Thursday Afternoon, October 31, 2013

Plasma Science and Technology
Room: 104 C - Session PS-ThA

Low Damage Processing

Moderator: E.V. Johnson, LPICM-CNRS, Ecole Polytechnique, France

2:00pm **PS-ThA1 Damage Control: Electron Beam Generated Plasmas for Low T_e Processing**, ***S.G. Walton***, Naval Research Laboratory**INVITED**

The advantages of plasma-based materials processing techniques are numerous. The capability to modify large (> 10^3 cm^2) areas with precision down to the nanoscale is one reason plasmas are widely used in the materials and surface engineering communities. However, with the rapidly evolving demand for new materials in applications ranging from organic and nanoelectronics to biosensors, some of the limitations of conventional plasma sources are becoming apparent. The lack of process control and excessive ion energies in the processing of soft or very thin materials are examples.

The Naval Research Laboratory (NRL) has developed a processing system based on an electron beam-generated plasma. Unlike conventional discharges produced by electric fields (DC, RF, microwave, etc.), ionization is driven by a high-energy (~ 2 keV) electron beam. This approach provides a solution to many of the problems associated with conventional plasma processing systems, making it potentially useful in the development of a wide variety of novel materials. Importantly, high plasma densities (10^{10}-10^{11} cm^{-3}) can be produced in electron beam generated plasmas, while the electron temperature remains between 0.3 and 1.0 eV. Accordingly, ions leaving the plasma impact surfaces with energies in the range of 1 to 5 eV. This provides the ability to slowly etch and/or controllably engineer both the surface morphology and chemistry, critically important features for applications requiring atomically thin or smooth materials.

An overview of NRL's research efforts in developing this technology with a focus on source development, plasma characterizations, and materials processing will be presented. Particular attention will be given to current efforts in the processing of polymers and 2-d materials such as graphene, where we take advantage of the unique attributes of electron beam generated plasmas to engineer the surface properties of these materials for electronic and sensing applications. This work is supported by the Naval Research Laboratory base program.

2:40pm **PS-ThA3 Numerical Simulation of Oxidation Process in Silicon by O_2 Gas Cluster Beam**, ***K. Mizotani***, *M. Isobe, S. Hamaguchi*, Osaka University, Japan

A surface modification process based on a gas cluster ion beam (GCIB) is known to be less damaging to the surface than that based on an ordinary atomic or molecular ion beam. In a GCIB process, several thousands of atoms or molecules aggregated by Van der Waals interactions form a gas cluster and such gas clusters are ionized and accelerated up to a high kinetic energy (typically in the range of several keV) toward a surface that is to be processed. Although the total acceleration energy for each cluster can be very high, each atom or molecule has relatively low kinetic energy. Therefore a GCIB process is essentially a low energy beam process. In this study, we use molecular dynamics (MD) computer simulations to examine surface oxidation processes for silicon (Si) by oxygen-molecule GCIBs at various incident energies and compare the results with those of earlier experimental studies. Especially in this study, we focus on extremely low energy processes, where incident oxygen molecules in gas clusters have kinetic energies close to thermal energy at room temperature. It has been found in MD simulations that only the top surface layer of the substrate can be oxidized with little damage to the surface in GICB processes. This is in contrast with oxygen molecular-ion beam processes, where oxygen hardly sticks to the Si surface when the beam kinetic energy is sufficiently low (so that the chemical bond of O_2 cannot be broken). If the kinetic energy is high, then the surface can be oxidized but the beam impact causes surface damage. It has been observed that, in the case of low-energy gas cluster beam incidence, each gas cluster sticks to the Si surface for dozens of picoseconds until the gas cluster is sublimed by heat transport from the substrate. While a cluster remains on the substrate surface, a large number of oxygen molecules with a solid density are directly exposed to the substrate surface, which increases the probability for the formation of Si-O bonds only on the top surface.

3:00pm **PS-ThA4 Ultra-low k Dielectric and Plasma Damage Control for Advanced Technology Nodes (10-nm and Below)**, ***F. Lazzarino***, IMEC, Belgium, *M. Krishtab*, KU Leuven, Belgium, *S. Tahara*, TEL, Belgium, *M. Baklanov*, IMEC, Belgium

The continuous decrease of the critical dimension together with the introduction of new porous low-k materials (k-value lower than 2.5) make plasma etch more and more challenging. Besides the morphological aspect (profile of the structure or bottom roughness), the degradation of the dielectric properties of the low-k film is another important point that needs to be understood and well-controlled. In this work, we compare and analyze the damage (loss of Si-CH3 groups and moisture absorption) caused by different types of fluorocarbon-based chemistries and we propose a new damage-free chemistry to pattern advanced low-k materials identified for the most advanced technology nodes.

In the first part of the study, the low-k film is exposed to a selection of few conventional C4F8-based chemistries. In all cases, a significant level of damage is observed and is mainly attributed to the diffusion of fluorine radicals coming from the fluorocarbon polymer layer deposited on the low-k surface. As fluorine cannot be suppressed from the discharge, two options are considered to reduce its concentration in the passivation layer. First, a less polymerizing gas like CF4 is used to replace C4F8 then a carbon-free molecule like NF3 is considered to fully modify the nature of the passivation layer. Both approaches led to a very low level of damage. However, all CF4-based chemistries show very low etch rate and exhibit a poor selectivity towards masking layers like TiN. In contrast, a much higher etch rate and a greater selectivity is observed when NF3 is used to replace C4F8. Concerning the damage, an extremely thin (~1-nm) but very hydrophilic carbon depleted layer is formed at the low-k surface and a rough surface appears while the etch front progresses. We characterized and understood these issues using FTIR spectroscopy, Auger analysis and AFM and we fixed both instabilities together by slightly adapting the chemistry. The optimized chemistry leads to a very low level of water absorption within an extremely thin and smooth damaged layer. Finally, a comparative study including k-value, surface roughness and composition of the damage layer using TOF-SIMS is presented applying our best C4F8-, CF4- and NF3-based chemistries on two potential low-k candidates for the 10-nm technology node.

To conclude, it is shown that a very low level of damage is obtained by using a C-free NF3-based chemistry. The two side effects like the surface roughness and the high moisture uptake were characterized and the chemistry was tuned in order to overcome both issues. This new chemistry is rated as the best candidate to pattern ultra-low k dielectrics for the most advanced technology nodes.

3:40pm **PS-ThA6 High Temperature Etching of GaN Preserving Smooth and Stoichiometric GaN Surface**, *R. Kometani, K. Ishikawa, K. Takeda, H. Kondo,* ***M. Sekine***, *M. Hori*, Nagoya University, Japan

Plasma etching of GaN is necessary for fabricating high performance GaN devices, however plasma exposure generates defects and produces residues, which results in degradation. It is strongly required that the damage induced by plasma etching should be reduced. Post annealing can recover damages, however, preferentially N lost causes Ga-rich surface. The stoichiometric surface was reported to be deteriorated under annealing of 200 to 1000°C after N_2^+ sputtering at room temperature.[1] We have revisited the surface reactions at high temperature (HT).

We constructed a high-temperature plasma reactor,[2] where a CCP was generated by 13.56-MHz rf power to the substrate electrode. Ion bias energy was determined about 250 eV. SiC sample stage can be rapidly heated up to 800°C by an IR lamp as fast as 100°C/s.

As the GaN was exposed to Ar plasma at 600°C, a rough surface appeared with a root-mean-squared (RMS) value of 9.88 nm in AFM image. By XPS analysis of the shoulder peak at 18.9 eV in the Ga 3d region, it revealed Ga metallic state or Ga cluster formation. In contrast, no significant increase of roughness (1.46 nm) was observed after N_2 plasma exposure even at 600 °C.

On the other hand, for Cl_2 plasma, the etch rate increased at HT, from 293 to 534 nm/min for 300 to 600°C, and hexagonal pits were formed for 600°C etching. These mean that the heating would prompt the chemical reaction. The optical properties were investigated for YL (deep level defects such as N vacancy), BE (GaN band gap emission), and their ratio indicates crystal quality. Ar plasma exposure increased the YL/BE. It means crystal quality deterioration and deep level defects generation. The shallow level defects were also increased and not only YL but also lower energy side of BE increased. However, the crystal quality after Cl_2 plasma etching was much better than that of Ar plasma.

In Cl_2 plasma, no metallic gallium at any temperature, etch rate increasing and smooth surface was retained at HT except the hexagonal pits formation at 600°C. Consequently, HT etching is effective to enhance the surface chemical reaction and reducing plasma damages.

This work was supported by the Knowledge Cluster Initiative (Second Stage), MEXT, Japan.

1 Y. H. Lai et al., J. Phys. Chem. B 105, 10029 (2001).

2 R. Kometani et al., Appl. Phys. Express 6 (2013) 056201.

4:00pm **PS-ThA7 Investigation of Surface Roughness in III-V Semiconductors After an *In Situ* Hydrogen Plasma Clean Prior to PEALD**, ***E. Cleveland***, NRL-ASEE, *L. Ruppalt, B. Bennett, S.M. Prokes*, NRL

III-V compound semiconductors, such as GaSb, are attracting widespread attention as an alternative to Si in advanced complementary metal-oxide-semiconductor (CMOS) technologies; their high electron and hole mobilities, as well as relatively narrow bandgaps, makes them particularly well-suited for high-speed, low power applications. However, for high-performance device realization, the quality of the interface between the III-V semiconductor and the gate-oxide is crucial. Most III-V semiconductors have a highly reactive surface and unlike SiO_2, the native oxides are complex in structure and composition leading to the formation of heavily defected interfaces that pin the semiconductor Fermi-level near midgap and degrades device performance. A significant effort has been focused on surface preparations prior to ALD that removes the native oxide and passivates the III-V atoms in order to ensure the best possible interface. Current approaches typically rely upon wet-chemical etches to remove the defect-prone native oxide layer prior to dielectric deposition; however, this technique typically suffers from a lack of reproducibility, as well as potential interface contamination between processing steps.

Recently, we demonstrated the use of an in situ hydrogen plasma treatment prior to the deposition of plasma enhanced ALD (PEALD) Al_2O_3 on GaSb. Samples demonstrating good electrical characteristics correlated to the elimination of Sb-oxide, a decrease in elemental Sb, as well as an increase in Ga_2O_3 as determined by XPS. While using plasma has been shown to produce good quality interfaces and subsequent dielectric films, a significant amount of surface roughening can take place across the semiconductor surface. Although surface roughness may not greatly influence the capacitance modulation of a MOS capacitor, it could significantly hamper charge mobility within a field-effect transistor (FET). Therefore, we investigated the surface roughness of a GaSb surface after exposure to hydrogen plasma as a function of select plasma parameters: rf-power, substrate temperature, and exposure time. Surfaces were characterized using atomic force microscopy, transmission electron microscopy, as well as, electrical measurements. Furthermore, we investigated the surface roughness across GaAs samples of different facets when exposed to a hydrogen plasma prior to PEALD in order to gain a better understanding of surface interactions during plasma assisted ALD.

4:20pm **PS-ThA8 Fabrication of GaAs/AlGaAs Nano-Pillars using Bio-Template Combined with Neutral Beam Defect-Free Etching**, ***C. Thomas***, *Y. Tamura, A. Higo*, Tohoku University, Japan, *N. Okamoto, I. Yamashita*, Nara Institute of Science and Technology, Japan, *S. Samukawa*, Tohoku University, Japan

Quantum dot (QD) lasers have been extensively studied in the last few decades due to their device characteristics benefits. However, fabrication of a high density and uniform two-dimensional array of QDs is still a big challenge. We have developed the first damage-free top-down process for creating GaAs QDs by combining a high-density bio-template [1] and a neutral beam (NB) etching process [2]. The bio-template consists of a high-density (about $7x10^{11}$ cm^{-2}), two-dimensional array of cage-shaped proteins called ferritins with encapsulated metal oxide nanoparticles (NPs). After removal of the protein shell, 7 nm in diameter iron (Fe) or cobalt (Co) oxide NPs were used as etching masks. The NB etching consists of an inductively coupled plasma chamber separated from the process chamber by a carbon electrode with a high-aspect-ratio aperture array. As a result, the charged particles are efficiently neutralized whereas almost no UV photons can reach the sample.

A thin oxide layer was deposited on top of the single quantum well (GaAs, with $Al_{0.3}GaAs$ barrier layer) samples grown by using metal organic vapor phase epitaxy after removing the native oxide. Then, deposition of the 2D-array etching masks was conducted. An oxygen treatment was carried out to remove the protein shell, followed by a hydrogen radical treatment to remove the remnant oxide layer. Etching was performed using the NB technique. Defect-free nano-pillars [3] were obtained using both etching masks. It appeared that the nano-pillars with Co masks had a better etching profile than those with Fe masks. Indeed, the nano-pillars formed using Co NPs as the etching masks presented a vertical sidewall whereas the ones formed by using Fe NPs presented an etching profile with tapered angles of about 82°. Moreover, we have successfully achieved 15-nm-in-diameter and over 100-nm-high pillars by NBE process. The average height of the nano-pillars was larger when the Co masks were used. These results suggest that the etching selectivity of Co NPs is higher than that of Fe NPs. The maximum density of the nano-pillars was up to $5x10^{10}$ cm^{-2} and did not seem dependent on the chemical nature of the etching mask. The most important parameter for achieving high density, over that of conventional QDs grown by molecular beam epitaxy, is the interaction between the cores and the GaAs surface rather than the etching selectivity. The results showed that III-V compound nanodisk devices can be realized by this defect free top-down nanoprocess.

[1] I. Yamashita et al., Biochim. Biophys. Acta 1800 (2010) 845

[2] S. Samukawa et al., Jpn. J. Appl. Phys. 40 (2001) L997

[3] X. Y. Wang et al., Nanotechnology **22** (2011) 365301.

4:40pm **PS-ThA9 Conductive Carbon Film Formation at Low Temperature (R. T.) using Neutral-Beam-Enhanced Chemical-Vapor-Deposition**, ***Y. Kikuchi***, Tohoku University and Tokyo Electron, Japan, *S. Samukawa*, Tohoku University, Japan

Conductive carbon material such as graphite film is one of the primary materials used as an alternative for metal electrodes in various devices. However, it is difficult to precisely control their properties at low temperature depositions using conventional plasma-enhanced chemical vapor deposition (PECVD). We have developed a neutral-beam-enhanced chemical vapor deposition (NBECVD) process as an alternative to the conventional PECVD process for forming conductive carbon film to solve this problem. NBECVD can almost completely eliminate the irradiation of UV photons and electrons on the substrate surface by using a carbon aperture, resulting in a damage-free deposition process. Moreover, the NBECVD can form a film through the surface polymerization caused by the bombardment of an energy-controlled Ar neutral beam on a surface with absorbed precursors. We previously proposed controlling the molecular-level structures in SiOCH film by using the NBECVD process, which can control the film properties (k-value and modulus). Since the bombardment energy of the neutral beam can be precisely controlled, selective dissociation of the weak chemical bonds in the precursors is possible, which enables us to control the precursor structure when designing the film structure.

In this study, we used toluene as the precursor to grow an aromatic hydrocarbon structure in the film to obtain the conductive properties. As a result, we formed highly conductive carbon films using a low temperature process.

5:00pm **PS-ThA10 Numerical Simulation of Total Processes of Neutral Beam Etching from Generation of Neutral Beam by Collision of Ions against Graphite Sidewall to 3-dimensional Etching Profile**, ***N. Watanabe***, *S. Ohtsuka*, Mizuho Information & Research Inst., Japan, *S. Mochizuki*, Mathematical Systems, Japan, *T. Kubota*, Tohoku Univ., Japan, *T. Iwasaki, Y. Iriye, K. Ono*, Mizuho Information & Research Inst., Japan, *S. Samukawa*, Tohoku Univ., Japan

Neutral beam is an indispensable technology for fabrication of future nano-devices. Especially, a neutral beam source developed by Prof. Samukawa can achieve high neutralization efficiency, controllable energy, and realistic flux. It can perform damage-free processes and is expected to be used in mass production. To achieve production of such future devices, etching simulation is indispensable.

To construct the etching simulation by the neutral beam, simulations of (1) neutral beam generation process by collision of ions from plasma against graphite aperture wall, (2) energy and angular distributions and trajectories of ions and neutral beams passing through the aperture, (3) surface reactions such as etching and deposition, and (4) 3-dimensional etching profile evolution are needed. We performed these simulations and combined into an etching simulation.

First principles calculation was performed to simulate the neutralization process of chlorine ions. By using a larger unit cell, a planar electronic state which is located about 0.4 nm apart from the graphene sheet was found. Also, it was found that electrons emitted from chlorine particles were absorbed by the planar electronic state. It seems that the state plays an important role in a neutralization process. We have calculated neutralization efficiencies as a function of incident energy, incident angle, and number of collisions.

Based on the result, energy and angular distributions of neutral beam were calculated. In the stage of surface reaction simulation, reactions such as radical adsorption, desorption of products, beam-assisted reaction, physical sputtering, carbon adsorption, and so on were considered. Finally 3-dimensional etching simulator was developed by these results. By using the simulator we could reproduce the experimental results such as aperture aspect ratio dependence and bias dependence.

A part of this work was supported by the New Energy and Industrial Technology Development Organization (NEDO).

5:20pm **PS-ThA11 Controlling the Attributes of Electron Beam Generated Processing Plasmas**, ***D.R. Boris***, *E.H. Lock, R.F. Fernsler, S.G. Walton*, Naval Research Laboratory

Electron beam generated plasmas have a variety of unique features that make them distinctive plasma sources for materials processing. They are characterized by high plasma density, very low electron temperature, and unique gas phase chemistries that distinguish them from discharge based plasmas. This work presents measurements from suite of diagnostics (RF impedance probes and Langmuir probes, optical emission spectroscopy (OES), and energy resolving mass spectrometer) used to characterize the unique features of electron beam generated plasmas. The focus will be on the important role that gas chemistry plays in determining plasma parameters (kT_e, V_p, ion energy distribution) and the resulting flexibility of the processing system.

5:40pm **PS-ThA12 Time-resolved Discharge Observation of an Argon Plasma Generated by Commercial Electronic Ballast for Remote Plasma Removal Process**, ***T. Cho***, *Y. Sen, R. Bokka, S. Park, D. Lubomirsky, S. Venkataraman*, Applied Materials Inc.

Recently, a remote plasma reactor has been widely used to clean the wafer surface and especially for the removal of the silicon dioxide or silicon nitride over silicon with high selectivity in semiconductor manufacturing industry. In a remote plasma process, plasma is generated within a plasma reactor and delivers only radicals to the process chamber. Absence of plasma in the process region decreases the physical damages of the substrate by ion bombardment and the radicals created by the plasma results in chemical reactions at wafer surface. For a stable supply of radicals to process chamber, a plasma reactor has to be designed very carefully. In Applied Materials, Inc, the plasma reactor adopting a hollow cathode type electrode is being used as a remote plasma source. An argon plasma generated between the cone-shaped electrode powered by commercial electronic ballast and grounded plane electrode has been investigated. Since the electronic ballast has positive and negative cycle in a period, two different discharge modes of remote plasma reactor - the normal glow discharge mode and the hollow cathode discharge mode – have been observed. The hollow cathode discharge mode has wider operation window in gas pressure than the glow discharge one. The glow discharge started to be extinguished at higher pressure than 4.1 Torr and turned suddenly to another hollow cathode discharge mode in the holes on ground plate, while the hollow cathode discharge mode kept growing until 10 Torr. These results show that the stable operation window of the system could be defined by the glow discharge mode rather than the hollow cathode discharge mode and could be improved by optimizing the applied voltage waveform and electrode configuration.

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