

Tuesday Morning, November 5, 2002

Plasma Science

Room: C-103 - Session PS-TuM

Atmospheric Pressure and Other Emerging Plasma Applications

Moderator: R. Blumenthal, Auburn University

8:20am **PS-TuM1 Instabilities in a Dielectric Barrier Discharge at Atmospheric Pressure**, *M.C.M. Van de Sanden, E. Aldea*, Eindhoven University of Technology, The Netherlands, *C.P.G. Schrauwen*, TNO TPD, The Netherlands

Due to their enormous potential for cost-efficient industrial applications, atmospheric low temperature (300-500 K) plasmas at atmospheric pressure received large attention in recent years. From the points of view of power density and plasma stability the most efficient solution was proved to be the dielectric barrier configuration in which the electrodes are covered with a insulator. The procedure used to generate plasma is simple but the physical mechanism underlying the plasma generation is still unclear. The generation of homogeneous plasma at atmospheric pressure is assumed to be related to the gas pre-breakdown pre-ionisation by metastable-metastable collisions,¹ but there are not yet unambiguous experimental evidences of a significant pre-ionization due to this mechanism. In this paper the work was focussed on the investigation of the role of metastables in the excitation or ionisation processes in a plasma generated in Ar, nitrogen and air between two electrodes (electrode gap 0.3-5 mm) covered by a dielectric mounted in a gas tight cabinet. A study of dependence of plasma stability and filamentation on the electrode gap, surface temperature, voltage pulse frequency or shape was also performed and the optimum conditions range was defined. The importance of metastables is evaluated on basis of the plasma rovibrational and excitation temperatures derived from the optical emission spectroscopic data, and on the study of the correlation between temporal dependence of the plasma emission and of the current pulse. It is demonstrated that metastable-metastable collisions cannot be responsible for a significant pre-ionization. Therefore other factors must play a role in plasma stability.

¹N. Gherardi, G. Gouda, E. Gat, A. Ricard, F. Massines, Plasma Sources Sci. Technol. 9 (2000), 340.

8:40am **PS-TuM2 Atmospheric Pressure Plasma Processing**, *R.F. Hicks*, G.R. Nowling, M. Moravej, X. Yang, University of California, Los Angeles, G. Ding, Applied Materials, S.E. Babayan, Surfx Technologies LLC

INVITED

Atmospheric pressure plasma discharges have emerged as exciting new tools for materials processing. There are many different sources to choose from depending on the application, including dielectric barrier discharges, microwave plasmas, transferred arcs and inert-gas-stabilized capacitive discharges. At UCLA, we have developed a novel low-temperature plasma source, in which reagent gases are mixed with helium or argon and passed through two closely spaced, perforated electrodes. By applying radio frequency power at 13.56 to 100.0 MHz to one of the electrodes, the gas becomes ionized with the dissociation of about 1% of the reagent molecules into atoms and radicals. This source exhibits a charged particle density of about 10^{11} cm^{-3} and an electron temperature from 2 to 4 eV. By contrast, the neutral temperature ranges from 300 to 450 K, depending on the process conditions. Many different gas mixtures may be fed through the source, including oxygen, nitrogen, hydrogen, carbon tetrafluoride, ammonia, etc. The concentration of ground-state atoms, e.g., O or N, varies from about 1.0 to $10.0 \times 10^{15} \text{ cm}^{-3}$. These species may be used to drive a variety of downstream surface treatment processes, including polymer activation, organic residue removal, glass or metal etching, and chemical vapor deposition. At the meeting, I will briefly review atmospheric pressure plasma sources, and then describe our work on the physics and chemistry of these systems.

9:20am **PS-TuM4 Atmospheric Pressure Plasma Treatment of Polypropylene**¹, *R. Dorai, M.J. Kushner*, University of Illinois at Urbana-Champaign

Atmospheric pressure plasmas, corona and dielectric discharges in particular, are used to modify polymer films to improve their wetting and adhesion properties. Production of O and OH radicals in humid air discharges produce surface oxidation of the polymer and result in the formation of Low-Molecular Weight Oxidized Material (LMWOM). Although a widely used industrial process, the fundamental plasma surface interactions which produce LMWOM and modify surface properties are not well understood. In this paper, results from a computational investigation of

corona treatment of polypropylene will be discussed with the goal of determining the reaction mechanism which produce LMWOM. The investigation was performed using a global plasma chemistry model linked with a surface site balance model for the plasma-surface interactions. The surface reaction mechanism distinguishes between processes which produce hydrophilic and hydrophobic groups. Comparisons can then be made with experimental data for corona treated polypropylene based on wettability (contact angle), densities of different surface groups and erosion rates. With the validated reaction mechanism, parameterizations of the important variables affecting the adhesion properties namely, energy deposition and relative humidity will be performed.

¹Work supported by 3M, Inc. and the National Science Foundation.

9:40am **PS-TuM5 Simulation of the Plasma Dynamics and Chemical Phenomena in Dielectric-barrier Controlled Atmospheric-pressure Glow Discharges**, *X. Yuan, L. Raja*, University of Texas at Austin

Large-volume atmospheric-pressure glow (APG) discharges are emerging as an important new class of glow discharges with several potential applications in materials processing. These discharges operate in a previously inaccessible regime of plasma parameter space and have properties that resemble classical low-pressure glow discharges, but at atmospheric or near-atmospheric pressures. Important classes of APG discharges include a high-frequency capacitively coupled configuration with closely spaced parallel electrodes and a low-frequency dielectric-barrier configuration with parallel plates and an intermediate dielectric layer. In this talk, we will present detailed one-dimensional simulation results for a dielectric-barrier APG discharge for varying discharge parameters such as gap length, dielectric capacitance, and frequency. The mechanism of pulsed glow formation and extinction will be discussed for a noble gas (helium) and a molecular gas (nitrogen) APG plasma. Ion impact energy characteristics at the surfaces will be analyzed and its implications for in situ material processing will be reported. Simulation results will be verified with experimental data where available.

Supported by NSF-CAREER grant.

10:00am **PS-TuM6 Plasma Enhanced Chemical Vapor Deposition of Hydrogenated Amorphous Silicon at Atmospheric Pressure**, *M. Moravej*, S. Babayan, G.R. Nowling, X. Yang, R.F. Hicks, University of California, Los Angeles

The plasma enhanced chemical vapor deposition (PECVD) of hydrogenated amorphous (a-Si:H) and hydrogenated microcrystalline (uc-Si:H) silicon has been examined at ambient pressure. A hydrogen and helium gas mixture flowed through two electrodes supplied with 50 W RF power at 13.56 MHz. Silane was added downstream from this plasma, and the reactive mixture directed onto a heated glass substrate. After growth the thickness of the films was determined using a profilometer. The deposition rate increased with the H₂ and SiH₄ partial pressures and saturates at approximately 70 Å/min for both parameters. The deposition rate also increased with substrate temperature following an Arrhenius relation with an activation energy of 3.44 kJ/mol. However the growth rate decreased from 92 Å/min to 13 Å/min as the electrode-to-substrate distance increased from 10.5 mm to 5 mm. Fourier-transform infrared spectroscopy, Rutherford backscattering spectroscopy, and Raman spectroscopy were used to determine the structure and chemical composition of the films. The effect of the process conditions on the hydrogen content and degree of crystallinity of the films will be discussed at the meeting.

10:20am **PS-TuM7 Low Energy Electron Enhanced Etching (LE4) for Reduced Process Damage in Compound Semiconductor Devices**, *H.P. Gillis*, S.H. Lee, University of California, Los Angeles, D.I. Margolese, S.J. Anz, Systine, Inc.

INVITED

Dry etching for defining device features is a key process in manufacturing integrated circuits because it controls critical dimensions much more tightly than does wet etching. Indeed, the ability to etch transistor features at dimensions progressively smaller than 0.25 μm has been a mainstay of the computer industry, and is one of the foundations of Moore's Law. As a side effect, the conventional dry etch methods inflict "etch process damage" caused by the surface ion bombardment needed for high resolution feature definition. Consequently, the need arises for developing alternative dry etch processes and for characterizing "etch process damage" in material terms to guide its control and elimination. We will describe an alternative dry etch method in which electrons with energies below about 15 eV stimulate high-resolution etching of features as small as 0.020 μm with no apparent damage. Along with high-resolution feature definition, this method gives mirror-smooth etched surfaces and maintains stoichiometry of compound materials. We will relate these results to plasma conditions including the

electron temperature and energy distribution. The discussion will emphasize compound semiconductor materials and applications for optical and wireless communications.

11:00am **PS-TuM9 Coulomb Crystals in Plasma Processing Reactors¹**, **V. Vyas**, *M.J. Kushner*, University of Illinois at Urbana-Champaign

Many plasma deposition systems operate in regimes whereby large densities of small particles are nucleated in the gas phase. Given sufficient densities of these particles, they can exhibit collective behavior and form Coulomb solids. These structures typically form at moderate gas pressures, small particle sizes and lower powers in capacitively coupled, radio frequency discharges. Lattices having different radial structure functions $[g(r)]$, non-ideality factors and geometrical shapes can be formed given somewhat subtle changes in discharge properties. Having scaling laws for their behavior would be desirable to minimize unwanted feedback to the plasma or film properties. To address these phenomena, a 3-dimensional dust transport simulation has been developed and incorporated into a plasma equipment model. The forces included in the dust transport model are electrostatic, ion-drag, thermophoretic, fluid-drag by neutrals, gravity and particle-particle Coulomb interactions. We will discuss formation of plasma crystals as function of operating conditions in rf discharges and, in particular, the formation of voids in the plasma crystal at high substrate biases. The negative ion fluxes in electronegative gas mixtures alter the ion drag force acting on the dust particle leading to qualitatively different crystal morphologies than those found in electropositive plasmas. For example, addition of electronegative gases such as Cl_2 and O_2 to Ar causes voids in the plasma crystals to close. The effect of ion streaming on dust particle motion will be discussed, as will the effect of surface topology on radial compression of the plasma crystal producing changes in interparticle spacing and $g(r)$.

¹ Work was supported by Sandia National Laboratory and the National Science Foundation.

11:20am **PS-TuM10 Simplified Model for Calculating the Pressure Dependence of a DC Planar Magnetron Discharge and Experimental Verification**, **G. Buyle***, *D. Depla*, *K. Eufinger*, Ghent University, Belgium, *W. De Bosscher*, Bekaert Advanced Coatings, Belgium, *J. Haemers*, *R. De Gryse*, Ghent University, Belgium

A simplified model for the DC planar sputter magnetron discharge allowing to simulate the pressure dependence over a wide range is presented. The model is based on the assumption that the discharge is built up by arch shaped regions which are determined by the orbits of the electrons emitted from the cathode by ion bombardment (secondary electrons). This assumption, combined with relatively simple schemes for the ionization, target erosion and secondary electron production, forms the core of the simplified model. Although the presented model has not the same accuracy as more advanced models based on the Monte-Carlo method, it has the major advantage of being much less computing intensive. This allows for quickly assessing the influence of a variety of discharge parameters and has proven to be well sufficient to explain our experimental results. We observed that at high gas pressures (above approximately 0.5Pa) there is a very weak pressure dependence of the observed discharge parameters, but for lower pressures an increase in the discharge voltage, cathode sheath thickness and erosion profile width is observed. Our modeling revealed the necessity to integrate recapture of secondary electrons by the cathode to explain the observed pressure dependence. To our knowledge, recapture in planar magnetron discharges has not been acknowledged yet. This is because the small initial energy of the secondary electrons, which enables recapture, is neglected in recently published simulations. Given the good agreement between experiment and simulation in this study, it appears that recapture is essential for accurately modeling the planar magnetron discharge at low pressures and that the presented model, in spite of its simplifications, is a valuable tool for this.

11:40am **PS-TuM11 Conformal and Anisotropic Deposition of Cu Films using Hassisted Plasma CVD**, **M. Shiratani**, *K. Takenaka*, *M. Onishi*, *K. Koga*, *Y. Watanabe*, Kyushu University, Japan, *T. Shingen*, Asahi Denka Kogyo K.K., Japan

We have developed Hassisted plasma CVD (HAPCVD),^{1,2} which realizes conformal and anisotropic deposition of Cu films in trenches for Cu interconnects of small width below 100 nm. Conformal deposition is aimed at creating thin Cu seed layer for Cu electroplating, while anisotropic deposition is aimed at filling trenches completely. We have obtained the results 1-4) using fluorine(F)-free complex, $\text{Cu}(\text{EDMDD})_2$ and the result 5) using $\text{Cu}(\text{HFAC})_2$. The following conclusions are obtained in this study. 1) H irradiation is effective in removing impurities from the surface and inside of Cu films for a substrate temperature above 170°C. 2) Initial nucleation

densities of Cu on TiN, TaN, and SiO_2 layers are above $5 \times 10^{15} \text{ m}^{-2}$ which is quite high compared to those for thermal CVD. The high nucleation density is favorable to realizing smooth thin Cu films and their strong adhesion to under-layer. 3) Deposition of Cu films of a low resistivity, $1.85 \mu\Omega\text{cm}$ and a strong adhesion above 10 MPa to TiN diffusion barrier layer has been demonstrated. Concentrations of C and O in the Cu film are much less than 0.1%, while those values at the interface between Cu and TiN are 1 and 0.2%, respectively. 4) Conformal deposition of smooth Cu films of 20 nm in thickness in trenches 0.5 μm wide and 2.73 μm deep has been demonstrated. 5) Anisotropy, which is defined as a ratio of film thickness at bottom of trench to that at its side wall, increases from 100% to 550% with increasing energy of irradiating ions from 20 V to 220 V, while H-irradiation reduces anisotropy. Promising anisotropic filling of trenches 3.5 μm wide, 2.73 μm deep has been demonstrated.

¹ M. Shiratani, et al., *Sci. and Technol. of Adv. Mater.*, 2, 505 (2001).

² K. Takenaka, et al., *Proc. of Int. Symp. of Dry Process*, pp.169 (2001).

Authors Index

Bold page numbers indicate the presenter

— A —

Aldea, E.: PS-TuM1, **1**
Anz, S.J.: PS-TuM7, **1**

— B —

Babayan, S.: PS-TuM6, **1**
Babayan, S.E.: PS-TuM2, **1**
Buyle, G.: PS-TuM10, **2**

— D —

De Bosscher, W.: PS-TuM10, **2**
De Gryse, R.: PS-TuM10, **2**
Depla, D.: PS-TuM10, **2**
Ding, G.: PS-TuM2, **1**
Dorai, R.: PS-TuM4, **1**

— E —

Eufinger, K.: PS-TuM10, **2**

— G —

Gillis, H.P.: PS-TuM7, **1**

— H —

Haemers, J.: PS-TuM10, **2**
Hicks, R.F.: PS-TuM2, **1**; PS-TuM6, **1**

— K —

Koga, K.: PS-TuM11, **2**
Kushner, M.J.: PS-TuM4, **1**; PS-TuM9, **2**

— L —

Lee, S.H.: PS-TuM7, **1**

— M —

Margolese, D.I.: PS-TuM7, **1**
Moravej, M.: PS-TuM2, **1**; PS-TuM6, **1**

— N —

Nowling, G.R.: PS-TuM2, **1**; PS-TuM6, **1**

— O —

Onishi, M.: PS-TuM11, **2**

— R —

Raja, L.: PS-TuM5, **1**

— S —

Schrauwen, C.P.G.: PS-TuM1, **1**
Shingen, T.: PS-TuM11, **2**
Shiratani, M.: PS-TuM11, **2**

— T —

Takenaka, K.: PS-TuM11, **2**

— V —

Van de Sanden, M.C.M.: PS-TuM1, **1**
Vyas, V.: PS-TuM9, **2**

— W —

Watanabe, Y.: PS-TuM11, **2**

— Y —

Yang, X.: PS-TuM2, **1**; PS-TuM6, **1**
Yuan, X.: PS-TuM5, **1**