Plasma Science and Technology
Room 314 - Session PS1-ThM

Plasma-Surface Interactions: Deposition

Moderator: S.M. Han, University of New Mexico

8:20am **PS1-ThM1 Reactive Sputtering of Metallic Tin in a Mixture Ar - O2 : Comparison between an Amplified and a Classical Magnetron Discharge***, R. Snyders,* Mons-Hainaut University, Belgium

Industrially, magnetron sources are widely used for coating and surfaces treatments. The problem encountered by "classical" magnetron sputtering is the shadowing effect when complex substrates have to be treated. Neutral particles arrive on the substrate surface with a broad angular distribution of trajectories and as a consequence the deposited film is of poor quality. Ionizing the sputtered particles can solve this problem. Velocity control and normal trajectory of the ionized species can be achieved by applying a bias voltage to the substrate. For that purpose, a R.F. (13.56 MHz) power supplied copper coil (diameter of 4 cm) has been set up, between the DC tin magnetron target and the substrate holder. The applied R.F. power used to create the secondary plasma can be raised up to 200 W. The aim of this work is to estimate the RF coil influence on the chemical behaviour of both the discharge and the films during the deposition of SnOx thin films in a mixture Ar - O2. During the deposition, the discharge is characterized by the target voltage, the deposition rate and glow discharge mass spectrometry whereas the prepared films compositions are obtained from in-situ XPS measurements. During the work, we have observed the influence of both the gas mixture composition and the RF power on the discharge and on the films. By increasing the RF power on the coil, we have observed on both the plasma and the films compositions an increase of the oxidation level for the same ratio O2 / Ar. On the other hand, the metal â€" compound transition at the target, observed on the discharge voltage and on the deposition rate measurements are not influenced by the coil. So, using the RF coil the films oxidation can be reached at lower reactive gas flow and consequently at higher deposition rate.

8:40am **PS1-ThM2 Selective Plasma-induced Deposition of Fluorocarbon Films on Metal Surfaces for Actuation in Microfluidics***, P. Bayiati,* ***A. Tserepi****, E. Gogolides, K. Misiakos,* National Center for Scientific Research (NCSR) "Demokritos", Greece

Plasma-induced deposition of polymer films on surfaces is an important issue in etching plasmas, since on one hand it allows selective etching of materials,@footnote 1@@footnote 2@ while on the other it provides side wall passivation necessary for anisotropic high-aspect ratio etching. The present work focuses on the selective deposition of fluorocarbon (FC) films on metal surfaces, specifically on aluminum, over SiO@sub 2@ surfaces, in order to obtain surfaces of distinct wettability. If, in addition, the wettability of the modified metal surface can be controlled electrostatically and consequently the surface be varied from a hydrophobic to a hydrophilic one, such plasma-modified metal surfaces can be used as electrodes employing electrowetting for actuation of fluid transport in microfluidic devices.@footnote 3@ Since polymer layers on surfaces are easily formed in fluorocarbon discharges with high concentrations of radical CFx species, fluorocarbon gases such as C@sub 4@F@sub 8@ and mixtures of CHF@sub 3@/CH@sub 4@ were used in our experiments. For the selection of conditions appropriate for selective deposition of FC films on Al over SiO@sub 2@, plasma parameters such as plasma power, bias voltage, electrode temperature, and gas composition were varied. The wettability of SiO@sub 2@ and Al surfaces exposed to FC plasmas under different plasma deposition conditions was characterized by contact angle measurements (without and with voltage application). Contact angles as a function of the applied voltage were used to yield the thickness of the FC film deposited on Al, and to indicate the breakdown voltage for the films under consideration. The results demonstrate the feasible use of such plasma-deposited films on Al for electrostatic actuation with application of relatively small voltages (less than 10 V). @FootnoteText@ @footnote 1@G. Oerlein, Surface Science 386, 222 (1997); and G. Oerlein et. al., J.Vac. Sci. Technol. A 12(2), 333 (1994).@footnote 2@L.Rolland, M.C. Peignon, Ch. Cardinaud, G. Turban, Microel. Engin. 53, 375 (2000).@footnote 3@M. Pollack, R. Fair, A. Shenderov, Appl. Phys. Lett. 77(11), 1725 (2000).

9:00am **PS1-ThM3 Deposition of Transparent Tin Oxide Films by PECVD on Polymers***,* ***F. Arefi-Khonsari****, J. Pulpytel,* Laboratoire de Genie des Procedes Plasma et Traitement de Surface ENSCP, France*; H. Cachet,* UPR15-CNRS, France **INVITED**

Transparent conductive tin oxide films have been deposited at low temperature(< 50°C) from a mixture of O@2sub@/Ar/TMT on two substrates for two different applications : 1) biofouling reduction for underwater instrumentation on polymer windows and 2)as sensitive layers of gas microsensors on silicon wafers. In order to obtain carbon free tin oxide films, mass spectrometry was performed by using a calibration mixture composed of inert gases. The latter allowed us to determine the molar fraction of the stable species produced in the discharge, such as CO & CO@2sub@ namely those which witness the carbon etching of the organometallic precursor. For this study the role of the two major parameters i.e. power and oxygen partial pressure in the reactor have been studied. The biofouling reduction was based on seawater electrolysis at the optical surface for producing active chlorine species. In order to limit the ageing effect of tin oxide films deposited on polymers, they were doped with fluorine atoms which gave rise to higher conductivities and limited also the ageing effect. Precursors such as SF@6sub@ and C@4sub@F@6sub@ were introduced in the plasma mixture in order to dope the tin oxide films in a one step process. In the case of SF@6sub@, an increase of the electrical conductivity and charge carriers were obtained for very small flow rates of SF@6sub@ introduced in the discharge. For higher flow rates, a sharp decrease of the conductivity was observed. For such flow rates, competitive etching and functionalization processes, assisted by fluorine atoms present in the discharge, took place giving rise to a sharp decrease of the deposition rate and the incorporation of Sn-F and C-F bonds in the deposited films. This has been explained by the formation of new species such as S O@2sub@, SOF, SOF@2sub@ and HF. Oxygen being consumed to form such species, it is much less involved in forming CO, CO@2sub@ and H@2sub@O species, therefore leading to the incorporation of carbon species in the deposit which explains the sharp decrease of the conductivity of the films.

10:20am **PS1-ThM7 Temperature Dependence of the SiH@sub 3@ Surface Reactivity During Plasma Deposition of a-Si:H Studied by Time-resolved CRDS***,* ***J.P.M. Hoefnagels***[1]*, Y. Barrell, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

The surface reactivity of SiH@sub 3@ - the dominant radical during deposition of hydrogenated amorphous silicon (a-Si:H) from SiH@sub 4@ plasmas - has been investigated to obtain information on the elemental surface reactions during a-Si:H film growth. To do so, we have measured the surface reaction probability @beta@ of SiH@sub 3@ for substrate temperatures in the range of 50-450 °C by means of the novel time-resolved cavity ringdown spectroscopy (@tau@-CRDS) method. In this method, the highly-sensitive CRDS absorption technique is used to map the temporal decay of the SiH@sub 3@ radical density (probed at the Ã@super 2@A@sub 1@'<-@td X@@super 2@A@sub 1@ transition) after a minor periodic modulation of the density during regular plasma operation. From measurements of the SiH@sub 3@ loss time versus the SiH@sub 4@ partial pressure, it has been verified that SiH@sub 3@ is not lost by gas phase reactions, as is, e.g., the case for the Si radical. The surface reaction probability of SiH@sub 3@ has been deduced for different substrate temperatures from the pressure dependence of the SiH@sub 3@ loss time using information on the gas temperature and the diffusion of SiH@sub 3@ towards the surface. The gas temperature - determined from Doppler broadening of Si absorption lines - is ~1500 K and is unaffected by the substrate temperature. This procedure has revealed that the surface reaction probability of SiH@sub 3@ is independent of the substrate temperature with a value of @beta@=0.30±0.03. For comparison, the surface reaction probability of Si has been determined for 200 °C and is very close to unity (0.95<@beta@@<=@1). These observations will be discussed in terms of the contribution of different plasma radicals to film growth and the possible SiH@sub 3@ surface reactions taking place. The results suggest a two-reaction step growth mechanism for a-Si:H with a temperature-independent abstraction reaction of H from the surface as the rate-limiting step.

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[1] **PSTD Coburn-Winters Student Award Finalist**

10:40am **PS1-ThM8 Creation of SiOF Films with SiF@sub 4@/O@sub 2@ Plasmas: from Gas-Surface Interactions to Film Formation***, **J. Zhang**, E.R. Fisher,* Colorado State University

Fluorinated SiO@sub 2@ (SiOF) films have been studied because of their relatively low dielectric constant and their potential as a replacement for SiO@sub 2@ in the microelectronics industry. Despite the intense scrutiny, many of the details of the mechanisms for SiOF film deposition remain unclear. Here, we deposited SiOF films using SiF@sub 4@/O@sub 2@ plasmas. The plasma parameters of SiF@sub 4@ percentage in the feed gases (%SiF@sub 4@) and applied rf power (P) were studied as well as the effects of ion bombardment and substrate temperature on film deposition. Fluorine incorporation in the film increases with increasing %SiF@sub 4@ and P. Film deposition rate also increases with P, whereas its dependence on %SiF@sub 4@ is more complex. Ion bombardment decreases the film deposition rate and affects film composition significantly. On the molecular level, we examined the surface reactivity of SiF and SiF@sub 2@ during SiOF film deposition using the imaging of radicals interacting with surfaces (IRIS) technique. SiF shows high surface reactivity, R, which varies from 0.95 ± 0.08 to 0.60 ± 0.07, depending on plasma parameters. In contract, SiF@sub 2@ shows significant surface production. The scattering coefficient, S, varies from 1.12 ± 0.08 to 2.52 ± 0.16. The surface interactions of SiF and SiF@sub 2@, along with plasma gas-phase composition, were correlated with film characteristics to reveal the possible film-deposition processes.

11:00am **PS1-ThM9 Study of Fluorocarbon Deposition Mechanism with a Small Gap Structure in Fluorocarbon Plasmas***, **L. Zheng**, X. Li, X. Hua, L. Ling, G.S. Oehrlein,* University of Maryland, College Park*; E.A. Hudson,* Lam Research Corp.

We designed a small gap structure to study the deposition of fluorocarbon film in a high aspect ratio feature in an inductively coupled rf plasma (ICP) reactor in an effort to provide information on fluorocarbon film formation mechanisms for highly selective dielectric etching processes. The small gap structure exhibits three regions for fluorocarbon film formation: A region exposed to the full plasma, transition region and a completely shadowed region where only long-lived species can arrive after multiple collisions with the walls. Both in situ (real time) and external He-Ne ellipsometers were used to monitor the deposition rate of the fluorocarbon film on the base wafer. X-ray photoelectron spectroscopy (XPS) was used to analyze the detailed surface chemistry of the fluorocarbon film. CFx (x = 1-3) radicals produced in fluorocarbon discharges act as precursors for the formation of fluorocarbon film. Effects of different gases (C4F8, C4F6), Ar addition, gap height, pressure on refract index and deposition rate of the fluorocarbon film in the three regions were studied and a simple model based on Knudsen diffusion mechanism was developed to describe the fluorocarbon film deposition in the completely shadowed region. We also will describe an equivalent set of studies performed in a 40 MHz (source power) - 13.56 MHz RF (bias power) dual frequency capacitively coupled system.

11:20am **PS1-ThM10 Plasma Chemistry and the Growth Kinetics of Silicon Nitride Deposited by the SiH@sub 4@-N@sub 2@ Reactant Mixture***, **F.J.H. Van Assche**, J. Hong, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Plasma ions and radicals in a remote plasma operated on an Ar-H@sub 2@-N@sub 2@-SiH@sub 4@ mixture have been studied by several diagnostics such as Langmuir probe measurements, ion mass spectrometry, cavity ringdown spectroscopy, and threshold ionization mass spectrometry. It is shown that the H radicals that emanate from the plasma source react with the SiH@sub 4@ admixed downstream and create a high SiH@sub 3@ density. Si and SiH radicals have also been measured but they have a much lower density in the downstream plasma. Ground-state N radicals emanating from the plasma source do not react with the SiH@sub 4@ injected downstream leading to a high N density under the silicon nitride deposition conditions. This has lead to the conclusion that N and SiH@sub 3@ radicals dominate the silicon nitride growth process as has also been confirmed by the correlation between the SiH@sub 3@ and N density in the plasma and the incorporation flux of Si and N atoms into the silicon nitride films. Furthermore, from this correlation very reasonable sticking probabilities of the N and SiH@sub 3@ radicals have been obtained. >From these results, the following kinetics for silicon nitride growth from the N@sub 2@-SiH@sub 4@ reactant mixture are proposed: During deposition an amorphous silicon-like surface layer is created by the SiH@sub 3@ radicals and simultaneously this amorphous silicon-like surface layer is nitridated by the N radicals leading to silicon nitride formation. Further support for this mechanism is obtained by experiments in which silicon nitride films have been created by exposing amorphous silicon films to a high flux of N radicals.

11:40am **PS1-ThM11 Molecular Dynamics Simulations of Organic Polymer Etching by H@sub 2@/N@sub 2@ and NH@sub 3@ Plasmas***, **H. Yamada**, S. Hamaguchi,* Kyoto University, Japan

Using classical molecular dynamics (MD) simulations, plasma-surface interactions have been investigated for organic polymer etching processing with H@sub 2@/N@sub 2@ and NH@sub 3@ plasmas. To perform MD simulation in such systems, we have developed an interatomic potential model applicable to systems consisting of H, C, and N atoms [i.e., (H,C,N) systems]. Further we have also worked with the Abel-Tersoff-Brenner (ATB) potential proposed for (H,C) systems. Reducing the dielectric constants of insulating materials for interconnect circuits is of significant importance for the manufacturing of fast computer chips based on the copper wiring. For this purpose, organic polymers with low dielectric constants (i.e. low-k) have been studied recently as an alternative to SiO@sub 2@. In addition to such use, organic polymers have been studied for other applications, for example, substrates of healthcare chips and optical waveguides. Hydrogen and nitrogen based plasmas such as N@sub 2@+H@sub 2@ or NH@sub 3@ plasmas are often used to etch such polymer surfaces with micron and submicron structures. The goal of this work is to study plasma-surface interactions of polymer etching process, using classical MD simulations. To represent surface reactions correctly, it is critical to employ realistic interatomic potential functions for MD simulations. In this work, therefore, we present interatomic potential functions for (H,C,N) systems, extending the Stillinger-Weber potential with some modification such as the inclusion of double and triple bonds. To compare simulation results with our potential model with those with other potential models, we have also run MD simulations with the ATB potential. Because many low-k organic polymers contain Benzene-like rings, we use poly (1,4-phenylene) as our model substrate. Preliminary results of the MD simulations will be presented.

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