

Wednesday Afternoon, November 15, 2006

Advanced Surface Engineering Room 2007a - Session SE2-WeA

Pulsed Plasmas in Surface Engineering

Moderator: M.J. Brett, University of Alberta Edmonton

3:40pm **SE2-WeA6 In-Situ Ellipsometric Studies of HPPMS Deposited Chromium Thin Films**, *S.L. Rohde, J. Li, S.R. Kirkpatrick*, University of Nebraska-Lincoln

Chromium thin films have been deposited using high power pulsed magnetron sputtering (HPPMS). In order to study the sputter etch conditions used to clean surfaces prior to depositions of hard coatings, the films were deposited for 30 minutes with a base pressure of 3mTorr and a large DC substrate bias of -1000V. The substrate bias was run in both the on (-1000V) and off condition and an unbalanced magnetic coil current was run at both 0 and 5 A to observe their effect on the process. The deposition process was monitored at the substrate using a 44 wavelength ellipsometer. Deposition rates varied between 0.5 and 1 Angstroms/second as measured by ellipsometry and confirmed with profilometry. Ellipsometric data indicates initial island growth followed by layer growth. Ellipsometry also indicates increasing roughness during the deposition at about 1 Angstroms/minute. Lower roughness rates and slower deposition rates resulted with magnetic coil assisted depositions.

4:00pm **SE2-WeA7 Plasma Spectroscopy of Carbon Nanotubes**, *J.G. Jones, C. Muratore, A.R. Waite, A.A. Voevodin*, AFRL/MLBT

Carbon nanotubes (CNTs) have unique properties of thermal and electrical conductance, as well as structural properties. Samples of vertically aligned CNTs on silicon substrates were plasma treated in different background gas environments including argon/hydrogen, and argon/nitrogen for the purposes of functionalization. A high power pulsed plasma treatment was used to modify CNT surface by attaching N and H atoms. In situ spectroscopy was used to detect atomic and molecular excitation for each of the background gas environments including mixtures of argon/hydrogen, pure hydrogen, pure nitrogen and argon/nitrogen. The result demonstrated the presence of both atomic and ionized species at the vicinity of the CNT sample surfaces. In situ X-ray photoelectron spectroscopy (XPS) was performed on the treated samples to determine the chemical bonding structures, both before and after treatment. The analyses shows formation of both C-N and C-H bonds for CNT surfaces. Correlations of the plasma characteristics and chemistry and bonding of the modified CNT surfaces is discussed for different environments pulsed plasma process settings.

4:20pm **SE2-WeA8 Pulsed RF PECVD of a-SiN_x:H Alloys: Film Properties, Growth Mechanism and Applications**, *R. Vernhes, O. Zabeida, J.E. Klemberg-Sapieha, L. Martinu*, Ecole Polytechnique of Montreal, Canada

In PECVD of thin films, control of plasma chemistry and plasma-surface interaction during the growth are critical for the tailoring of film composition and microstructure. In this context, pulsing the plasma provides additional parameters (frequency, duty cycle) to control the deposition process, while decreasing the thermal load on the substrate. In this work, we present the pulsed PECVD of a-SiN_x:H alloys, the films' properties being varied simply by adjusting the duty cycle of the RF power, while keeping the N₂/SiH₄ gas mixture constant. Spectroscopic ellipsometry analysis in the UV-VIS-NIR and FIR ranges, atomic force microscopy, and elastic recoil detection reveal strong variations of optical properties (1.88 ≤ n ≤ 2.75, 10⁻⁴ ≤ k ≤ 5 × 10⁻² at 550 nm), microstructural characteristics (1.3 nm ≤ surface roughness ≤ 8.3 nm), and chemical composition (0.3 ≤ x ≤ 1.3) of the coatings as a function of duty cycle. This behavior is interpreted in terms of radical concentration changes in the gas phase and variations of the average ion bombardment energy at the film surface, leading to modifications of the growth mechanism. Using this process, we fabricated two types of a-SiN_x:H-based thin film devices, namely (i) a high-quality Fabry-Perot optical filter deposited on plastic substrate without monitoring, and (ii) a superlattice structure displaying a photoluminescence signal four times higher than the reference single layer. These two examples of applications point out the main advantages of this pulsed RF PECVD process, in particular low deposition temperature, reproducibility, versatility and ease of use.

4:40pm **SE2-WeA9 The Role of Oxygen Impurities in Anisotropic Etching of Crystalline Silicon by Atomic Hydrogen, and in the Deposition of Single-Phase Nanocrystalline Silicon**, *S. Veprek*, Technical University Munich, Germany; *Ch.L. Wang*, Consultant; *M.G.J. Veprek-Heijman*, Technical University Munich, Germany

Nanocrystalline silicon, nc-Si (and germanium) was originally prepared by means of chemical transport in hydrogen plasma, which combines the etching of silicon in the charge zone with the formation of monosilane as the main product, Si(s) + 4H → SiH₄, and the decomposition reaction SiH₄ → nc-Si + 2H₂ in the deposition zone. The etching rate is highest at a temperature of about 60-80 °C and it strongly decreases to essentially zero above 350 °C. After a sufficiently long dwell time, partial chemical equilibrium with monosilane concentration of about 0.3 - 0.5 mol.% is established in glow discharge hydrogen plasma at a temperature of 40 - 80 °C, regardless if monosilane, or solid silicon and hydrogen are used as reactants. In the present paper we shall show, that minor oxygen impurities of about 5 - 10 at. ppm (atomic parts per million) strongly decrease the reaction rate, and above 50 - 60 ppm of oxygen this reaction cannot occur. The etching by atomic hydrogen is isotropic below about 5 ppm of oxygen impurities, whereas controllable addition of a few 10 ppm of oxygen in combination with negative bias to the crystalline silicon results in highly anisotropic etching with thin oxide acting as sidewall passivation. Oxygen impurities also hinder the formation of single-phase nc-Si and cause occurrence of a significant fraction of a-Si in the deposited films. Oxygen impurities of about > 0.5 at. % in the hydrogen plasma can completely hinder nc-Si to form. In a pure hydrogen glow discharge plasma, single-phase nc-Si without any detectable a-Si tissue can be deposited under conditions close to the partial chemical equilibrium. S. Veprek and V. Marecek, Solid-State Electronics 11(1968)683. S. Veprek and A. P. Webb, Chem. Phys. Lett. 62(1979)173. Z. Iqbal, A. P. Webb and S. Veprek, Appl. Phys. Lett. 36(1980)163. J. J. Wagner and S. Veprek, Plasma Chem. Plasma Process. 2(1982)95.

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