Hafnium-aluminum-zinc-oxide Thin Film Transistors, ***Ju-Hee Park,*** *S Lee, H Jun, J Park,* Hanyang University, Republic of Korea

Amorphous oxide semiconductors (AOSs) have demonstrated their advantages as applications for flat panel displays (FPDs) due to their electrical performance, transparency in visible light, and room-temperature deposition. Oxygen vacancies in AOS materials play the role of generating carriers and thus provide a conducting path and at the same time, they are components that may deteriorate the stability of the AOS-based thin film

transistors (AOS-TFTs) by forming defects. To improve the stability of AOS-TFTS, the oxygen vacancies have to be reduced. Recently, a number of studies regarding the incorporation of materials with a low standard electrode potential (SEP) into AOS materials, such as yttrium (Y), hafnium (Hf), and zirconium (Zr), have been reported. Particularly, Hf has a lower SEP (- 1.56 eV) than that of Zn (- 0.76 eV) and HfO_2 has a larger bandgap (5.8 eV) than that of ZnO (3.3 eV). Thus, the addition of Hf to the indium-zinc-oxide (IZO) system is expected to control the electrical characteristics of the films and improve the stability of TFTs by controlling oxygen vacancies. Recently, K. Ghaffarzadeh et. al. introduced TFTs using hafnium-indium-zinc-oxide (HIZO) as an active layer. They showed that the stability of the HIZO TFTs due to bias-stress and photo-stress was improved as a result of the reduced interface charge trapping. However, when Hf is used in TFTs, it may decrease the channel mobility due to the reduction of carrier concentration, leading to the significant decrease of the on-current. Furthermore, the In element used in the HIZO TFTs is an earth-rare material. For this reason, some studies without using In in AOS-TFTs have recently been reported to aim at maintaining high channel mobility.

In this study, we have fabricated a TFT using the channel layer with a hafnium-aluminum-zinc-oxide (HAZO) thin film in order to enhance the device performance and stability. The HAZO films were deposited on SiO_2/Si substrates at room-temperature via co-sputtering where separate targets of hafnium-oxide and aluminum-zinc-oxide were used. The structural, optical, and electrical characteristics of HAZO films were evaluated using various methods, such as X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), UV/visible spectrophotometer, Hall measurements, and I-V characteristics analyzer. The electrical characteristics of the HAZO-TFTs as well as the stability of the devices due to bias-photo stress were also analyzed as functions of Hf and Al contents.

CP-11 Electrical and Magnetic Properties of (Al, Co) co-doped ZnO Films Deposited by RF Magnetron Sputtering, ***Yu-Wei Lin**, S Chen,* Ming Chi University of Technology, Taiwan*; H Sun,* Ocean University of China, China*; C Wang,* Ming Chi University of Technology, Taiwan*; C Wen, T Chuang,* National Taiwan University, Taiwan*; X Wang,* Ocean University of China, China

In this work, (Al, Co)-ZnO films were co-sputtered on glass substrate through radio frequency sputtering at 100 °C. The film's structure, electrical and magnetic properties as a function of Al doping content is investigated. The results indicate that (Al, Co)-ZnO films crystallinity can be suppressed by Co doping or (Co, Al) co-doping. With the substitution of Zn by Al , the film's conductivity improves. All the films present ferromagnetic behavior at room temperature. With increasing Al doping amount, the film's saturation magnetization expresses a carrier-concentration dependent behavior. Three different regions can be defined, where BMP model and carrier-mediated exchange mechanisms play a role in the various regions.

CP-13 Development of Low Temperature TiO_2 Mesoporous Scaffold for Perovskite Solar Cells, ***Gwomei Wu,*** Chang Gung University, Taiwan

Perovskite solar cells have become attractive candidates for modern thin-film photovoltaic devices due to their high performance and promising cost-competitiveness. The prevailing fabrication methods involve spin-coated materials and vapor-deposited thin films. They are much less expensive than the high-vacuum deposition equipments used in the semiconductor industry. The organic-inorganic hybrid solar cells combine a mesoporous scaffold, a perovskite light absorber and an organic hole transporter. However, it requires a high annealing temperature up to 500℃ to sinter the mesoporous layer. Thus, it is interesting to develop lower temperature processing schemes by different chemical sources for the solution spin-coating techniques. The different film-forming characteristics should be investigated. In this report, TiO2 nanoparticles could be coated from a binder-free colloid to form the mesoporous scaffold with low processing temperature. The different chemical formulations were prepared for solution-processed spin-coatings on glass substrates. The low temperature processed multi-layered photovoltaic structures were examined and presented in this study. This work was supported in part by the Ministry of Science and Technology under research grants MOST105-2221-E182-059-MY3 and NERPD2E0481.

CP-15 Atmospheric Plasma Deposition of Oxide Semiconductors, ***Blake Emad,*** University of Dayton, USA*; J Ferguson,* Materials and Manufacturing Directorate, Air Force Research Laboratory, USA*; C Muratore,* University of Dayton, USA

Atomic layer deposition (ALD) is unsurpassed as a technique for application of uniform, conformal, and continuous thin films on a broad range of useful substrates, especially those with ultra-high aspect ratios or complex morphologies, as the precursors are in the gas phase and easily fill all spaces with characteristic lengths greater than 0.5 nm. Three principal shortcomings of conventional ALD include: (1) reliance on vacuum pumps to reduce the pressure in the growth chamber and pull gas in resulting in long individual half cycle times—many of which are required to apply films of appreciable thickness (~50 nm), (2) contamination from precursor gas reactions that only proceed to a fraction of total completion, and (3) challenges (high temperature, high vacuum, containment within vacuum reaction vessel, etc.) associated with integration into additive manufacturing which could lead to custom components with integrated antennas and other device functionality especially in components employing conformal nature of the ALD coatings. Novel atmospheric plasma-based processes for synthesis of semiconducting oxides such as ZnO, GaO, IGZO (indium gallium zinc oxide) are presented. Techniques include a rapid ALD process where gas is cycled thru microvolumes adjacent to the substrate, rather than filing and vacating an entire processing chamber with the necessary series of vapor phase precursors to increase the effective growth rate of materials substantially. The precursors are selected so gaseous byproducts after ALD film formation are safe for exposure to open air. Results from optical spectroscopy of the atmospheric plasma processes is presented to demonstrate relationships between process characteristics and the structure and composition of the materials. For example, the degree of ZnO crystallization will play a critical role in its transport properties, and will therefore be thoroughly characterized using Raman spectroscopy and X-ray diffraction. The composition will first be measured with XPS, which has a resolution of approximately 1 atomic percent. Once contaminants are below this level, property measurements will be most useful for understanding atomistic-scale defects such as impurity atoms or vacancies. Nanocrystalline ZnO grown via pulsed laser deposition is a semiconductor material reported to possess high charge mobility (>100 $cm^2\ V^{-1}\ s^{-1}$), an extremely high on/off ratio (>10^{12}), and be useful for high frequency (500 MHz) device operation. These parameters set the baseline for our comparisons of atmospheric pressure plasma enhanced ALD, where the aim is to match or surpass these values of mobility, on/off ratio, and maximum operating frequency.

CP-18 Structural and Magnetic Properties of Perovskite $SrMnO_3$ Thin Films Grown by Molecular Beam Epitaxy, ***Jiawei Bai,*** East China Normal University, China

In this work, we report the structural and magnetic properties of the ~30 nm epitaxial (001) $SrMnO_3$ thin films grown on (001) $SrTiO_3$ substrate by molecular beam epitaxy (MBE). In situ reflection high energy electron diffraction (RHEED) intensity oscillation is used to precisely adjust the stoichiometry by tuning the shuttered time during the growth. The structural properties of the $SrMnO_3$ thin film is characterized by atomic force microscopy (AFM), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The surface of the thin film with obvious steps is observed to be atomically flat. The epitaxial single crystal $SrMnO_3$ thin film which is grown along the direction of (001) STO substrate is typical cubic crystal structure. The film is confirmed to be four-fold symmetric along the <001> azimuth by X-ray diffraction ϕ scan. The XRD reciprocal space map indicates that the $SrMnO_3$ thin film is fully strained in the present thickness. Due to the tension strain, the $SrMnO_3$ film exhibits ferromagnetic behavior while the bulk $SrMnO_3$ is antiferromagnetic at the same low temperature.

CP-19 Yb-doped Zinc-Tin-Oxide Thin Film and its Application to Solar Cell, ***Youngsang Park**, W Kim,* Yeungnam University, Republic of Korea*; G Ferblantier, A Slaoui, A Dinia,* CNRS-Université de Strasbourg, France*; H Jung, S Alhammadi, S Kwon,* Yeungnam University, Republic of Korea

The use of rare earth elements with semiconductor materials has attracted a lot of interest due to its unique properties. In this paper, we investigated ytterbium(Yb)-doped zinc tin oxide (Yb:ZTO) thin film characteristics and its application to a potential down-converter of Cu(InGa)Se2 (CIGS) thin-film solar cells. Yb:ZTO thin films were deposited by reactive sputtering of Zn and Sn metal with an oxygen flow. A few pieces of Yb were embeded in Zn metal target and thus Yb elements were supplied during Zn sputtering process. The relatively composition of Zn and Sn was controlled by changing the sputtering power(10-70W) of Sn with the fixed sputtering power for Zn(70W). Also, the substrate temperature varied from room

temperature to 400 degC. It was confirmed that smaller amount of Sn with lower sputtering power led to more incorporation of Yb into ZTO. The X-ray photoelectron spectroscopy analysis confirmed that incorporation of Yb in ZTO, and photoluminescence measurement demonstrated Yb emission. The glazing incidence X-ray diffraction showed the shift of ZTO peaks induced by the difference in composition of Zn and Sn. Finally, CIGS solar cells with a Yb:ZTO layer have been fabricated. The results suggested that cells with the highest Yb PL emission showed the highest short circuit current density and cell efficiency.

CP-20 Mo-patterning on Graphene-coated Glass Substrate for a Bifacial Cu(InGa)Se2 Thin Film Solar Cell, ***Dohyun Park***, *W Kim,* Yeungnam University, Republic of Korea

The Molybdenum (Mo) has been used as a back-contact electrode for high-performance chalcopyrite Cu(InGa)Se2 (CIGS)-based thin film solar cells, which were recently reported to have the world-record cell efficiency of 22.7 % (ZSW, 2016). The substrate-type typical CIGS cell structure is glass/Mo/CIGS/CdS/ZnO. In this paper, to investigate the feasibility of CIGS cell for the application to bifacial solar cells, Mo layer has been patterned and a few layers of transparent conducting graphene were inserted to glass/Mo interface yielding glass/graphene/Mo(patterned) substrate. The graphene sheets grown on Cu foil by chemical vapor deposition were transferred to glass substrates by a simple wet-based graphene transfer process. Then, Mo was deposited onto glass/graphene by DC sputtering. The diverse design of Mo patterning for light transparency was achieved by using custom-designed masks during Mo deposition. It was confirmed that glass/graphene/Mo thin films showed lower sheet resistance than glass/Mo samples, and the sheet resistance was monotonically decreased with the number of graphene layers inserted. The resulting CIGS device results will be also discussed.

CP-21 Enhanced Stability of Plasmonic Metal-dielectric Thin Films by CVD Grown Graphene Transfer, *T Del Rosso, Q Zaman, E Cardona Romani, F Lazaro Freire Jr., O Pandoli, R Queiroz Aucélio,* ***Marco Cremona***, Pontifícia Universidade Católica do Rio de Janeiro, Brazil

The major problem to practical application of plasmonic devices is the chemically instability of the metal-dielectric interfaces which easily oxidize and degrade influencing the performances of the thin film plasmonic substrates [1]. Here we use angle interrogation scheme of Surface Plasmon Resonance spectroscopy to study the stability of plasmonic devices constituted by metal-dielectric thin films covered with graphene grown by CVD on copper foil [2]. The gold (Au) and silver (Ag) thin films deposited on glass slides functionalized with (3-ercaptopropyl) trimethoxysilane were monitored by AFM measurements up to 24 hours, in order to observe the morphological changes of the metal surfaces during the interaction with atmosphere.

Taking advantage of the high impermeability property of graphene to gases and liquids [3], we demonstrate that a graphene on metals substrates can be used to prevent it from chemical reactions and degradation of the adhesion of the metal deposition over the glass substrates. Raman spectroscopy has been used to verify the existence and quality of graphene after transfer process over gold and silver thin films.

The stability measurements where performed in atmosphere, and are based on the monitoring of SPR angle and full width half maximum (FWHM) during time.

Our results demonstrate that graphene protected gold (Au) and silver (Ag) depositions exhibit greater stability as compared to unprotected samples (exposed to air), similar to the one associated to samples protected by typical OLEDs encapsulation technique [4]. We observed a shift in the SPR angle of about 0.005^0 for Ag /graphene and Au/graphene samples after 4 hours of observation. Such a change is comparable to the zero angle determination and limits the time interval useful for the characterization of thin films in air. Similar results were obtained for graphene covered dielectric loaded waveguides (DLWGs).

The presented stability enhancement is very important both for the graphene optical characterization [5] as well as to the use of graphene in biosensing application [6].

1. V. G. Kravets, R. Jalil, Y.-J. Kim et al., Scientific Reports, 4 (2014) 05517.

2. X. Li, L. Colombo, R. S. Ruoff, Adv. Mater. 28 (2016) 6264.

3. Y. Su, V.G. Kravets, S.L. Wong, J. Waters, A.K. Geim, Nature communication 5 (2014) 4843.

4. T. Del Rosso, J. E. H. Sanchez, R. Dos Santos Carvalho, O. Pandoli, M. Cremona, Optics Express 22 (2014) 18915.

5. H. Jussila, H. Yang, N. Granqvist, Z. Sun, Optica 3 (2) (2016) 151–158.

6. O. Salihoglu, S. Balci, C. Kocabas, Appl.Phys. Lett. 100 (2012) 213110.

CP-23 Optical Characterization and Structural of ZnO Thin Film Prepared by Reactive Electron Beam Evaporation with Ion-Assisted Deposition from Metal Zinc, ***Hung-Pin Chen***, *W Cho,* Instrument Technology Research Center, National Applied Research Laboratories, Taiwan*; C Lee,* National Central University, Taiwan*; Y Lin,* National Tsing Hua University, Taiwan*; C Hsiao,* Instrument Technology Research Center, National Applied Research Laboratories, Taiwan

Zinc oxide thin films were fabricated by reactive electron beam evaporation with ion assisted deposition using metal zinc as a starting material. The transmittance spectra were measured by a UV/VIS/NIR spectrometer and the optical constants of the Zinc oxide films were calculated from the transmittance spectra using envelope method. The refractive indices were close to bulk value of 2 and the extinction coefficients were lower than $1x10^{-3}$ in the visible light ranges when the substrate temperatures exceeded 200°C. After annealing at 600°C for 2 hours in air, the extinction coefficients of Zinc oxide films prepared at room temperature increased as the annealing temperature increased, especially in short wavelength region. The ZnO films prepared at high temperatures exceeding 200°C were polycrystalline and had a preferred orientation of (100).

CP-24 Opto-electrical Properties of Few-layer $ReSe_2$ FETS for Phototransistors, ***DongJin Lee***, *M Yoo, N Kim, G Cho, P Ko,* Chosun University, Republic of Korea

The two-dimensional (2D) materials, including graphene, h-BN, layered transition metal–chalcogenides (TMC) and layered transition metal-dichalcogenides (TMDCs), are the next generation of the opto-electronic devices. Ultra-thin devices based on the 2D materials still under development, and many of the 2D materials remained almost unexplored field. Recently, there have been reports on photodetectors based on multilayered 2D materials such as GaSe, $MoSe_2$, WSe_2 et al. In this research, we fabricated field-effect transistor (FET) based on few–layered $ReSe_2$ on substrate (Ti / p–Si / SiO_2). The electrodes (Ti) deposited by electron-bean (EB) evaporation at room temperature on silicon substrates (doped p+, conductivity: 0.003 – 0.007 Ω cm) covered with 300 nm of thermally oxidized silicon dioxide (SiO_2). The thickness of the $ReSe_2$ flake was measured by atomic force microscopy (AFM) using a Pico plus 5500 AFM (Agilent Technologies, USA). The electrical characterization was carried out using Semiconductor Parameter Analyzer 4155-A (Hewlett Packard, USA). The layered $ReSe_2$ phototransistors were high values, underscoring that $ReSe_2$ is a promising 2D material for phototransistor applications. Acknowledgement: This work was supported by the Korea Institute of Energy Technology Evaluation and Planning(KETEP) and the Ministry of Trade, Industry & Energy(MOTIE) of the Republic of Korea (No. 20164010201020).

CP-28 UV Photosensitivity in Metal-Oxide-Semiconductor Structures based on SiO_x Films containing Si Nanoparticles, *M Curiel,* ***Oscar Perez***, *N Nedev,* Universidad Autónoma de Baja California, Mexico*; D Nesheva,* Institute of Solid State Physics, Mexico*; B Valdez,* Universidad Autónoma de Baja California, Mexico*; E Manolov,* Institute of Solid State Physics, Mexico*; A Arias, D Mateos,* Universidad Autónoma de Baja California, Mexico*; O Contreras,* Universidad Nacional Autonoma de Mexico, Mexico*; V Dzhurkov,* Institute of Solid State Physics, Mexico*; R Nedev,* Universidad Politecnica de Baja California, Mexico*; J Paz,* Universidad Autónoma de Baja California, Mexico

Metal-Oxide-Semiconductor (MOS) structures using SiO_x films as gate insulators are promising for application in different types of optoelectronic devices. In this work we present results for the effect of UV light on the electrical characteristics of MOS structures containing crystalline or amorphous Si nanoparticles in the gate insulator.

SiO_x films with thickness of ~50 nm and various compositions, x varies between 1.15-1.5, were deposited by thermal evaporation in vacuum on n-type crystalline Si. After the deposition the samples were annealed at temperatures in the 250 - 1000 °C range for 30, 60 and 120 min. High temperature annealing at T ≥ 700 °C leads to formation of amorphous and/or crystalline Si nanoparticles in SiO_x layers. The formation of nanocrystals in the samples annealed at 1000 °C was verified by Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS). High resolution TEM images revealed that the nanocrystal size depends on the composition and the annealing time; for example, samples with x = 1.15 and 1.3 annealed at 1000 °C for 60 min exhibit nanocrystals with diameters of approximately 4 and 6 nm,

respectively. The XPS results showed that the annealing at 1000 ^{o}C leads to complete phase separation and formation of Si in SiO_2.

Lateral currents between two metal contacts on the top of the Si/SiO_x structure were measured in dark and under visible and UV light illumination. The dark and visible light I-V characteristics coincide, while the UV light leads to an increase of the current through the structure. The UV effect is more pronounced with the increase of the annealing temperature. The observed effect may be explained assuming UV light assisted transport between neighbor nanocrystals of electrons injected from the crystalline silicon wafer.

The obtained results indicate that the studied SiO_x layers have a potential for application in UV sensors.

CP-29 Photoresponse and Electrical Properties for Photodiodes from Graphene Oxide (GO)*, Asmaa Hendi,* King Abdulaziz University, Saudi Arabia

The nanocomposites of zinc oxide/graphene oxide (ZnO-GO) were synthesized to fabricate the photodiodes. The ZnO-GO/p-Si and ZnO-GO/n-Si diodes were prepared for various GO contents. The electrical characteristics of the ZnO-GO/p-Si and ZnO-GO/n-Si diodes were analyzed under dark and light illuminations. The photocurrent of ZnO-GO/p-Si and ZnO-GO/n-Si diodes increases with increasing GO content.

The ZnO-GO/p-Si diode having 0.03 M ratio of GO:ZnO exhibited the highest photoresponsivity with 0.5 A/W under 100 mW/cm2. It is evaluated that ZnO-GO composites can be used in fabrication of high photo sensitivity diodes.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Royal Palm 1-3 - Session C4
Energetic Materials and Microstructures for Nanomanufacturing

Moderators: Karsten Woll, Karlsruhe Institute of Technology (KIT), Ibrahim Gunduz, Purdue University, USA

8:00am **C4-1 Investigation of Dynamic Processes in Energetic Materials by Ultrafast Transmission Electron Microscopy at the Nanoscale**, ***Volkan Ortalan,*** Purdue University, USA **INVITED**

The ignition of exothermic chemical reaction in energetic materials has long been known to occur after locally heated regions of the material called "hot spots" are formed by various mechanical processes. Once formed, these hot spots either fail to react chemically due to thermal diffusion or react exothermically creating an ignition site. These ignition sites then grow in temperature, size, and pressure, rapidly consuming the energetic material. Despite of its significance, direct experimental evidence of such hot spots, however, is exceptionally limited; mechanisms for their generation are poorly understood and methods to control their locations remain elusive. A complete fundamental understanding of the mechanisms and dynamics of thermo-mechanical processes of energy localization at nanoscale, and the role of the microstructure in the complex energetic materials can only be obtained by directly observing their response to different stimuli at the relevant time and spatial scales. However, although the recent progresses in picosecond spectroscopy are promising, there is currently no single technique alone satisfying the required resolutions (spatial, temporal and energy) relevant to the energetic reaction events to visualize the dynamic processes occurring in energetic materials. However, recently developed ultrafast transmission electron microscopy (UTEM) opens up new possibilities for visualization of these complicated ultrafast processes.

The high time resolution of a UTEM is achieved by creating short electron pulses that are used to illuminate the specimen. A UV laser pulse stimulates photoemission of electrons from a photocathode. The resultant bunch of electrons is then accelerated and sent into the electron-optical column. It is then focused onto the specimen and magnified to produce the image. The response to be studied (chemical reactions in energetic materials, a phase transformation, shock propagation, structural change, chemical reaction, etc.) in the experiment is stimulated by a second laser pulse and the delay between the two laser pulses sets the timing of the observation. The realization of UTEM is a revolutionary step for the *in-situ* investigation of dynamic processes in materials with high spatiotemporal resolution and the capabilities of UTEM provide an ideal platform to probe dynamic phenomena through a combination of imaging, spectroscopy, and diffraction on their natural length and time scales. Here, the results of dynamic UTEM experiments performed on energetic materials, such as HMX and composite metal-organohalide materials (mixture of aluminum nanoparticles dispersed in a fluoropolymer oxidizer matrix), will be presented.

8:40am **C4-3 A Closer Look at Determining Flame Speeds w ith Imaging Diagnostics**, *R Bratton, M Pantoya,* ***Connor Woodruff,*** Texas Tech University, USA

A comparison of flame speed measurements of reacting powders utilizing various filtering and illumination techniques is presented. Reactive energetic composites are often highly luminescent and quantifying reaction propagation can often be difficult because of sensor saturation. To explore the influence of image saturation on flame speed measurements, experiments were designed using micron-sized aluminum (Al) and micron-sized molybdenum trioxide (MoO_3) mixtures and further studied with nano powders of Al +MoO_3. The micron powder mixtures were loaded into tubes at a constant bulk density of 43% of Theoretical Maximum Density (TMD), approximately an average sample mass of 1260mg. The nano powder mixture samples were loaded into tubes at a constant bulk density of 12.5% of TMD. These respective bulk densities were selected in order to maintain sample consistency and prevent density gradients. Regulating the mass and bulk density per sample is of great importance because of the significant effect of variance in bulk density in observed flame speeds. The flame speeds for each powder mixture were determined using a high speed camera and applying a series of neutral density filters to the camera's lens. This technique reduces the oversaturation effect on the camera and allows flame speed to be determined through better tracking of the reaction front. For ultimate oversaturation removal, use of a Copper Vapor Laser (CVL) and coupled 511 nm notch filter was employed to illuminate the reaction and filter the majority (i.e., >99.9%) of reaction illumination. This technique provides a perspective of the solid material and its transition from reactant to product without the interference of light emission from the reaction. The results show that the flame speeds measured through the filtering techniques were not affected by the various levels of filtration. This conclusion is evidenced by the greatest percent difference in average flame speeds in the micron powder mixtures was 15% and in the nano powder mixtures 4.2%. With this conclusion we can say that the filtration applied to the front of the camera for deflagration reactions will not impact the observed flame speed. Also with extreme filtering techniques such as a single bandwidth filter and single wavelength illumination, a more detailed view of thermite powder reaction can be observed. This advanced filtration technique can be used to analyze and characterize combustion phenomena.

9:00am **C4-4 Modeling and Experimental Study of Propagating Exothermic Reactions in Al/Pt Multilayers**, ***David Adams***, *M Abere,* Sandia National Laboratories, USA*; R Reeves,* Sandia National Laboratories, USA, US*; C Sobczak,* Sandia National Laboratories, USA

The propensity of sputter-deposited Al/Pt multilayers to undergo rapid, self-propagating formation reactions is evaluated across a broad range of stoichiometry (nAl:mPt) and layer periodicity. Experiments demonstrate self-propagating reactions in ~1.6 micron-thick Al/Pt multilayers when the molar ratio of reactants is in the range 4Al:1Pt to 1Al:4Pt. This rather large compositional range is characterized by different heats of reaction, reaction rates and reaction modes. High-speed photography shows that equimolar Al/Pt multilayers undergo the most rapid reactions with wavefront speeds as large as 80 m/s. Al- and Pt-rich multilayers react at reduced rates with speeds as low as 1 m/s. A previously developed, analytical method by Mann et al. (J. Appl. Phys. 1997) is utilized to reveal additional details of reactions in the various Al/Pt multilayers. Models that account for the reactant layer thicknesses, composition, the adiabatic temperatures, the flame temperatures, and the measured heats of reaction are used to predict wavefront speeds that closely match measured values. These results are further analyzed to extract information regarding the mass transport characteristics of reactant species.

9:20am **C4-5 Sub-critical Hotspots to Quench Reactions in Ni-Al Nanofoils**, *I Gunduz,* ***Matthew Beason,*** Purdue University, USA

Identification of intermediate reactions in reactive nickel aluminum nanofoils is challenging due to the rapid thermal front velocities up to 13 m/s and very thin reaction zones estimated to be on the order of 5-20 micrometers. We present a novel method to quench reactions at rates beyond 10^8 K/s, which are comparable to the self-heating rates in these foils. A thin aluminum wire is used to produce a microscale spark-heated spot on the surface of the foil with an energy below the self-propagation threshold. Upon the application of the spark that lasts approximately 50 ns, the reactions that are initiated are rapidly quenched due to the conductive heat losses to the rest of the foil and stop the conversion of intermediate species. SEM micrographs and TEM analysis using selected area diffraction show a transition zone of 3 micrometers, where amorphous Al solid solution, $NiAl_3$, Ni_2Al_3 and NiAl are sequentially formed at bilayer interfaces. The reactions appear to propagate faster along smoother bilayers compared to the kinked sections that form during the sputtering process, forming a fingered reaction front in the thickness direction starting from the ignited spot.

9:40am **C4-6 Laser Pulse Duration Dependence on Ignition of Al/Pt Reactive Multilayers**, ***Michael Abere***, *C Yarrington, D Adams,* Sandia National Laboratories, USA

Sputter deposited Al/Pt nano-laminates with bilayer thicknesses of 328 nm, 164 nm and 65 nm were ignited via laser irradiation resulting in rapid, self-propagating reactions. Laser ignition of these foils was characterized over eleven decades (10 ms to 150 fs) of pulse duration. For laser ignition with milli- and microsecond pulses, the go/no go threshold is equivalent to the laser intensity at which the heating time required for ignition equals the pulse duration. The heating time required for ignition at a given laser intensity was determined experimentally with high-speed photography and calculated with finite element simulations. Reducing the pulse duration to 150 fs leads to a breakdown of this Joule heating based mechanism as the ignition threshold becomes spot size invariant. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin

Corporation, for the US Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

10:00am **C4-7 Microstructural Evolution during Thermal Ignition of Self-Propagating Reactions in Ru/Al Multilayers***, **Karsten Woll,*** Karlsruhe Institute of Technology (KIT), (IAM-WBM), Germany*; C Pauly, F Muecklich,* Saarland University, Germany

The ignition of the self-propagating reaction represents one of the crucial processes for reactive materials. Whereas the characterization of reaction initiation often uses macroscopic parameters, such as ignition temperatures or ignition energies, the characterization lacks the knowledge about the underlying microstructural transitions, such as the phase transformations. We take this as motivation and analyze the ignition in sputter deposited Ru/Al multilayers. In greater detail, we thermally ignite free standing Ru/Al foils as well as samples on a substrate. In our experiments we use ignition temperatures and energies just below the ignition threshold. This approach enables us to arrest the reaction immediately after ignition. Eventually, we create characteristic microstructures that help us to infer the phase transformations and microstructural changes during thermal ignition. To analyze the microstructures after igntion we use the transmission electron microscope in combination with chemical analysis, such as atom probe tomography. Finally, based on the experimental observations we suggest a mechanism for thermal ignition in Ru/Al multilayers and deduce characteristics of the ignition process in reactive multilayers in general.

10:20am **C4-8 Waves of Crystallization in Amorphous Metallic Glass Films obtained by Spinning of Melts***, **Alexander Rogachev,*** National University of Science and Technology "MISIS", Russian Federation*; S Vadchenko, A Aronin,* Russian Academy of Sciences, Russian Federation*; A Mukasyan,* University of Notre Dame, USA

Metallic and semiconducting amorphous materials and films possess unique combination of properties that cannot be obtained in the crystalline materials, such as high mechanical strength, corrosion and radiative resistance, specific electrical and magnetic properties. It promotes applications of the amorphous films in contemporary industrial technologies and growing interest in scientific research of the amorphous structures formation and its transition into crystalline state. Despite of significant amount of scientific research, mechanisms and dynamics of amorphous-crystalline transition has not been studied adequately yet, especially, as related to self-propagating waves of crystallization. Propagating waves of crystallization in the vacuum-deposited films of Si, Ge, Sb and other metal or semiconductor material, have been studied for decades ("explosive crystallization") and found some prospective applications, e.g., as a new method of fine-grained polycrystalline silicon films production for solar cells. In this work, we report existence of the self-propagating waves of crystallization in the amorphous metal allows films produced by spinning of the melts. It is shown that self-propagating waves of amorphous-crystalline transformation can be initiated in the foils CuTi, $Fe_{84}B_{16}$, $Fe_{76}Si_{13}B_{11}$ and other compositions. Using thermal vision (up to 200 fps) and high-speed video (up to 20000 fps) cameras, we have measures propagating velocities, temperature-time profiles and other characteristics of the waves. Crystal structure and microstructure transformations have been studied. Characteristics of a new class of self-propagating thermal waves are compared with those of explosion crystallization in deposited films and reactive waves in multilayer bimetal nanofilms. Promising routes of utilization of this phenomenon for production sub-micron and nanocrystalline metal films are discussed.

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