Plasma Science and Technology
Room: 305 - Session PS1+TF-ThM

Plasma Deposition and Plasma Assisted ALD
Moderator: Sumit Agarwal, Colorado School of Mines

8:00am **PS1+TF-ThM1 Sputtering Growth of High-Quality ZnO-based Semiconductors for Optoelectronic Applications**, ***Naho Itagaki***, Kyushu University, Japan **INVITED**

ZnO and its related semiconductors are remarkable multi-functional materials with a huge range of existing and emerging applications including transparent conducting oxides (TCO) and light emitting diodes (LED). In order to obtain physical properties required for such applications, control of the crystallinity (grain size, crystal axis alignment, crystal defects) is of great importance. We have recently developed a new fabrication method based on magnetron sputtering, "Impurity mediated crystallization (IMC)", where crystal nucleation and the growth are controlled by impurity atoms adsorbed on the film surface [1,2]. Here we demonstrate sputtering deposition of two kinds of ZnO films by utilizing buffer layers fabricated via IMC method. One is polycrystalline TCO films fabricated on glass substrates, and the other is single crystalline films on sapphire substrates for LED applications. Effects of impurity during the crystal growth of ZnO are studied by observing the evolution of film morphology by means of atomic force microscopy (AFM).

IMC-ZnO buffer layers have enabled fabrication of single-crystalline ZnO films even on large lattice-mismatched (18%) sapphire substrates by a conventional sputtering method. The ZnO films have atomically-flat surfaces with steps of 0.26nm-hight, corresponding to a half of c-axis length of ZnO. AFM observation of IMC-ZnO buffer layers revealed that impurity atoms inhibit the crystal growth and thus increase in the grain density, which reduce the strain energy caused by the large lattice mismatch between ZnO and sapphire. IMC-ZnO buffer layers have also improved the film quality of ZnO based TCO fabricated on glass substrates. The most remarkable effect is a reduction in the resistivity of the films thinner than 100 nm. The resistivity of ZnO:Al films fabricated by conventional sputtering increases substantially from 6.3×10^{-4} W×cm to 1.5×10^{-3} W×cm with decreasing the film thickness from 100 nm to 20 nm, while the resistivity of ZnO:Al films with IMC buffer layers is low of 2.8-3.2×10^{-4} W×cm in the thickness range 20-100 nm. The role of impurity here is to suppress the nucleation and allow the crystal growth with larger grains from the very early stage of deposition.

We believe that IMC method will not only accelerate the commercialization of ZnO in optoelectronic devices but also open up a new pathway for development of other oxide semiconductors, some examples of which including In_2O_3:Sn will be presented at the conference.

This work was partially supported by JSPS (25630127), JST-PRESTO, and AOARD.

[1] N. Itagaki, et al., Appl. Phys. Express 4 (2011) 011101. [2] K. Kuwahara, et al., Thin Solid Films 520 (2012) 4507.

8:40am **PS1+TF-ThM3 Novel Composite Materials Fabricated by Plasma-enhanced CVD of Carboranes and Pyridine or Benzene**, ***Robinson James***, *U. Chiluwal*, University of North Texas, *E. Echeverria*, University of Nebraska-Lincoln, *R. Gapfizi, J. Tae*, University of North Texas, *P.A. Dowben*, University of Nebraska-Lincoln, *J.A. Kelber*, University of North Texas

Altering the electronic structure of carborane-derived boron carbides by incorporating aromatic compounds is of scientific and technological interest in neutron detection and microelectronics. The fabrication of novel composite materials derived from ortho-carborane or meta-carborane with benzene or pyridine by plasma enhanced chemical vapor deposition (PECVD) at room temperature may lead to improved device performance over conventional boron carbides. The chemical composition and electronic structure of the resulting films were studied using in-situ x-ray and ultraviolet photoelectron spectroscopy (XPS, UPS) respectively. XPS of composite films of carboranes with pyridine shows the evidence of B-N bond formation during the PECVD process. Pyridine incorporation in the boron carbide materials resulted in the improved adhesion of physical vapor deposited Cu (PVD Cu) overlayers on the surface. XPS indicates that no thermal induced diffusion/dewetting of Cu was observed in the ortho-carborane and pyridine composite films even after annealing up to 1000K in UHV. In contrast, pure boron carbide films exhibited poor adhesion of Cu overlayers on the surface resulted in the significant dewetting during 400-600 K annealing although no diffusion of Cu was observed even after annealing up to 1000 K. Composite films of ortho-carborane or meta-carborane with benzene were also grown on Si substrates by PECVD. These carborane: benzene composite films exhibit augmented B-C bond formation due to linking of benzene with the icosahedral carborane units as evidenced by XPS.

9:00am **PS1+TF-ThM4 Engineering High-k Dielectric Gate Stacks using *In Situ* Spectroscopic Ellipsometry**, ***Yuanxia Zheng***, Penn State University, *G.B. Rayner*, Kurt J. Lesker Company, *A. Agrawal, S. Datta, R. Engel-Herbert*, Penn State University

The development of Ge-based field effect devices requires the integration of a high quality dielectric that forms an electrically well behaved semiconductor dielectric interface. Although GeO_2/Ge has been found promising, the thermodynamic instability as well as the relatively low dielectric constant of GeO_2 requires an alternative approach. The utilization of an ultrathin Si layer to move the semiconductor/dielectric interface from Ge into Si has been successfully demonstrated; however, the introduction of a planar thin layer into the gate stack is incompatible with a 3D FinFET manufacturing process flow. It is thus desirable to develop a multilayer gate stack by atomic layer deposition process, where an ultrathin GeO_2 layer can be thermodynamically stabilized and combined with a high-k dielectric film to meet the stringent requirement of low interface trap density and large capacitance density while maintaining a low gate leakage.

In this talk, we will present an approach of developing a multilayer gate-stack of $HfO_2/Al_2O_3/GeO_2$ for Ge using in-situ processing control in plasma-enhanced atomic layer deposition (PEALD) by utilizing real-time monitoring capabilities of in-situ spectroscopic ellipsometry (SE). Pristine Ge-surface is obtained by removing native GeO_x using H-plasma and an ultrathin GeO_2 layer is grown thereafter by O-plasma anneal; in-situ SE is used to monitor the process and to control GeO_2 thickness. An ultrathin bilayer of alumina and hafnia is subsequently grown using thermal ALD and large capacitance densities with equivalent oxide thicknesses (EOT) below 1 nm and gate leakages below 1×10^{-4}A/cm^2 at -1V (EOT=0.7 nm) are demonstrated. The impact of the thickness of the individual dielectric layers on interface trap density, determined by the conductance and the Terman method, leakage current and EOT is discussed. We will further discuss how in-situ SE is used to optimize process-relevant parameters for native oxide etching, intentional oxidation and deposition of high-k dielectrics. The potential of this in-situ real-time process metrology is projected for the development of high quality high-k dielectrics on other high mobility low band gap semiconductor materials.

9:20am **PS1+TF-ThM5 Impact of Low Frequency Addition to RF Power in PECVD Process: Case of TiN and GeTe**, ***Christophe Vallee***, *F. Piallat, M. Aoukar, P.D. Szkutnik*, LTM - CEA/LETI, France, *R. Gassillloud, P. Noé, P. Michallon*, CEA, LETI, MINATEC Campus, France

In Dual Frequency plasma etching, one frequency is chosen to be much higher than the other in order to achieve an independent control of ion bombardment and electron density (i.e. ion flux). It is assumed that high frequency control the density and low frequency (LF) the energy. Recently, many groups have simulated the effect of LF addition to RF source. Depending on the model, it has been reported that the plasma density may be reduced due to sheath width variation as well as it may be increased due to highly energetic secondary electrons. Donko *et al* have shown how the γ coefficient of the secondary electrons may be used to interpret contradictory published papers [1] and they concluded that there is only a small pressure process window for which the effect of secondary electrons on the ionization compensates the effect of the frequency coupling.

The interest of adding LF to RF plasma in order to enhance the deposition reaction mechanisms is demonstrated here. An in depth investigation of plasma by Optical Emission Spectroscopy shows that the plasma density increases when adding LF (350 Khz) in a RF (13.56 Mhz) metal deposition process. In this case, the plasma enters a γ-mode due to secondary electron heating. This mode is not obtained when depositing semiconductors (GeTe) or dielectric, i.e. depending on the biased nature of the surface of showerhead electrode during the process. Adding LF to RF also modifies the sheath thickness of the plasma and increases the electron temperature of the gas [2]. In our experiments, all the deposited materials show different properties and new emission peaks are observed by OES for all precursors. Carbon content, density and growth rate are strongly modified by adding LF. For example, in case of TiN we found that the deposition rate is increased by a factor of two while in the same time the resistiviy is strongly reduced (50%) and the density is going from 3.4 to 3.8 g.cm^{-3}[3]. We also studied the plasma impact on the Equivalent Oxide Thickness (OET) regrowth of a TiN/HfO_2 integrated MOS capacitors. For phase change material (PCM) applications, very different cycles (amorphous to crystalline) are observed for devices with RF GeTe or LF+RF GeTe. All the

deposition processes are performed in 200 (GeTe) and 300 mm (TiN) pulsed liquid injection PEMOCVD chambers from AltaCVD Advanced Materials^{TM}, located in CEA-LETI cleanroom.

[1] Z. Donkó, *et al*, Appl. Phys. Lett. **97** (2010) 081501

[2] W-J Huang *et al*, Phys. Plasmas **16** (2009) 043509

[3] F. Piallat *et al*, *J. Phys. D: Appl. Phys.***47** (2014) 185201

11:00am **PS1+TF-ThM10 Surface Reactions during Ammonia-Plasma-Assisted Atomic Layer Deposition of Silicon Nitride**, ***Dennis Hausmann***, Lam Research Corporation, *R. Ovanesyan, S. Agarwal*, Colorado School of Mines

The advent of FinFETs with high-aspect-ratio 3-D geometries increases demands on conformality of the SiN_x films. These stringent requirements on conformality and low thermal budget can be simultaneously met using atomic layer deposition (ALD). While there are a few reports in the literature that show that SiN_x can be conformally deposited via ALD at <400 °C, these films are not sufficiently dense to serve as moisture or oxidation barriers. Hence, improvements in this area are needed via a fundamental understanding of the surface reaction processes. Recently, we have developed a novel ALD processes for the growth of Si_3N_4 thin films using trisilylamine ($Si(NH_3)_3$, TSA) and silane precursors, and an NH_3 plasma. This ALD process with TSA provides dense films with a conformal coverage over aspect ratios typical for the applications; 10:1. To understand the underlying film growth mechanism, the specific surface reactions involved during each half-reaction cycle of this ALD process were monitored with *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. ZnSe internal reflection crystals were used as substrates since ZnSe is transparent in the infrared up to 700 cm^{-1}. This spectral range, combined with the high sensitivity achieved with ATR-FTIR spectroscopy, allows us to identify and monitor in real time the different surface species generated and consumed due to sequential exposure of the growth surface to Si-containing precursors and an NH_3 plasma. The vibrational modes that were monitored include the surface SiH_x and NH_x stretching modes in the 2100 and 3400 cm^{-1} region, respectively, and Si_3N_4 phonon modes, which appear in the 800-900 cm^{-1} region. The corresponding surface reaction products were monitored using quadrupole mass spectrometry. Further, these films were extensively characterized using a suite of *ex situ* diagnostic tools.

11:20am **PS1+TF-ThM11 Plasma Assisted Atomic Layer Epitaxy of III-N Ternaries for Next Generation Devices**, ***Neeraj Nepal***, *J.K. Hite, V.R. Anderson, V.D. Wheeler, S. Qadri, C.R. Eddy*, Naval Research Laboratory

III-Ns (InN GaN and AlN) and their alloys have been attractive semiconductor materials for application in a wide range of device technologies. The most common growth methods of this material system are CVD and MBE, but these conventional growth techniques have challenges in achieving alloys without phase separation over the entire stoichiometric range, ultimate thickness control at the atomic level, and the ability for *in situ* growth of complete device structures. Plasma-assisted atomic layer epitaxy (PA-ALE) is a promising method to grow III-N alloys and incorporate them into device structures as it allows low temperature growth and precise control of thickness, stoichiometry and uniformity. Recently, PA-ALE has been used for the growth of III-N binaries at low temperatures (≤500°C)[1,2]. Ternary growth at these low temperatures could eliminate miscibility gaps, which has been an issue for conventional growth methods.

We present the growth and characterization of III-nitride ternaries by PA-ALE over a wide stoichiometric range including the range where phase separation has been an issue for MBE and CVD. Using our previously reported optimal growth conditions for GaN, InN [1], and AlN [2], $Al_xGa_{1-x}N$, $In_xAl_{1-x}N$ and $In_xGa_{1-x}N$ ($0 \leq x \leq 1$) alloys were grown at 250–500 °C. Group III-B metal contents in these alloys were varied with binary cycle ratios and the alloy compositions were determined by XPS and XRD and reflectivity measurements. Since the growth rate (GR) of InN is slower than that of AlN, a digital alloy produced from 3 cycles of InN for every cycle of AlN results in an $Al_{0.83}In_{0.17}N$ film. The GaN GR, however, is slower than InN, and $In_{0.54}Ga_{0.46}N$ alloy was grown for every alternating cycle of GaN and InN. Additionally, 4 cycles of GaN for every cycle of AlN gave $Al_{0.5}Ga_{0.5}N$ alloy and the measured concentration was confirmed optically. By this digital alloy growth method, we are able to grow In containing ternaries by PA-ALE in the spinodal decomposition region (15-85%). The surface roughness of III-N alloys on GaN were the same as the starting roughness of 0.4 nm. Optimal ternary growth conditions were used to synthesize III-N based device structures on GaN and demonstrated 2DEG at the interface. We will present electrical and optical data on ALE III-N heterojunctions on GaN templates.

These early efforts suggest great promise of PA-ALE for addressing miscibility gaps issue encountered with conventional growth methods and realizing high performance optoelectronic and electronics devices involving ternary/binary heterojunctions, which are not currently possible.

[1] N. Nepal et al., JCGS **13,**1485 (2013).

[2] N. Nepal et al., APL **103**, **0**82110 (2013).

11:40am **PS1+TF-ThM12 Plasma-enhanced Atomic Layer Deposition: Prospects and Challenges**, ***Hyungjun Kim***, Yonsei University, Korea **INVITED**

Due to various benefits such as atomic level thickness control and excellent conformality, atomic layer deposition (ALD) is expected to play an important role in future device fabrication. Especially, plasma enhanced ALD (PE-ALD) allows deposition at significantly lower temperatures with better film properties than conventional thermal ALD. This low temperature process makes PE-ALD more attractive for emerging nanoscale device fabrication. In addition, since ALD is surface-sensitive deposition technique, surface modification by plasma exposure can be used to alter nucleation and adhesion. In this presentation, the basic characteristics and several examples of PE-ALD processes for various applications such as semiconductor/display devices fabrication will be presented. The PE-ALD is a valuable tool to deposit very thin metal layers with good properties including little nucleation delay and high purity. Co, Ni, Ru films with good conformality was deposited by PE-ALD using NH3 plasma. Film properties as well as applications for emerging electronic devices of the metal PE-ALD will be discussed. Also, the use of plasma for ALD enables improvements in electrical properties of next generation semiconductor devices. Various high k oxides including HfO2, CeO2, La2O3 and doped high k oxides were deposited by PE-ALD from metal organic precursors and oxygen plasma. Especially, comparative study between PE-ALD and thermal ALD has shown that the interface defect density and leakage current are better for PE-ALD. Also, PE-ALD of ZnO thin films was investigated for thin film transistors. We studied the modulation of device parameters of PE-ALD ZnO based TFTs using UV light exposure. Finally, PE-ALD TiO2 thin films have shown high photocatalytic effects on various substrates. These indicate that the PE-ALD processes are versatile methods enabling nano scale manufacturing in emerging applications.

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