Plasma Science and Technology Division
Room: 202 - Session PS+SS-WeM

Plasma Surface Interactions (Fundamentals & Applications) I
Moderator: C. Labelle, GLOBALFOUNDRIES

8:00am **PS+SS-WeM1 Investigation of Sidewall Passivation Mechanism in a 'CMOS-compatible' Plasma Etching Process for InP-based Photonic Devices**, ***S. Bouchoule***, CNRS-LPN, France, *L. Vallier*, CNRS-LTM, France, *L. Gatilova, G. Patriarche, S. Guilet, L. Le Gratiet*, CNRS-LPN, France

Inductively coupled plasma (ICP) etching of II-V semiconductors is now widely used for the development of high-performance emitters, and various chlorine- or HBr- containing chemistries have been proposed for the patterning of InP-based heterostructures required to reach the NIR region. Smooth and anisotropic etching is generally a key-requirement, but only few studies exist on the understanding of the sidewall passivation mechanisms occurring during the etching of InP and related materials. We have shown for the Cl_2-H_2 and HBr chemistries [JVSTB 26, 666 (2008)] that a silicon oxide layer acting as a lateral etch-inhibitor can build-up on the etched sidewalls of InP-based heterostructures, when a Si wafer is used as the sample tray. This configuration corresponds to most commercial ICP etch systems having an electrode diameter of 4-in or more, used to etch III-V samples of 2-in or less size. However, this may not be the case for future large surface processing of III-V when the III-V wafer will have the same size as the electrode or when III-V dies bonded onto a 200/300 mm wafer have to be etched, where most of the wafer surface is covered by a protecting layer that is not silicon. This may occur in III-V/Si photonic technologies. We have shown that high-aspect- ratio etching of the photonic patterns via a SiO_x sidewall passivation mechanism independent of the electrode surface can be obtained when a Si-containing gas such as SiH_4, or $SiCl_4$ added [JVSTB 29, 020601 (2011)]. A more detailed analysis of the plasma has shown that hydrogen may promote the deposition of a Si-rich passivation layer on the sidewalls of the etched patterns. SiOCl sidewall passivation takes place during Si ICP etching using Cl_2-HBr-O_2 chemistry in CMOS technology. We have therefore investigated $SiCl_4/Cl_2/HBr/O_2/Ar$ plasma for the etching of InP dies in a 300-mm CMOS etching tool. This gas mixture provides the Si,O, and H species required for the build-up of a SiO_x passivation layer on the InP sidewalls. We show that the passivation mechanism is enhanced when the HBr concentration is increased in the feed gas. We have performed a local analysis of the passivation layer deposited on the InP sidewalls using EDX spectroscopy coupled to TEM. We show that the nature of the passivation layer can be changed from a-Si or nc-Si to SiO_2 depending on the hydrogen and oxygen concentrations in the gas mixture. Finally we demonstrate smooth and anisotropic etching of ridge waveguide and vertical Bragg reflector patterns in the CMOS etching tool.

8:20am **PS+SS-WeM2 Coupling of Surface Mixed-Layer Kinetics and Monte Carlo Modeling for Profile Evolution in Patterning Complex Oxides**, ***N. Marchack****, *C.D. Pham, J.P. Chang*, University of California Los Angeles

As the downscaling of integrated circuit devices continues, minute variations in the feature profiles from processing techniques such as plasma etching significantly affect device performance. With the increasing introduction of novel materials into integrated circuits, the need to predict surface response during etching of these materials, such as complex oxides, becomes critical to attainable device performance. In this work, a phenomenological model[1] based on high-k oxide etching in chlorine based plasmas is adapted into a translated mixed layer (TML)[2] kinetics-based format to be used a Monte Carlo-based feature profile simulator. To accurately represent the kinetics involved, experiments are conducted in this work in an inductively coupled plasma (ICP) reactor equipped with a quadrupole mass spectrometer (QMS) for analyzing etch products and a quartz crystal microbalance (QCM) for measuring the etch rate *in situ*. This reactor is connected to a UHV transfer tube which allows the surface composition to be studied via x-ray photoelectron spectroscopy (XPS) without exposure to ambient conditions. In the TML model, surface reactions such as ion impingement, neutral adsorption, physical sputtering and chemically enhanced ion etching are accounted for, and reaction parameters are either measured directly or extracted by comparing the model to etch yield data. The MC model used ion incident angle dependence and an elliptical energy deposition model to capture the effects of surface morphology on the profile evolution under the bombardment of energetic and directional ions. The material systems studied include HfLaO and HfSiON etched in Cl_2/BCl_3 plasmas, for both blanket films and trenches patterned by e-beam lithography. Very good agreement was demonstrated between the phenomenological and TML models, as well as between simulated profiles and cross-sectional SEM images of the patterned material systems.

[1] Martin et al. Journal of Vacuum Science and Technology A 27(2) 2009

[2] Kwon et al. Journal of Vacuum Science and Technology A. 24(5) 2006

8:40am **PS+SS-WeM3 Plasma Diagnostics and Nanoscale Surface Processing - Application to SiO_2, High-k PVD and ALD**, ***T. Kitajima***, National Defense Academy, Japan **INVITED**

Introduction

Reactive plasmas are widely used for surface processings due to its controllable ion energy and radial fluxes.

Nano size feature control with plasma processing requires nonthermal chemistry with low energy ion exposure. Metastable atoms with internal energy of a few eV become important for the quality and throughput of deposition as ion energy is reduced.

Minimizing the processing target to the nanoscale also reveals the new properties of materials interacting with plasmas due to the size effect. Namely, sticking coefficients of radicals on metal significantly increase.

In the presentation, some recent results on metastable radical induced deposition including HfO2 ALD are shown. The latest findings of nano particle interaction with reactive plasmas are introduced for the model case of PVD based HfSiON film growth.

Reactive metastables for oxide growth : SiO2 and HfO2

The density of metastable O(1D) (1.9eV) in Ar-diluted O2 ICP shows maximum at O2 fraction of 1% and the flux shows significant increase due to the reduced quenching by O2. O(1D) density is measured by Vacuum UltraViolet Absorption Spectroscopy (VUVAS). The XPS analysis shows the stoichiometry of the grown SiO2 is comparable to the thermal oxide as well as the electrical breakdown.

The scheme is applied to the plasma enhanced atomic layer deposition (PEALD) of HfO2. The reagent is TEMAH and the oxidant is Ar-diluted O2 ICP. The increased O(1D) flux enables less particle film surface with fewer carbon contamination.

Reactive surface nano particles interacting with plasma : HfSiON growth

Hf nanoparticles self assembled on SiO2/Si(100), origin of HfSiON, have sticking coefficient of N radicals close to 1 in the initial stage of N2 ICP exposure. The reactivity of the nanoparticles with underlying SiO2 is enhanced by the plasma exposure, results in the formation of carbon free HfSiON film.

Concluding remarks

Metastables are important reactant for low temperature non-biased deposition processes

Metastable flux is controllable with the base gas chemistry

Nanoscale surface features are current concerns for plasma deposition

Nano sized surface has totally different reaction kinetics including interface with underlayer

Nano size effect of the surface is evident for radical reactivity

Self assembly (bottom up scheme) is highly important for next generation nano scale plasma processing as well as lithographic techniques (top down scheme)

Acknowledgement

This work was supported by MEXT Grant-in-Aid for Scientific Research on Innovative Areas （22110520） and JSPS Grant-in-Aid for Young Scientists (B) (21760033).

9:20am **PS+SS-WeM5 Nitric Oxide Reactivity Investigation via Plasma Processing**, ***J.M. Blechle***, *E.R. Fisher*, Colorado State University

With increasing concern about environmental health, there is a greater need to investigate fundamental reactivity of pollutant species with and without the influence of surface effects. Here, inductively coupled plasmas are used to examine the catalyzed conversion of industrial exhaust, with an emphasis on elucidating the surface and gas-phase chemistry. Literature studies have thus far failed to explore the primary driving forces present in these catalytic plasma systems. The present work focuses on investigating the

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properties of nitric acid within plasmas formed from a collection of precursor gases including NO, NO_2, N_2O, and N_2+O_2. The behavior of the NO radical is determined by various methods that include catalytic surface reactivity measurements via the imaging of radicals interacting with surfaces (IRIS) technique as well as kinetic formation and destruction via time-resolved optical emission spectroscopy (TR-OES). Species density, surface scatter coefficients (*S*), along with vibrational and rotational temperatures establish inherent characteristics of NO. Results from these studies show the density of NO is strongly dependent on system pressure, which is in part attributable to formation of gas-phase dimers. In addition, *S*(NO) using non-catalytic surfaces (e.g. Si) increases with increasing plasma power. Additional results from studies of NO formation through bimolecular reactions in N_2/O_2 plasmas will be presented. Collectively, these data allow for unparalleled insight into the properties of atmospheric species during plasma processing and the interactions they undergo in the presence of catalytic substrates.

9:40am **PS+SS-WeM6 Near-Threshold Ion-Enhanced Silicon Etching**, ***H. Shin**, W. Zhu, V.M. Donnelly, D.J. Economou*, University of Houston

Nearly mono-energetic ion energy distributions (IED) were obtained on the substrate electrode in a Faraday-shielded inductively couple plasma. This was accomplished by pulsing the plasma, and applying a synchronous DC bias on a "boundary" electrode, during a specified time window in the afterglow. Both the peak ion energy and the width of the IED could be controlled.[1] The ability to precisely control the IED enabled a study of ion-enhanced etching of silicon with chlorine, at near-threshold ion energy. Unlike "beam" experiments, where there is no plasma over the substrate, this work involves etching under "realistic" plasma conditions. The progress of etching in an argon-diluted chlorine plasma was monitored as a function of pressure and ion energy using optical emission spectroscopy. The silicon etch rate was measured using infrared laser interferometry. The etch rate of a p-type blanket silicon substrate was proportional to Cl-atom density, but did not depend on ion energy for sub-threshold (less than ~ 20 eV) ions. Under these conditions, however, the etch rate was much higher than that expected based on reported experiments in downstream plasmas where the surface is exposed to Cl atoms alone. Above threshold, the etch rate increased with the square root of ion energy. A comparison with n-type silicon substrate was also made. The carrier-mediated mechanisms of p-type Si etching in a plasma under very low energy ion bombardment will be proposed and discussed.

Work supported by the DoE Plasma Science Center and NSF.

[1] H. Shin et al., to appear in *Plasma Sources Science and Technology.*

10:40am **PS+SS-WeM9 Atomic Chlorine Absolute Densities and Surface Recombination Coefficients in Inductively-Coupled Plasmas in Pure Cl_2**, ***J.-P. Booth***, LPP-CNRS, France, *N. Sirse*, NCPST Dublin City University, Ireland, *Y. Azamoum, P. Chabert*, LPP-CNRS, France

Two-photon laser-induced fluorescence (TALIF) at 233.2nm was used to measure the density of Cl atoms in a 13.56MHz Inductively-coupled plasma in pure chlorine. Initial attempts to use the technique proposed by Ono et al [1], to calibrate the signal using photolysis of CCl_4 gave unphysically high values, probably due to poor knowledge of the laser spatial profile at the focal point. Therefore we developed a new technique, based on 355nm (tripled YAG) photolysis of Cl_2 to generate a known density of Cl atoms. The variation of the absolute Cl density at the reactor centre was measured as a function of pressure and RF power in the range 3-90 mTorr and 20-500W. We also used the TALIF technique to determine the recombination coefficient, γ_{Cl}, of atomic chlorine at the reactor walls from the rate of decay of the Cl density in the afterglow of a pulsed discharge. The signal to noise ratio is good enough to make measurements far into the afterglow (50 ms), when the gas has cooled to the wall temperature, making a precise measurements possible. We found that γ_{Cl} varies in the range 0.05-0.15, decreasing with increased pressure and RF power, and increasing with gas residence time. We show that the latter effect is due to the increased proportion of O_2 due to inevitable small air leaks: the presence of 0.5% O2 was shown to double the value of γ_{Cl}. The origin of the pressure and power dependencies will be discussed.

Work partly supported by Agence Nationale de la Recherche project INCLINE (ANR-09 BLAN 0019)

[1] K. Ono, T. Oomori, M. Tuda, and K. Namba, Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films, **10**, 1071, (1992).

11:00am **PS+SS-WeM10 Silicon Etching Characteristics by Hydrogen Halide Ions (HCl^+ and HBr^+) and Ions of Desorbed Species ($SiClx^+$)**, ***T. Ito***, *K. Karahashi*, Osaka University, Japan, *S.-Y. Kang*, Tokyo Electron Ltd., Japan, *S. Hamaguchi*, Osaka University, Japan

In recent reactive ion etching (RIE) processes for Si, halogen and hydrogen halide gases, such as Cl_2 and HBr, have been widely used to achieve high selectivity, etching anisotropy, and high etching rates. Furthermore, in some highly selective silicon etching processes, higher gas-pressure processes have been found to be more effective. In higher-pressure systems, chemical compounds formed from the input gas and some of desorbed species containing Si may serve as additional etchants. To develop etching equipments based on such plasma chemistry, it is important to understand basic etching reactions on silicon surfaces by energetic ion species associated with silicon and/or hydrogen containing species. To clarify the roles of SiClx, SiBrx, HCl, and HBr in silicon etching processes, we have employed a mass-analyzed ion beam system that can irradiate a sample surface with a specific ionic species under an ultra-high vacuum condition and evaluated the etching yields. The change in chemical nature of the substrate surface during the process can be observed in situ by X-ray photoelectron spectroscopy (XPS) installed in the reaction chamber. Time of Flight (TOF) measurement of species desorbed from the sample surface in a pulsed ion beam operation is also possible with the use of a differentially pumped quadrupole mass spectrometer (QMS). In this study, etching yields of silicon by Cl^+, $SiCl^+$, $SiCl_3^+$, Br^+, H^+, HCl^+, and HBr^+ ion beams were evaluated with incident energies of 100 – 1000 eV. A typical ion dose for each ion irradiation was 2– 4E17/cm2. Yields by some of these ionic species have been known and our etching yield data are confirmed to be in good agreement with the earlier data. It is found that, for a given incident energy, the etching yield by $SiCl_3^+$ ions is higher than that by Cl^+ ions whereas the etching yield by $SiCl^+$ ions is lower than that of Cl^+ ions, which may be accounted for by the number of Cl atoms and a possible deposition effect of Si. It has been also observed that deposition occurs under $SiCl^+$ ion irradiation when the injection energy is lower than 300eV. Energy dependence of etching yields and effects of hydrogen will be discussed in detail.

11:20am **PS+SS-WeM11 Interaction of Chlorine Plasma with Si_xCl_y Coated Plasma Reactor Chamber Walls**, ***R. Khare****, *A. Srivastava, V.M. Donnelly*, University of Houston

The interplay between chlorine plasmas and silicon chloride (Si_xCl_y) coated reactor walls has been studied by line-of-sight mass spectrometry in a radio frequency (rf) inductively coupled Cl_2 plasma (ICP), using the spinning wall method. A bare silicon wafer was etched in a 400 Watt Cl_2 ICP, with rf power applied to the stage resulting in a -110 VDC self-bias. Etch products were deposited on the plasma reactor walls and the rotating substrate surface, resulting in a thick layer of Si_xCl_y that was characterized *in situ* by Auger electron spectroscopy. Some oxygen also incorporated into the film due to erosion of the fused silica discharge tube. The reactions of chlorine plasmas with this prepared surface were then studied by line-of-sight mass spectrometry. Without substrate bias, the chlorine plasma etches the Si_xCl_y layer to form products that result in detection of $SiCl_x$ (x = 1-4) m/e components, as well as oxy-silicon-chloride products (m/e= 177, 247, 307, 361). In one experiment, after the deposition of dense Si_xCl_y layer on reactor and substrate surfaces, substrate rotation was stopped and the film was etched from the reactor walls with the chlorine plasma, leaving only the Si_xCl_y layer on 2/3rd of the substrate surface that was out of the plasma. Upon resuming rotation, and exposing the Si_xCl_y loaded surface to the Cl_2 plasma, $SiCl_x$ products were detected, but at suppressed levels, indicating that the evolution of etch products is a complex "recycling" process in which these species deposit and desorbs from the walls many times, and repeatedly fragment in the plasma. These and other experiments will be discussed. This work is supported by the National Science Foundation and Lam Research Corporation.

11:40am **PS+SS-WeM12 Numerical Simulation of Enhanced Oxygen Diffusion in Silicon as a Cause of Si Recess**, ***K. Mizotani***, *M. Isobe*, Osaka University, Japan, *M. Fukasawa, T. Tatsumi*, Sony Corporation, Japan, *S. Hamaguchi*, Osaka University, Japan

In a gate etching process, the formation of hollowed Si profiles around the polysilicon (poly-Si) gates, which is now widely known as "Si recess," has raised serious concern in the semiconductor processing community as such hollows on a Si surface can severely degrade the device performance and reliability. In a typical process that causes Si recess, a plasma based on HBr and oxygen gases are used to etch polysilicon gates anisotropically. A recent study [1] based on multiple-beam and plasma experiments has shown that Si recess is caused by ion assisted oxygen diffusion, i.e., oxygen diffusion enhanced by hydrogen ion injections. In this study, we have used molecular dynamics (MD) simulations to understand the mechanism of enhanced oxygen diffusion in Si under such conditions. In the simulations, energetic hydrogen ions and low-energy oxygen atoms (with kinetic energies close to room temperature) are simultaneously injected into a crystalline Si substrate initially covered with a native oxide layer. Simulation results are in good agreement with ion beam experiments

* Coburn & Winters Student Award Finalist

performed under similar conditions given in Ref. [1]. In our simulations, O atoms are transported into the bulk Si due to momentum transfer from energetic hydrogen ions. In other words, the enhanced ion transport is not typical “diffusion” associated with thermal motion in solid. However, random walk characteristics of O atoms in Si under such conditions are interestingly similar to those of diffusion. In this study, we relate this oxygen transport to diffusion transport and present its effective diffusion coefficient as a function of hydrogen ion injection energy.

[1] T. Ito, K. Karahashi, M. Fukasawa, T. Tatsumi and S. Hamaguchi, “Si recess of Poly-Si Gate Etching: Damage Enhanced by Ion Assisted Oxygen Diffusion,” Jpn. J. Appl. Phys. (2011) *in press*.

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