Atomic Scale Processing Mini-Symposium
Room Oregon Ballroom 203-204 - Session AP-TuP

Atomic Scale Processing Poster Session

AP-TuP-2 in-Situ Laser Diagnostics of Plasma Surface Interactions by fs-TALIF*, **Mruthunjaya Uddi,*** Advanced Cooling Technologies*; A. Dogariu,* Texas A&M University*; E. Kudlanov,* Advanced Cooling Technologies*; G. Urdaneta,* Texas A&M University*; Y. Xiao, D. Jensen, C. Chen,* Advanced Cooling Technologies

Plasma surface interaction has been a critical area of research for many applications such as Plasma-Enhanced Atomic Layer Deposition (PEALD). To meet the demanding needs of more advanced atomically controlled microfabrication methods, the physics of PEALD needs to be better understood to enable high quality, repeatable and controllable deposition process. Several challenges that need to be addressed regarding PEALD include damage to the substrate from highly energetic species and UV radiation, need for precise amorphous/crystalline modulated selective layer deposition, conformality in coating non-uniform substrates, achieving an aspect ratio of >100, repeatability and controllability of the finish. To address these challenges, we are developing laser diagnostics methods to measure species over substrates by advanced laser diagnostics such as femtosecond- Two-Photon Absorption Laser Induced Fluorescence (fs-TALIF) to image atomic species over substrates. Here we present measurements of N atom densities over a substrate with high spatial (< 10 microns) and temporal resolution (<1 ns) using fs-TALIF at pressures of 5-150 mTorr.

AP-TuP-3 Characteristics of Hydrogenated Amorphous Carbon Thin Films Fabricated by Plasma-Enhanced Chemical Vapor Deposition of Cyclohexane Precursor*, T. Poche, R. Chowdhury, **Seonhee Jang,*** University of Louisiana at Lafayette

The characteristics of the hydrogenated amorphous carbon (a-C) films can be determined by the composition of sp^3, sp^2, and sphybridized structures depending on the bond type of four valence electrons. The C-C bonds with sp^3, sp^2, and sp correspond to diamond, graphite/graphene, and carbyne, respectively. Mixed hybridization determines different carbon allotropes such as graphyne (sp and sp^2), nanotube and graphene quantum dots (sp^2 with sp^3), fullerene (sp^2 and sp^3), carbon dots (sp^3 with sp^2), and yne-diamond (sp and sp^3). Different mechanical, electrical, chemical, and optical properties are obtained depending on the mixture of sp^3, sp^2, and sp. For example, the sp^3 bond shows some advantages including mechanical strength, wide band gap, and chemical and electrochemical inertness, however it is unfavorable for a strip process after etching. The a-C films are characterized according to the composition ratios among a sp^3, sp^2, and hydrogen. When the hydrogen content is large, polymer-like a-C films can be formed with low film density due to high content of sp^3. When the hydrogen content is small, the content of sp^3 becomes low, resulting in a diamond-like a-C with high film density and hardness. When the hydrogen content becomes smaller, the content of sp^2 is high and a graphite-like a-C can be obtained. Depending on the deposition conditions, the sp^2/sp^3 hybridization ratio can vary over a wide range of values. The a-C thin films were fabricated by plasma-enhanced chemical vapor deposition (PECVD) of cyclohexane (CHex, C_6H_{12}) precursor. The a-C films were deposited at room temperature of 25 °C with a pressure of 26.7 Pa. The RF plasma power with 13.56 MHz was chosen from 20 to 80 W. The thickness, refractive index, and extinction coefficient of the a-C films were measured by ellipsometer. Surface morphology and roughness of the films were observed by atomic force microscopy (AFM). The functional groups of the films were identified using Fourier transform infrared (FTIR) spectroscopy. The FTIR spectrum consisted of C-H stretching, C-C stretching, and C-H bending modes. The C-H_x stretching peak at 3100-2800 cm^{-1} was deconvoluted to determine the bonding structure of hydrogen in the a-C films and the fractions of sp^3 CH_2 stretching and sp^3 CH_3 stretching modes was investigated depending on deposition parameters. The structural arrangement of the carbon bonds was analyzed by Raman spectroscopy and showed E_{2g} G and A_{1g} D breathing modes. The chemical composition of the films was determined by X-ray photoelectron spectroscopy (XPS). The deconvoluted C1s revealed sp^2 C=C and sp^3 C-C bonding peaks along with oxygen functional groups of C-O, C=O, and O-C=O.

AP-TuP-4 Fabrication Related Impurities Study of Aluminum Transition Edge Sensors*, **Ghadendra Bhandari,*** West Virginia University*; T. Stevenson, E. Barrentine,* NASA*; M. Holcomb,* West Virginia University

Superconducting aluminum-based microwave kinetic inductance detectors (MKID) are being developed to be used in space technology. These detectors operate at extremely low temperature regime which improves signal to noise ratio.We have studied the residues and adsorbates during different stages of the device preparation processes using x-ray absorption spectroscopy (XAS). We have observed oxidation and fluorination of aluminum during the fabrication process. We have observed aluminum oxidize as a-Al_2O_3 phase and fluorination at AlF_3. Additionally, we studied the effectiveness of residue removal processes with the help of reference samples.

AP-TuP-5 Plasma-Induced Surface Defects and Their Impact on the Surface Chemistry of Silicon Nitride and Silicon Carbonitride*, **Ting-Ya Wang**, G. Hwang,* University of Texas at Austin

As integrated circuits continue to shrink, the challenge of resistive-capacitive (RC) delay is becoming increasingly prevalent. Implementing low-κ dielectric materials using techniques such as atomic layer deposition (ALD) has become a popular approach to decreasing capacitance and improving film conformality. However, there are still many technical challenges that need to be addressed. Although plasma is widely used in semiconductor processing, it can negatively impact the achievement of high-quality low-κ materials.

A thorough understanding of surface structure and reactivity is essential. Currently available experimental methods are rather limited in their ability to study reaction mechanisms and non-invasively observe surfaces at the atomic level. Therefore, we have utilized computational methods, such as density functional theory (DFT) and Monte Carlo (MC), to investigate the underlying mechanisms of ALD, with a focus on silicon nitride (SiN) and silicon carbonitride (SiCN) thin films.

Based on DFT calculations, we have identified several active sites induced by plasma irradiation. For N_2 plasma treatment, previous studies are mainly focused on under-coordinated sites such as >Si=N- site, while other potential surface sites remain incompletely understood. Our work demonstrates that N_2 dimers can also act as reactive sites towards Si precursors. Moreover, we have found that under-coordinated Si and N defects can exhibit different electronic states and thus significantly different reactivity. In addition, plasma treatment can trigger bridging reactions that produce Si-N=C=N-Si bridges, which could also be active sites.

Different types of precursors, depending on the presence of carbon and chlorine, are commonly used to grow SiN or SiCN thin films. However, experimental studies have shown that precursors have different favorability over the reactive surfaces created by different plasmas. To better understand the phenomena, we have investigated the mechanisms underlying the reactions between various surface defects and these precursors. Moreover, we will also briefly touch our recent efforts of using DFT results as input data for MC simulations to investigate the coverage of these surface defects and how they affect the surface chemistry involved in plasma-enhanced ALD.

AP-TuP-6 Electron Heating Mode Changes in Plasma Sources Used for Atomic Precision Processing*, **David Boris,*** U.S. Naval Research Laboratory*; M. Johnson,* Huntington Ingalls Industries*; J. Woodward, V. Wheeler, S. Walton,* U.S. Naval Research Laboratory

The inclusion of plasma in plasma enhanced atomic layer deposition (PEALD) applications generally offers the benefit of substantially reduced process temperatures, greater flexibility in tailoring the gas-phase chemistry to produce desired film characteristics, and the ability to affect film crystallinity and phase.

Many PEALD systems use inductively coupled plasma (ICP) sources in materials synthesis.These sources can undergo changes in electron heating modes which can be induced by changes in applied power, pressure, or gas phase chemistry. Generally, these mode changes cause substantial variations in the electron energy distribution function and plasma density, which can impact the delivery of reactive and energetic species to substrates. This presentation explores the effects of heating mode changes on reactive species production and downstream plasma parameters (electron temperature, plasma potential, and plasma density).We discuss the use of probes and optical emission spectroscopy to characterize changes in the plasma parameters and how these changes affect the delivery of reactive and energetic species to the material surface. The discussion will include the results from select processing applications, where changes in plasma properties are linked to differences in material properties.This work supported by the Naval Research Laboratory Base program

AP-TuP-7 $NaHF_2$ as an Alternative Hydrogen Fluoride (HF) Source for Thermal Atomic Layer Etching and Deposition*, **Marcel Junige**, R. Hirsch, V. Ghodsi, S. George,* University of Colorado Boulder

Thermal atomic layer etching (ALE) and deposition (ALD) are defined by an alternating sequence of separate, self-limiting surface reactions. ALE modifies and volatilizes a thin film surface, thereby removing ultra-thin layers of material. ALD adsorbs a precursor and, depending on the co-reactant, adds ultra-thin layers of film material. ALE and ALD processes have been developed for a wide range of film materials, including metals and semiconductors, as well as their oxides, nitrides, and fluorides. ALE and ALD provide precise control of shrinking critical dimensions, conformality in complex 3D structures, and wafer-scale uniformity.

A vital step for ALE and ALD is the fluorination reaction using hydrogen fluoride (HF). For example, thermal ALE of alumina (Al_2O_3) cycles between HF to fluorinate and trimethylaluminum (TMA) to ligand exchange at elevated temperatures. Thermal ALD of aluminum fluoride (AlF_3) also cycles between TMA adsorption and HF to remove methyl groups and form AlF_3 below 250℃. One problem with HF is that its toxicity presents a challenge to health and safety. To address safety concerns, solvents may reduce the HF vapor pressure. For example, a 70% HF in 30% pyridine solution, commonly known as Olah's reagent, is used by organic chemists for fluorination reactions.

Other thermal ALE processes have also widely employed HF-pyridine. However, care is required during handling in a glovebox. Further difficulties are encountered in cleanup and waste management. To address these issues, this study tested sodium bifluoride ($NaHF_2$), a salt that was safer to handle because $NaHF_2$ exhibits negligible HF vapor pressure at room temperature. When heated to 150℃, $NaHF_2$ delivered HF vapor pressures up to 15 Torr. In addition, this solid salt was easier to clean up and reduced waste.

HF volatilization was observed by temperature-ramped quadrupole mass spectrometry. ALE experiments were conducted in a hot-wall, viscous-flow vacuum reactor equipped with an *in situ* spectroscopic ellipsometer. Thermal Al_2O_3 ALE using sequential HF/TMA exposures served as a standard reference to evaluate $NaHF_2$. HF from $NaHF_2$ exhibited diffusion-limited fluorination of Al_2O_3 and an etch per cycle consistent with previous results using HF-pyridine. X-ray photoelectron spectroscopy detected no sodium on the surface after ALE, indicating that sodium fluoride remained in the source cylinder. These studies indicated that $NaHF_2$ can be considered as an alternative HF source for fluorination reactions in thermal ALE or ALD on the laboratory scale.

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