Tuesday Evening Poster Sessions, November 14, 2006

Plasma Science and Technology
Room 3rd Floor Lobby - Session PS3-TuP
Advanced Plasma Deposition Poster Session

PS3-TuP1 Room Temperature Crystallization of Amorphous Thin Films using RF Plasma, ***Y. Shibayama***, *M. Suzuki, A. Kinbara, T. Watanabe, H. Ohsaki,* The University of Tokyo, Japan

Crystallization of amorphous thin films was achieved by using a RF plasma treatment. Sol-gel TiO@sub 2@ / Si wafer, sputtered ITO / glass and sputtered Si / glass are crystallized by 2 minute-treatment and the sample temperature is lower than 150°C during the plasma treatment. Sol-gel derived TiO@sub 2@ films with about 66% packing density was densified to 91% and crystallized into anatase. Plasma-crystallized anatase films show photo-induced super-hydrophilicity and photocatalytic activities while as-coated sol-gel TiO@sub 2@ does not indicate such phenomena. Amorphous ITO films were deposited on soda-lime glass with alkali-barrier silica film without substrate heating. Resistivity of ITO films decreased by the plasma treatment and the surface of the ITO films was kept smooth after the treatment. Amorphous Silicon film including a small amount of randomly orientated crystallites were prepared by sputter method and XRD peaks grew by the plasma treatment with keeping the XRD peak height ratios almost the same as ones of polycrystalline Silicon. Amorphous Silicon films with preferred oriented crystallites were also prepared by sputter method. It can be concluded from XRD analyses that the plasma treatment realizes preferential crystal growth. In the presentation, the details of this plasma crystallization technology will be presented.

PS3-TuP2 Formation of Ultra Water-Repellent Thin Films in Organosilane Plasma by PECVD Method, ***Y.S. Yun***, *T. Yoshida, N. Shimazu, Y. Inoue, N. Saito, O. Takai,* Nagoya University, Japan

Ultra water-repellent films, inspired by water-repelling lotus leaves, have been attracted over the last few years to both fundamental research and practical applications. We have succeeded in fabricating ultra water-repellent thin films at room temperature by microwave plasma enhanced CVD using organosilicon compounds as raw materials. However, activated reactions in the PECVD process are too complicated to make clear its deposition mechanism. In this study, we investigated reactions in organosilane plasma by using optical emission spectroscopy and mass spectrometry in order to understand the formation reaction of ultra water-repellent thin films in the PECVD process. Surface morphology, chemical composition and bonding states of the films were analyzed. From the results, we found that there are several stages in formation of ultra water repellent thin films. That is, at the first stage of the growth, the nano-clusters seem to fall randomly on the surface. These clusters probably originate from a polymerization process in the gas phase and deposit on the substrate. When the film was deposited for several tens of seconds, the nano-clusters show a tendency to form chains or islands, which means the clusters must have a spatial preference. Finally, these films have particular nano-textures with nano-scale pores of a few hundreds nanometer in size among the cancellous web-like structure of the nano-cluster agglomerates. The rough surface of the films results in the water contact angles greater than 150 degree.

PS3-TuP3 Controlling the Fluxes of Carbon Supply for Carbon Nanotube Growth in CH@sub 4@/H@sub 2@ Plasma, ***A. Okita***, *Y. Suda, A. Ozeki,* Hokkaido University, Japan*; A. Oda,* Nagoya Institute of Technology, Japan*; J. Nakamura,* Tsukuba University, Japan*; K. Bhattacharyya, H. Sugawara, Y. Sakai,* Hokkaido University, Japan

Carbon nanotubes (CNTs) exhibit unique properties such as high chemical stability and current density. We are interested in LSI applications of CNTs utilizing their electronic properties. However, LSI technology demands the precisely control of CNTs growth with regard to placement, length, diameter and number density. We have focused on the growth speed of CNTs in order to fulfill the above demands. The purpose of this paper is to investigate the growth speed of CNTs by controlling the fluxes of carbon source. We have used plasma-enhanced chemical vapor deposition (PECVD) for CNT growth.@footnote 1@ PECVD can effectively decompose gas molecules and produce the precursors for CNTs such as ions and radicals. In this experiment, Al@sub 2@O@sub 3@/Fe/Al@sub 2@O@sub 3@ (1/1/1 nm) thin films were used as catalyst (Fe)/support (Al@sub 2@O@sub 3@) materials, and vertically-aligned CNTs were obtained using CH@sub 4@/H@sub 2@ plasma. The degree of catalyst activities and oxidation states were observed by X-ray photoelectron spectroscopy (XPS), and CNTs obtained were evaluated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).@footnote 1,2@ In addition, CH@sub 4@/H@sub 2@ plasma was simulated by one-dimensional fluid model to analyze the correlation with the CNTs growth and plasma gas phase.@footnote 1@ This simulation results correlating to experimental condition enable us to predict the fluxes of carbon-containing species onto the substrate. As the results, average length of CNTs became shorter by applying positive DC bias to the substrate. We will discuss the effect of bias voltage on CNT growth speed and compare the simulation results in terms of the difference of fluxes of carbon-containing species. @FootnoteText@@footnote 1@A. Okita, et al., J. Appl. Phys. 99 (2006) 014302, @footnote 2@A. Okita, et al., Jpn. J. Appl. Phys., (accepted).

PS3-TuP4 Pulsed PECVD Processes with E-beam Generated Plasmas, ***D. Leonhardt***, *S.G. Walton,* US Naval Research Laboratory

Plasma enhanced chemical vapor deposition (PECVD) processes open up wide parameter spaces (most notably lower substrate temperatures) than CVD techniques. This is because the plasma electrons can directly impart energy into the gas species on the order of 1 eV (> 10,000 K) instead of relying on strictly thermal surface processes. Modulated plasmas in turn can provide even greater control over the deposition conditions by tailoring a gas/surface phase synergy to achieve optimum growth conditions for the desired films. This work will discuss recent progress on PECVD of Si-based films using pulsed electron beam generated plasmas with organic precursors such as TEOS and HMDSO. In these systems, pulse lengths were varied from below 1 millisecond to multiple milliseconds to determine the effects of less total power being imparted to the plasma and gas constituents. Shorter pulse lengths, comparable to gas and surface phase reaction times were expected to have a significant effect on the process deposition rate and the final film quality. These film characteristics will be discussed and compared with complementary time-resolved ion flux measurements (in situ mass spectrometry) and global plasma parameters (from electrostatic probes). Films compositions were varied from SiO@sub x@, SiN@sub x@, and polymeric Si-O complexes, tailored for display applications on flexible substrates (low temperature, low damage) and large area capacitor fabrication. @FootnoteText@ This work supported by the Office of Naval Research.

PS3-TuP5 Diagnostics of Microwave Plasmas Applied for Organic Layer Deposition, ***S.F. Dribinskiy***, *G. Franz,* Munich University of Applied Sciences, Germany*; D. Voss,* Plasma-Parylene Coating Services, Germany

Polyparylene, a non-critical, non-toxic layer material for long-term applications in the human body, has been deposited by plasma-enhanced chemical vapor deposition of the monomeric species. For that end, a microwave discharge in a pulsed mode has been applied. Important plasma parameters have been evaluated by simultaneous application of Langmuir probe and trace rare gas optical emission spectroscopy. Plasma densities and electron temperature have been found to cover values from an almost dark Langmuir plasma up to 10@super 10@/cm@super 3@ and between 1 and 3.5 eV, respectively. Differences in electron temperature between the two methods were less than 20 %. Due to the skin effect which is already effective beyond plasma densities of some 10@super 9@/cm@super 3@, the plasma is spatially inhomogenous which has been taken care of by measuring at three different positions with the Langmuir probe. Entering from the radially outmost position, the inverted V-shape profiles for plasma density and electron temperature peak in the border reagion. This holds true for argon and parylene. However, the plasma density in parylene is lower by a factor of nearly 10 indicating that this molecule and/or its fragments exhibit a strong power for electronic attachment. The skin effect is also responsible for the decreasing plasma density with growing discharge pressure. Finally, the decay constant has been determined and modeled.

PS3-TuP6 Behavior Analysis of Various Organosilicon Molecules in PECVD Processes, ***T. Yoshida***, *Y.S. Yun, N. Shimazu, Y. Inoue, N. Saito, O. Takai,* Nagoya University, Japan

Plasma enhanced chemical vapor deposition (PECVD) using organosilicon reactants are one of the most promising deposition processes because of its ability to prepare several functional films such as low-k films for semiconductor devices and ultra water-repellent coatings.ã??Although large number of studies has been made on the relations between film properties and functions, fewer studies has been devoted to the plasma itself. Therefore, the behavior of organosilicon molecules in PECVD processes has been poorly understood. To control the film property, it is absolutely imperative to clarify the behavior of organosilicon molecules. In this study, we investigate the behavior of reactant organosilicon molecules

in plasma by means of Optical emission spectroscopy (OES), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and other analysis. The hydrocarbon-doped silicon oxide films were prepared with an inductively-coupled rf PECVD system. Trimethylmethoxysilane (TMMOS), hexamethyldisiloxane (HMDSO) and hexamethylcyclotrisiloxane (HMCTS) are used as reactants. Si(100) substrates were kept at around room temperature during deposition. The OES of HMDSO and HMCTS plasmas were very similar and are dominated by H, H2 and CH emissions. On the other hand, we could observe not only H, H2 and CH but also CO and OH emissions in TMMOS plasma. It propose that the oxygen atoms of methoxy groups in TMMOS molecules can be dissociated easily in the plasma and behave as a kind of oxidizing agent whereas siloxane bondings in HMDSO and HMCTS are hardly expel oxygen atoms.

PS3-TuP7 Amorphous Carbon Coating Mixed with Nano Crystalline Diamonds*, **N. Sakudo**, N. Ikenaga, Y. Tashiro, A. Sakamoto,* Kanazawa Institute of Technology, Japan

We have developed new carbonic coating that can be applied to machine tools and dies. The coating, which we named hybrid nano-diamond coating, consists of multi layers with nano crystalline diamonds and amorphous carbon that is so-called DLC (diamond like carbon). Usually pure diamond coating had been carried out at a high substrate temperature of around 1000 K by microwave plasma CVD (chemical vapor deposition) using methane diluted with hydrogen. On the other hand, pure DLC coating had been carried out at a lower substrate temperature than 500 K by PVD (physical vapor deposition) using hydrocarbon gases like ethylene, ethane, acetylene and so on. In order to make the new carbonic coating on low temperature substrate, we constructed an apparatus that has two different plasma generators. One is a 2.45 GHz microwave-plasma source with slotted rectangular waveguide surrounding the plasma chamber, and the other is an inductively-coupled plasma source with one-turn loop antenna driven by 13.56 MHz RF power. The microwave plasma is used for nano diamonds and RF plasma for DLC, respectively. The substrate temperature can be kept lower than 500K during the whole process. The coating was applied to cutting-tool chips for a milling machine and the tool life was tested by machining aluminum alloys. In comparison with conventional DLC coating, the hybrid nano diamond coating showed longer life.

PS3-TuP8 Polymer Surface Modification using Electron Beam-Generated Plasmas*, **S.G. Walton**, D. Leonhardt,* US Naval Research Laboratory

Electron beam-generated plasmas have several unique characteristics that make them attractive for polymer modification or other processing applications where substrate material sensitivity is an issue. The US Naval Research Laboratory has developed a plasma processing system that relies on a magnetically collimated, sheet of multi-kilovolt electrons to ionize the background gas and produce a planar plasma. High-energy electron beams are efficient at producing high-density plasmas (n@sub e@ > 10@super 11@ cm@super -3@) with low electron temperatures (T@sub e@ < 0.5 eV) over the volume of the beam, resulting in large fluxes of low-energy ions (< 3 eV) at surfaces located adjacent to the electron beam. Most relevant to the processing of sensitive materials is the ability of these sources to provide large fluxes of reactive species and limiting ion kinetic energies to values near common bond strengths, all of which is achieved under low pressure operating conditions and small source-to-substrate distances. In this work, we discuss the processing of common polymers such as polyethylene using pulsed, electron beam-generated plasmas produced in pure argon and mixtures containing reactive gases such as SF@sub 6@ and O@sub 2@. This work focuses on tailoring the surface energy while minimizing substrate damage. Plasma diagnostics used to provide a more complete understanding of the system are also presented. We include the processing of porous polymer substrates using a dual source system specifically designed for the treatment of thin, porous or fibrous sheets. This work was supported by the Office of Naval Research.

PS3-TuP9 Chemical Modification of the Poly(Vinylidene Fluoride-Trifluoroethylene) Surface through Fluorocarbon Ion Beam Deposition*, **W.-D. Hsu**, I. Jang, S.B. Sinnott,* University of Florida

Classical molecular dynamics simulations are used to study the effects of continuous fluorocarbon (FC) ion beam deposition on a poly(vinylidene fluoride-trifluoroethylene), P(VDF-trFE), surface. Fluorocarbon plasma processing is widely used to chemically modify surfaces and deposit thin films. It is well-accepted that polyatomic ions and neutrals within low-energy plasmas have a significant effect on the surface chemistry induced by the plasma. The deposition of mass selected fluorocarbon ions is useful to isolate the effects specific to polyatomic ions. This research focuses on the differences in the chemical interactions of C@sub 3@F@sub 5@@super +@ ions and CF@sub 3@@super +@ ions with P(VDF-trFE) surface. The incident energy of the ion beams is 50 eV/ion. The CF@sub 3@@super +@ ions are predicted to be more effective at fluorinating the P(VDF-trFE) surface than C@sub 3@F@sub 5@@super +@ ions. At the same time, the C@sub 3@F@sub 5@@super +@ ions are predicted to be more effective in growth of fluorocarbon thin film. The simulations also reveal possible mechanisms that could produce these differences, which will be discussed. This work is supported by the National Science Foundation (Grant number CHE-0200838).

PS3-TuP11 Atmospheric Plasma Deposition of Silicon Dioxide Coatings on Metal*, **A.M. Ladwig**,* University of California - Los Angeles*; S.E. Babayan,* Surfx Technologies*; M.D. Smith, W. Highland,* National Nuclear Security Administration's Kansas City Plant Operated by Honeywell Federal Manufacturing and Technologies*; R.F. Hicks,* University of California - Los Angeles

The deposition and properties of silicon dioxide on metal substrates was investigated using atmospheric pressure plasma-enhanced chemical vapor deposition. The plasma, generated with radio frequency power at 27.12 MHz, was fed helium, oxygen and two types of silicon precursors, hexamethyldisilizane and tetraethylorthosilicate. After deposition, the films were analyzed for composition, adhesion and dielectric strength. X-ray photoelectron spectroscopy revealed that the glass films contained approximately 25 percent silicon, 50 percent oxygen and 25 percent carbon with negligible nitrogen. Scratch tests indicated that the films were strongly adherent to the substrates. The glass films achieved direct current dielectric strengths between 50 and 250 V for a thickness range of 0.5 to 1.3 µm. The maximum breakdown voltage measured was 400 V. Scanning electron microscopy revealed that breakdown occurred at cracks and other defects in the films. These defects appeared to form around areas of surface roughness and contamination. The process conditions and their effects on the properties of silicon dioxide will be presented.

PS3-TuP12 Properties of Various Polyparylenes Deposited by Conventional and Plasma-Enhanced Chemical Vapour Deposition*, **G. Franz**, S.F. Dribinskiy,* Munich University of Applied Sciences, Germany*; D. Voss,* Plasma-Parylene Coating Services, Germany

Polyparylene, a non-critical, non-toxic layer material for long-term applications in the human body but also a very promising candidate for a low-@kappa@ dielectric, has been deposited by conventional and plasma-enhanced chemical vapor deposition of the monomeric species (types C and N), and partly with CF@sub 4@. For that end, a microwave discharge in a pulsed mode has been applied. The characterization of the layer parameters has been compared with conventionally prepared cvd data. The analytical tools were scanning electron microscopy and atomic force microscopy to determine the surface roughness and density of voids in the film; the surface tension has been evaluated by contact angle measurements and the high-frequency dielectric constant by ellipsometry. Fourier-transform infrared spectroscopy served to define the occurrence of functional groups. The most prominent detail is the contact angle against water and the organic solvent CH@sub 2@I@sub 2@ which varies between very flat angles up to nearly 180° so it is possible to fabricate plasma-generated films which simultaneously exhibit hydrophobic and lipophobic character. Conventionally produced films, however, are more or less hydrophobic. Together with the very smooth surface which nearly completely lacks voids, we refer this conduct partly by physical reasons: the higher energy of the layer-composing molecules in the plasma case. In a chemical sense, this behavior is caused by the almost complete destruction of the benzene ring even in a relatively gentle plasma. Eventually, the tribological and dielectric film properties are correlated with the deposition conditions.

PS3-TuP13 Plasma and Surface Characterisation in the Pulsed Polymerisation of Acrylic Acid Films*, **J.W. Bradley**, S. Voronin,* University of Liverpool, UK*; M.R. Alexander,* University of Nottingham, UK

The pulsed-plasma polymerization of functional films from organic monomers struck at low pressure in RF discharge cells is a valuable technique for controlling surface chemistry and obtaining good functional retention.@footnote 1@ Despite the usefulness of the pulsed plasma technique, the relationship between the transient plasma parameters during the pulse cycle (typically several milliseconds duration) and the chemical and physical properties of the film has not been extensively investigated. Using state-of-the-art time-resolved mass spectroscopic and electrical probing techniques, the plasma parameters, (neutral and ion flux, ion energy distribution function, plasma density, electron temperature and

plasma potential) have been measured in a range of monomer flow rate to applied power ratios and pulse duty cycles and correlated with the surface chemistry obtained by XPS. We have evidence for the importance of heavy ionic species (e.g. [xM-H]@super +@ with x = 2, 3) originating from the plasma in the production of high functional retention films. A growth model for pulsed-plasma polymer films is being developed. @FootnoteText@ @footnote 1@ Rinsch CL, Chen XL, Panchalingam V, Eberhart RC, Wang JH, Timmons RB, Langmuir 12 (12) 2995-3002 1996

PS3-TuP15 Nanopantography: A New Approach for Massively Parallel Fabrication of Nano-Structures*, **M.K. Jain**, L. Xu, S.C. Vemula, S.K. Nam, V.M. Donnelly, D.J. Economou, P. Ruchhoeft,* University of Houston

Nanopantography is a new method for forming nano-structures on a massively parallel scale. A nearly monoenergetic ion beam (FWHM < 3 eV at 100 eV) is directed at a 3-layer (Cr/SiO@sub 2@/Si substrate) electrostatic lens structure built on a silicon wafer. A typical lens consists of a micron size hole etched through the metal and oxide layers down to the Si substrate. When the optimum potential is imposed on the metal layer, the ion "beamlets" entering the 1 µ hole openings focus to 10 nm size spots. Optimum potentials were obtained by ion trajectory simulations. Etching or deposition on the Si substrate can be accomplished depending on the choice of ions and effusive neutral beams. We performed etching experiments with 100 eV Ar@super +@ ions, formed in a pulsed ICP, and a Cl@sub 2@ effusive beam, and etched 10nm dia., 100 nm deep holes in Si with 950nm dia. lenses. When the sample was tilted 20@super o@ off normal with respect to the ion beam axis, the focused spot moved by 160nm off axis, in agreement with simulations. Thus, sample tilting will enable us to write lines and complex patterns with nanometer resolution. Deposition of ~50 nm dia. Ni islands was also accomplished with 20 eV Ni@super +@ ions formed by sputtering of a Ni target in the pulsed ICP.

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