## Atomic Scale Processing Focus Topic
## Room B130 - Session AP+BI+PS+TF-WeM

### Surface Reaction Analysis and Emerging Applications of Atomic Scale Processing

**Moderator:** Eric A. Joseph, IBM Research Division, T.J. Watson Research Center

8:00am **AP+BI+PS+TF-WeM-1 Open Spaces in $Al_2O_3$ Film Deposited on Widegap Semiconductors Probed by Monoenergetic Positron Beams***, **Akira Uedono**,* University of Tsukuba, Japan*; T Nabatame,* NIMS, Japan*; W Egger, T Koschine,* Universität der Bundeswehr München, Germany*; C Hugenschmidt, M Dickmann,* Technische Universität München, Germany*; M Sumiya,* NIMS, Japan*; S Ishibashi,* AIST, Japan **INVITED**

Positron annihilation is a useful technique for characterizing vacancy-type defects in semiconductors, and it has been successfully used to detect defects in GaN. This technique is also useful for detecting open spaces in thin amorphous films deposited on semiconductor substrates. When a positron is implanted into condensed matter, it annihilates with an electron and emits two 511-keV gamma quanta. The energy distribution of the annihilation gamma rays is broadened by the momentum component of the annihilating electron-positron pair. A freely diffusing positron may be localized in a vacancy-type defect because of Coulomb repulsion from positively charged ion cores. Because the momentum distribution of the electrons in such defects differs from that of electrons in the bulk material, these defects can be detected by measuring the Doppler broadening spectra of the annihilation radiation. Because the electron density in open spaces or vacancy-type defects is lower than that in the bulk, the lifetime of positrons trapped by such regions is longer than that of positrons in the delocalized state. Thus, the measurement of the positron lifetime also provides information of open spaces and vacancies in solid. In the present work, open spaces and defects in the $Al_2O_3$(25 nm)/GaN structure were probed by using monoenergetic positron beams.

$Al_2O_3$ films were deposited on GaN by atomic layer deposition at 300ºC. Temperature treatment above 800°C leads to the introduction of vacancy-type defects in GaN due to outdiffusion of atoms from GaN into $Al_2O_3$. The width of the damaged region was determined to be 40-50 nm from the $Al_2O_3$/GaN interface, and some of the vacancies were identified to act as electron trapping centers. In the $Al_2O_3$ film before and after annealing treatment at 300-900ºC, open spaces with three different sizes were found to coexist. The density of medium-sized open spaces started to decrease above 800°C, which was associated with the interaction between GaN and $Al_2O_3$. Effects of the electron trapping/detrapping processes of interface states on the flat band voltage and the defects in GaN were also discussed.

The present research suggests that the interaction between amorphous $Al_2O_3$ and GaN introduces not only vacancy-type defects in GaN but also changes the matrix structure of $Al_2O_3$ film. We also revealed that the electron trapping/detrapping processes of interface charge states are influenced by the defects introduced in GaN.

8:40am **AP+BI+PS+TF-WeM-3 Surface Reaction Analyses of Atomic-layer Etching by Controlled Beam Experiments***, **Kazuhiro Karahashi**, T Ito, S Hamaguchi,* Osaka University, Japan

In manufacturing of modern advanced semiconductor devices such magnetoresistive random-access memories (MRAMs), phase-change random-access memories (PRAMs), and three-dimensional integrated circuit (3D IC) devices, damage-free high-precision etching for various materials is an indispensable process technology. Halogenation of a surface layer combined with low-energy ion bombardment or ligand-exchange of organic molecules for the formation of metal complexes is a surface reaction that may be used for such highly selective etching processes with atomic-scale precision. A better understanding of surface reactions taking place during the etching process often allows one to control and optimize the process more effectively. In this study, we have developed a new surface-reaction analysis system with highly controlled beams of various species and examined surface reaction mechanisms of plasma-assisted or thermal atomic-layer etching (ALE) processes for silicon (Si), copper (Cu), and nickel (Ni) films. The beam experiment of this system offers an experimental "simulation" of actual ALE surface reactions. The system is equipped with differentially-pumped multiple beam sources that can irradiate the sample set in an ultra-high-vacuum (UHV) chamber with different types of beams, i.e., low-energy ions, thermal molecules, metastable radicals, and atomic/molecular clusters, independently. During the beam irradiation, scattered and desorbed species may be measured by a differentially pumped quadrupole mass spectrometer (QMS). Time-resolved measurements of QMS synchronized with pulsed beam irradiation facilitate detailed analysis of the beam-surface interactions. Chemical states of adsorbed species on the sample surface may be measured by X-ray photoelectron spectroscopy (XPS). In this presentation, we discuss the mechanisms of halogenated-layer formation on the Si, Cu, or Ni surfaces by their exposure to XeF2 or Cl2 gases and the removal mechanisms of halogenated species from the surface by low-energy ion irradiation or surface heating. Thermal desorption mechanisms of Cu or Ni by the metal-complex formation with organic molecules (such as diketones) from its oxidized surface are also discussed

9:00am **AP+BI+PS+TF-WeM-4 Surface Reaction Analysis of Fluorine-based Reactive Ion Etching (RIE) and Atomic Layer Etching (ALE) by Molecular Dynamics (MD) Simulation***, **Erin Joy Tinacba**, M Isobe, K Karahashi, S Hamaguchi,* Osaka University, Japan

Plasma etching has always been a useful process in semiconductor device fabrication. There are several ways of using plasma etching such as reactive ion etching (RIE), wherein the material surface is bombarded with energetic ions while it also exposed to chemically reactive radicals from the plasma. Because of the energy provided by bombarding ions and high chemical reactivity on the surface, the surface is etched even at a relatively low temperature due to the combination of physical and chemical sputtering effects. RIE is often suited to fast etching processes of high aspect ratio structures since it can provide high etching yields. Another application of plasma etching is plasma-assisted atomic layer etching (ALE), wherein chemical and sputtering effects of typical plasma etching are separated into two steps. In a typical ALE process, the first step is an adsorption step wherein chemically reactive molecules or radicals from a plasma are used to modify the material surface. The modified monolayer or a thin layer on the material surface is then etched during the subsequent desorption step (second step) where low-energy ions bombard the surface. The etching reaction stops when the modified layer is depleted. This cycle is repeated many times until the desired etched depth is reached. The ALE process might be slow but it can provide tight control in the etch variability for sub-10 nm technology applications.

In this paper, molecular dynamic (MD) simulation is used to understand the effects of ions and radicals of high fluorine (F) content on etching reactions of silicon (Si), silicon dioxide ($SiO_2$), and silicon nitride ($Si_3N_4$), which may be observed in RIE processes based on, e.g., $SF_6$, $C_2F_6$, or $NF_3$ plasmas. If such a plasma is used as a radical source and ion bombardment steps by inert gas ions are separated from the radical exposure steps, an ALE process may be performed with similar surface reactions. In typical RIE, a supply of a large amount of fluorine to the surface by increasing the flux of energetic ions containing multiple F atoms (such as $SF_5^+$, $C_2F_5^+$ and $NF_2^+$ ions) and/or by increasing a F radical flux to the surface results in high etch rates. It has been found that the etching rates by such highly fluorinated ions obtained from MD simulations are in good agreement with experimental observations and the deep fluorination of the surface accounts for their high etch rates. Although fluorine may be considered too corrosive to be used for ALE, we also analyzed by MD simulation an ALE process by fluorine-containing radicals such as NF2 and compared the results with experimental observations.

9:20am **AP+BI+PS+TF-WeM-5 Analysis of Metal Surface during Atomic Layer Etching with Gas Cluster Ion Beam and Organic Acid***, **Noriaki Toyoda**, K Uematsu,* University of Hyogo, Japan

Surface states of metal surface after atomic layer etchings (ALE) with gas cluster ion beam (GCIB) and organic acid were investigated using surface analysis tools (mainly X-ray photoelectron microscopy). In recent years, we have reported the usage of GCIB irradiation for the removal steps of ALE. Since GCIBs are aggregates of thousands of gas atoms or molecules, the energy/atoms or energy/molecules can be easily reduced to several eV even though the total energy of GCIB is several keV. This characteristic is beneficial for low-damage irradiation. In additions, since GCIBs induce dense energy deposition, the bombarded area experiences transient high-temperature and high-pressure conditions. As a result, chemical reactions are enhanced at low-temperature. These characteristics are suitable for the removal step in ALE.

In this study, we have investigated the surface state of metal (Ni, Cu) after ALE with GCIB and organic acid using in-situ XPS. Prior to GCIB irradiation, metal surfaces were cleaned by Ar ions. Then Ni or Cu surface were exposed to acetic acids or acetylacetones. The surface layer with adsorbed organic acid on metals were removed by subsequent GCIB irradiation. The

difference of the surface states of metal between Ar and $O_2$-GCIB irradiation are compared with in-situ XPS results. Etching mechanism by GCIB in the presence of the adsorbed organic acid will be discussed.

9:40am **AP+BI+PS+TF-WeM-6 In-situ Characterization of Growth Kinetics of Piezoelectric Films Grown by Atomic Layer Deposition Utilizing an Ultra-high Purity Process Environment***, **Nicholas Strnad**,* General Technical Services, LLC*; D Potrepka,* U.S. Army Research Laboratory*; N O'Toole, B Rayner,* Kurt J. Lesker Company*; J Pulskamp,* U.S. Army Research Laboratory

Recently, $PbZr_xTi_{1-x}O_3$ (PZT) was grown by atomic layer deposition (ALD) in a piezoelectric film stack that was micro-machined into electrically actuated cantilever beams. [1] ALD PZT is a process technology that may drive 3D PiezoMEMS that utilizes piezoelectric films deposited on micro-machined sidewall structures. AlN is also a desirable piezoelectric for 3D PiezoMEMS but integration has been hampered by its sensitivity to reactive background gases resulting in oxygen contamination of several atomic percent and above. [2] Reactive background gases can also impact oxide films by skewing the non-uniformity and growth-per-cycle (GPC). Thus, individual reactor conditions play a significant role in both the growth kinetics, and resulting quality of thin films grown by ALD. To address both of these issues there exists the need for ultra-high purity (UHP) process capability. Here, we present how the transition from non-UHP to UHP process environment affects ALD AlN and the constituent oxide films in ALD PZT. The UHP process environment also enables the rapid characterization of the reaction kinetics of ALD processes by in-situ ellipsometry. The reaction kinetics of several constituent oxides for ALD PZT are presented based on empirical in-situ observations.

References

[1] Strnad, N.A. (2019) Atomic Layer Deposition of Lead Zirconate-Titanate and Other Lead-Based Perovskites (Doctoral Dissertation) https://doi.org/10.13016/8dqx-7pev

[2] Chen, Z. (2019) Thermal atomic layer deposition of aluminum nitride thin films from AlCl3 (Master's Dissertation)

11:00am **AP+BI+PS+TF-WeM-10 Nanoscale Surface Modification of Medical Devices using Accelerated Neutral Atom Beam Technology***, **Dmitry Shashkov**, J Khoury, B Phok,* Exogenesis Corp. **INVITED**

Controlling surface properties of biomaterials is vital in improving the biocompatibility of devices by enhancing integration and reducing bacterial attachment. We use Accelerated Neutral Atom Beam (ANAB) technology, a low energy accelerated particle beam gaining acceptance as a tool for nanoscale surface modification of implantable medical devices. ANAB is created by acceleration of neutral argon atoms with very low energies under vacuum which bombard a material surface, modifying it to a shallow depth of 2-3 nm. This is a non-additive technology that results in modifications of surface topography, wettability, and chemistry. These modifications are understood to be important in cell-surface interactions on implantable medical devices. Similarly, ANAB could be used to modify surfaces of medical device coatings (small molecules and proteins)., creating a native drug elution barrier. In this study, we characterize the effects of ANAB on several materials including metals (Ti, CoCr) and polymers (PEEK, PP, PVC) and measure the differential ability of eukaryotic versus prokaryotic cell attachment on these modified surfaces. We also study the ability of ANAB to create an elution barrier on a drug coating without the use of binding polymers. We identified that eukaryotic cells including mesenchymal stem cells (MSC) and osteoblasts increase attachment and proliferation on treated surfaces as measured by MTS assay and cell visualization by microscopy. MTS assay shows that by day 14, control PEEK has 9,925±1,994 cells while ANAB-treated PEEK has 88,713±6,118 cells (n=3; p<0.0014). At the same time, we find that bacterial cells including *S.aureus* and *P.aeruginosa* have a decreased ability to bind on the ANAB-treated surface. This dichotomy of cellular attachment may be attributed to the nano-scale surface topography, favoring larger eukaryotic cells while inhibiting attachment of smaller bacterial pathogens. In studies focusing on drug elution, rapamycin was spray-coated on the surface of CoCr bare metal stents and either left as control or ANAB-treated the surface of the drug. These stents were then placed in a plasma elution assay for up to 7 days. We found that untreated stents eluted off most of the drug within 24 hours, and 100% of it by 48 hours post-elution. The ANAB-treated stents, however, showed a favorable elution profile slowly releasing the drug over the 7 day period. ANAB, therefore, has many possible uses in medical device technology in increasing integration, decreasing bacterial attachment and potentially biofilm formation, and, if desired, create an elution profile for a combination drug-device without the use of binding polymers.

11:40am **AP+BI+PS+TF-WeM-12 Chemically Enhanced Patterning of Nickel for Next Generation EUV Mask***, **Xia (Gary) Sang**, E Chen,* University of California, Los Angeles*; T Tronic, C Choi,* Intel Corporation*; J Chang,* University of California, Los Angeles

The ever-increasing demand in high-precision pattern definition and high-fidelity pattern transfer in the IC manufacturing industry calls for continuous advancement in lithography technology. Extreme Ultra-Violet (EUV) lithography is being widely adopted for defining sub-10 nm nodes. Due to its ideal optical properties, Ni is under active research as the future absorbing layer material in EUV masks, the profile of which determines the quality of resulting lithographic patterns. Contemporary techniques for patterning Ni rely on noble ion beam milling, which leaves considerable amounts of re-deposition on feature sidewall. Finding chemically selective patterning technique is thus of critical importance. Due to the etch-resistant nature of Nickel, removal at an atomic level is enabled by chemical modification of the surface through plasma exposure and subsequent introduction of organic ligands. Plausible chemicals are first screened by thermodynamic assessments from available databases, experiments were then conducted to validate the theoretical predictions.

Both blanket and patterned Ni thin films were studied using this reaction scheme. Organic chemistries, such as acetic acid and formic acid were first investigated to determine the feasibility of metal-organic formation through direct exposure. The efficacy of acetic acid and formic acid etching chemistries were confirmed through solution-based studies on Ni, the formation of Ni(CH3COO)2 and Ni(HCOO)2 were confirmed through mass spectrometry. Nickel oxide formation and subsequent removal were confirmed by quantifying the change in the relative intensities of peaks of metallic Ni (852.6 eV) and oxidized Ni (853.7 eV) by X-Ray Photoelectron Spectroscopy (XPS).

The chemical reactivity difference between Ni0 and Ni2+ was quantified in the work to explore the attainable etch selectivity. Due to the decrease in radical concentration and flux, vapor phase etching of metallic Ni resulted in small thickness reduction (~ 0.4 nm/cycle). It is then tested that surface modification, particularly oxidation, is capable of promoting subsequent reactions by lowering reaction energy barrier through metal oxide formation. An oxygen plasma treatment is added prior to acid vapor exposure, and this cyclic approach results in a relatively linear etch rate of ~ 2 nm/cycle, which translates to a 50:1 etching selectivity of NiO over Ni. The same cyclic approach was then applied to patterned samples, post-etch sidewall angle of ~ 85° is measured, which closely conserves the initial feature profile (~ 87°).

12:00pm **AP+BI+PS+TF-WeM-13 Surface Reactions of Low Energy Electrons and Ions with Organometallic Precursors and their Relevance to Charged Particle Deposition Processes***, **Rachel Thorman**,* Johns Hopkins University*; E Bilgilisoy,* FAU Erlangen-Nürnberg, Germany*; S Matsuda, L McElwee-White,* University of Florida*; D Fairbrother,* Johns Hopkins University

Focused electron beam induced deposition (FEBID) and focused ion beam induced deposition (FIBID) are nanofabrication techniques where beams of charged particles (electrons or ions) create metal-containing nanostructures by decomposing organometallic precursors in low pressure environments. Consequently, the interactions of electrons and ions with surface-bound organometallic precursors are fundamental processes in these deposition processes. Previously performed ultra-high vacuum (UHV) studies on low energy (below 100 eV) electron interactions with adsorbed precursors (e.g. $Pt(PF_3)_4$, $MeCpPtMe_3$, and $Co(CO)_3NO$) have revealed that electron-induced reactions of surface bound precursors occurs in two sequential steps: (1) an initial step characterized by precursor decomposition/deposition and partial ligand desorption followed by (2) decomposition of the residual ligands. However, a similar level of understanding does not exist for low energy ion interactions with organometallic precursors. In this presentation, I will show that a low temperature, UHV surface science approach can serve as a platform to study the reactions of both low energy electrons (500 eV) and low energy ions (<1kV $Ar^+$ ions) with organometallic precursors. Results from *in situ* X-ray photoelectron spectroscopy (XPS) and mass spectroscopy (MS) clearly show that low energy electron and ion-induced reactions of several surface-adsorbed species, including $(\eta^5\text{-Cp})Fe(CO)_2Re(CO)_5$, $Ru(CO)_4I_2$, $Fe(CO)_5$, and $Co(CO)_3NO$, are markedly different. Similarly to electron-induced reactions, low-energy ion-induced reactions proceed in a two-step process with an initial decomposition step primarily characterized by ligand

loss. However, ligand loss is typically must more extensive than is observed for electron-induced reactions; for example, in the case of ($\eta^5$-Cp)$Fe(CO)_2Re(CO)_5$ and $Fe(CO)_5$, all CO ligands desorb in this initial step. The second step in the ion induced reactions can be described as a regime primarily characterized by physical sputtering. These contrasting results are discussed in the context of different deposition mechanisms proposed for FEBID and FIBID.

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