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 $2\theta=56.64°$, 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.

Acknowledgements: This work was supported in part by a Grant-in-Aid for Scientific Research (No. 16H03869) from the Japan Society for the Promotion of Science.

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 (1st) attributed to the (0001) orientation and of about 66º (2nd) 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 2nd peak corresponding to the complex orientation decreased, whereas the 1st 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.

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