Plasma Science and Technology
Room: 306 - Session PS2-ThA

Plasma Deposition and Plasma Enhanced Atomic Layer Deposition and Etching
Moderator: W.M.M. Kessels, Eindhoven University of Technology, The Netherlands

2:00pm **PS2-ThA1 High Quality Thin Films Deposited at Low Temperatures by Plasma Enhanced ALD and CVD Techniques**, ***C.J. Hodson**, O. Thomas, Q. Fang*, Oxford Instruments, UK **INVITED**

Low temperature deposition of thin films is becoming increasingly important with a growing range of low thermal budget materials being used in device research. The rapid development and predicted future market for plastic electronics has resulted in a greatly increased focus on thin film depositions below 150ºC. This contribution will address the challenges of low temperature deposition in the context of some example applications including; depositing directly onto photo-resist for lift-off, Si_3N_4 MIM capacitor technology for MMIC and RF-MEMs[1] and Al_2O_3 moisture permeation barriers for polymer based devices such as flexible OLEDs.[2] The study will focus on two chemical vapour deposition (CVD) techniques ideally suited for low temperature deposition namely; Inductively Coupled Plasma CVD and Remote Plasma Atomic Layer Deposition. For any thin film CVD process it is widely true that film quality will degrade at lower temperatures. This degradation is most often measured by decreasing film density, refractive index, breakdown voltage and adhesion; and increasing film impurities and wet etch rates. By using the energetic and reactive plasma species to replace thermal energy it is possible to deposit films with acceptable quality at room temperature, i.e. 25ºC. By generating the plasma remotely such improved film quality can be achieved with low plasma damage to the substrate.

[1]Low temperature high density Si_3N_4 MIM capacitor technology for MMMIC and RF-MEMs applications. K. Elgaid, H. Zhou, C. D. W. Wilkinson and I. G. Thayne, Microelectronic Engineering, Volumes 73-74, June 2004, Pages 452-455

[2]Plasma-assisted atomic layer deposition of Al_2O_3 moisture permeation barriers on polymers. E. Langereis, M. Creatore, S.B.S. Heil, M.C.M. van de Sanden, and W.M.M. Kessels, Appl. Phys. Lett. 89, 081915 (2006).

2:40pm **PS2-ThA3 An Analysis of the Deposition Mechanisms Involved During Self-limiting Growth of Metal Oxides by Pulsed PECVD**, *M.T. Seman,* CMD Research LLC, *D.N. Richards,* ***C.A. Wolden***, Colorado School of Mines

Self-limiting deposition (~ 1 Å/pulse) of several metal oxides (Al_2O_3, TiO_2, ZnO, TiO_2) has been achieved by pulsed plasma-enhanced chemical vapor deposition (PECVD). In this process a metal precursor and O_2 are delivered continuously to a PECVD reactor while the rf power is pulsed at low frequency (~ 1 Hz). With proper reactor design and operation the net deposition rate of pulsed PECVD exceeds that of continuous wave operation, and the quantity of impurities is dramatically attenuated. The growth mechanism of alumina from trimethyl aluminum ($Al(CH_3)_3$, TMA) was investigated by comparing the results from pulsed PECVD with those of plasma-enhanced atomic layer deposition (PE-ALD). For both processes the rate/cycle saturated with ~200 L of TMA exposure. At 165 °C a rate of 1.37 Å/cycle was obtained using PE-ALD. For pulsed PECVD the rate scaled linearly with the TMA partial pressure, and its extrapolation was in good agreement with PE-ALD. The results suggest that deposition in pulsed PECVD involves an ALD component which is supplemented by PECVD growth, and that the contribution of the latter may be tuned using the TMA partial pressure. Experiments using patterned wafers supported this hypothesis. Conformal coatings were observed within 10:1 aspect ratio trenches using pulsed PECVD, however the deposition rate on the surface of these substrates was greater than within the trench. The ratio between the two corresponds well to the ratio of rates obtained from pulsed PECVD and PE-ALD on planar substrates. With cycle times < 1 s, net rates > 30 nm/min were obtained by pulsed PECVD while retaining high quality and digital control.

3:00pm **PS2-ThA4 Self-Limiting Growth of Titania by Pulsed Plasma-Enhanced Chemical Vapor Deposition**, ***N.G. Kubala**, C.A. Wolden*, Colorado School of Mines

In this presentation we describe the self-limiting deposition (~ Å/pulse) of titanium dioxide by pulsed plasma-enhanced chemical vapor deposition (PECVD) at low temperature (< 150ºC). In this process the titanium tetrachloride (TiCl4) and oxygen are mixed and delivered simultaneously in a remote PECVD configuration. The as-deposited films were characterized by spectroscopic ellipsometry, Fourier transform infrared spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS), and dielectric performance. In addition, the plasma chemistry in this system was characterized using quadrupole mass spectrometry (QMS) and optical emission spectroscopy (OES). QMS measurements confirmed that TiCl4 and O2 are inert in this system in the absence of plasma. During continuous wave plasma operation TiCl4 is completely consumed, no deposition is observed, and the main byproducts are Cl/Cl2. While no film growth is observed with the plasma on or off, self-limiting deposition was readily obtained by pulsing the plasma at low frequency (~1 Hz). The deposition kinetics and film quality were evaluated as a function of precursor exposure, plasma power, substrate temperature, and pulse parameters. The deposition rate per pulse scaled with the degree of precursor exposure during the plasma off step. Through appropriate control of the TiCl4 concentration and pulse duration, the depositing rate may be adjusted over a narrow range (0.6 – 1.3 Å/pulse). High refractive indices were obtained, scaling with exposure and plasma power over a range of 2.3 to 2.6 at 580 nm. The deposition rate also decreased with plasma power, and OES was used to highlight the role of atomic oxygen in this process. XPS analysis showed that the titanium was fully oxidized. At low plasma power a small amount of Cl contamination was observed, however no Cl was detected in films deposited at higher powers. FTIR characterization of these amorphous films display broad absorption features at low wavenumbers that are distinct from the sharp peaks associated with the crystalline phases of TiO2. A comprehensive analysis of dielectric performance is underway and will be reported at the symposium.

3:20pm **PS2-ThA5 Capillary Jet Injection of SiH_4 in the HDP-PECVD of SiO_2: What We Can Learn from It**, ***R. Botha**, T. Novikova, P. Bulkin*, LPICM, Ecole Polytechnique, France

This paper reports on the deposition of silicon dioxide films from a silane/oxygen gas mixture in a matrix distributed ECR PECVD system. In order to investigate the influence of the primary silane flux and the precursor consumption on the deposition rate and material properties, undiluted silane is first injected into the system through a gas ring positioned around the periphery of the substrate holder, at a distance of 3 cm. The same set of depositions is then done using a 1 mm diameter capillary tube located 3 cm vertically above the substrate surface. The microwave power, pressure, substrate bias and silane gas flow are varied. The material properties are studied using spectroscopic ellipsometry, FTIR spectroscopy and transmission measurements. The plasma is characterized using optical emission spectroscopy (OES) and differentially pumped quadrupole mass spectrometry (QMS). The maximal deposition rate when using a 16 sccm SiH4 and 40 sccm O2 gas mixture is found to increase from 1 nm/s up to 2.16 nm/s when the gas ring is replaced with the capillary jet injection system. This increase is attributed to the large increase in the primary flux of undissociated silane onto the substrate surface. Using an intentionally inhomogeneous deposition resulting from the capillary jet injection and studying the thickness normalized OH absorption in the deposited film at various distances from the capillary injection point, we gain insight into the contribution of the partial pressure of water (which is the main by-product of the reaction between silane and oxygen) on the OH content in the silicon oxide. It is observed that the silicon oxide deposited directly below the capillary injection point has an integrated OH absorption band intensity which is approximately half that of a point 3 cm away from it. Reducing the distance between the injection point and the substrate also leads to a narrowing of the OH absorption band, where the associated vibration mode at 3350 cm-1 practically disappears and only the isolated Si-OH vibration bonds at 3650 cm-1 are retained. By looking at the films thickness at various distances from the capillary jet, it is seen that the primary, beam-like SiH4 is the largest contributor to the deposition rate when using a capillary jet. A Direct Simulation Monte Carlo (DSMC) technique is used to model the flux of the precursor gases onto the substrate plane. The simulation results are compared with the experimental findings.

4:00pm **PS2-ThA7 High Quality TEOS Oxide Film CVD by Microwave RLSA Plasma**, ***H. Ueda**, Y. Tanaka, Y. Ohsawa, T. Nozawa*, Tokyo Electron Technology Development Institute, INC., Japan

A high-quality dielectric film CVD in low temperature is required in the processes of nano scale VLSI devices, FPDs, image sensors and flexible organic electronics. There have been many trials to form a high-quality low-temperature silicon dioxide using SiH4-O2 or TEOS-O2 PE-CVD methods. However, they have problems with not only their silicon oxide film qualities but also plasma-induced charging damages to underlying transistors during the plasma process. For example, with regard to the SiH4-O2 PE-CVD, it is hard to exclude Si-H and Si-OH bonds thoroughly to improve electrical properties such as leakage current and dielectric constant. For TEOS-O2 PE-CVD, unreacted TEOS precursor associated with carbon

contaminations causes reliability problems and the Si-H and Si-OH contamination was reduced by controlling the plasma source power and Ar gas addition. We report a new low temperature (< 400C) PE-TEOS CVD technology using Microwave (2.45GHz) RLSA (Radial Line Slot Antenna) plasma.[1] It realizes high quality silicon dioxide film without causing charging damages. The film property is as good as a HTO (> 800C) with a good step-coverage performance. The 5%HF wet etch rate of the film is less than that of HTO. One of the unique characteristics of the Microwave RLSA plasma is its plasma generation and transportation system. A very high electron temperature region to produce high density plasma is located just beneath a quartz plate under a microwave antenna. The plasma diffuses to wafer region and the electron temperature in the wafer region becomes less than a half of it in the plasma production region. The electron temperature and density above the wafer in the RLSA plasma chamber can be controlled to produce desired proper precursors for an excellent CVD film by adjusting the pressure, material gas mixture ratio and position of the gas injections. To make the excellent silicon oxide film, the RLSA plasma produces specific precursors with plenty of sufficient oxygen radicals in the gas phase and supplies to the substrate surface. It also seems to provide ions with certain range of energy, that inhibits remaining C=C or C=O bond in the film but enough to proceed surface reaction. In the system, plasma charging damages were never observed even in a MOS capacitor TEG with an antenna-ratio of 1 M, because of the low electron temperature and uniform plasma potential above the wafer surface.

[1]C. Tian, et al.: J. Vac. Sci. Technol. A24 (2006) 1421.

4:20pm **PS2-ThA8 Plasma Polymerization on Textiles: Deposition of Functional Nanostructured Thin Films**, ***S. Guimond***, *Y. Geng, A. Ritter, B. Hanselmann, D. Hegemann*, EMPA, Switzerland

A shift towards highly functional and added-value textiles is now recognized as being essential to the sustainable growth of the textile and clothing industry in developed countries. The demand for tailored surface modifications for water repellence, long-term hydrophilicity, anti-bacterial properties, etc, is therefore increasing. At the same time, the environmental restrictions concerning the waste water produced by conventional textile finishing techniques are getting more and more severe. In this context, plasma processing is seen as an attractive alternative method to add new functionalities to textiles since it is a versatile and eco-friendly (dry) technology. Because plasma processing results in a nano-scaled surface modification, it also has the advantage of preserving the bulk properties as well as the touch of the textiles. In this study, plasma polymer thin films have been deposited on various polyester fabrics of defined structure using $NH_3/C_2H_4/Ar$ low pressure RF glow discharges. The films were first characterized using XPS, FTIR and AFM as a function of the plasma process parameters. For a defined range of energy input and NH_3/C_2H_4 gas flow ratio, the coatings are nanostructured and contain predominantly amine functional groups. Interestingly, these films can thus serve as nanostructured templates for further surface functionalization. For example, they can be used to selectively bind acid dyestuff molecules, allowing a very efficient low temperature and substrate independent dyeing. The amine groups contained in the films were also derivatized with molecules containing OH and CF_3 groups. Due to the nano roughness and the high specific surface area of the films, super-hydrophilic or -hydrophobic properties are obtained. The hydrophilicity of the various coated fabrics was compared by monitoring the spreading of water droplets with infrared thermography. Results show that the textile structure has an important influence on the final properties. This is discussed in terms of capillary effects and accessibility of the textiles structures to the plasma species. Finally, the properties of the coated fabrics remain generally rather stable during abrasion tests, presumably due to the high crosslinking degree of the films. The scalability of the process investigated in this work has been demonstrated using a pilot-scale continuous web coater.

4:40pm **PS2-ThA9 Stable Super Hydrophobic Nanocoatings on Polymers Prepared by Gas Phase Deposition**, ***M. Puttaswamy***, University of Aarhus, Denmark, *K.B. Haugshoj, L. Christensen,* Danish Technology Institute, Denmark, *P. Kingshott*, University of Aarhus, Denmark

The demand for super hydrophobic and oleophobic coatings in technological applications is continuing to increase particularly on inert materials such as polymers. We utilize the method of molecular vapour deposition (MVD) as a gas phase process for depositing highly uniform and conformal nanocoatings on different laser structured polymer substrates using fluorinated silanes. The challenge with such an approach is optimizing the adhesion and stability of the silane layer, particularly under conditions where moisture is present. One approach we are pursuing is to perform several alternating pre-treatments of the polymer surfaces including O_2 plasma treatment followed by gas phase reaction of the resultant hydroxyl groups with trimethylaluminum ($Al_2(CH_3)_6$). Subsequently the surface is exposed to water vapour. The process of alternating exposures to trimethylaluminum and water, known as atomic layer deposition (ALD), is repeated a number of times, generating an alumina (Al_2O_3) surface highly reactive towards fluorinated silanes, perfluorodecyltrichlorosilane (FDTS) – $CH_3(CF_2)7(CH_2)2SiCl_3$. The chemical surface modification schemes when combined with femtosecond laser structuring results in super hydrophobic/oleophobic with contact angles above 150° (with water). The stable silicon dioxide adhesion layer on the structured surfaces is prepared from silicon tetrachloride and water by a CVD process. The so formed silicon dioxide adhesion layer when subjected to sweat test is found to be stable for almost 14 days at 65°C. The conditions for creating such a stable precursor adhesion layer are dependent on the polymer substrate to be coated. The polymers tested in this study include polyoxymethylene (POM), polyethylene terephthalate (PET), polycarbonate (PC) and polyethylene (PE), and the treatment conditions varied including the effect of plasma treatment, precursor composition, and other operational parameters such as temperature, gas flow and treatment time. So, the precise chemical reactions responsible for forming such a stable super hydrophobic coatings, is best understood using angle dependent XPS, TOF-SIMS and contact angle measurements. Characterization using C_{60} ion source on TOF-SIMS provided us the 'softer' depth profiling with increased ion yields. The results are discussed in terms of the molecular mechanisms of adhesion and polymers tested.

5:00pm **PS2-ThA10 Tunable Properties of Plasma-Polymerized Organosilicones**, ***V. Cech***, Brno University of Technology, Czech Republic

Plasma-polymerized organosilicones constitute a class of materials with a rich and varied scientific background. This class of materials possesses a special characteristic, which distinguishes it from other plasma polymers – the ability to vary and control the degree of its organic/inorganic character (i.e., the carbon content) by the appropriate choice of fabrication variables. This allows one to control many physicochemical properties over wide ranges resulting in an extraordinary potential for useful applications, which are only now beginning to be tapped. The organosilicon plasma polymers are widely recognized for their potential not only in optical and electronic applications, but also in composites and nanocomposites with controlled interphase. Plasma-enhanced chemical vapor deposition (PECVD) was used to prepare thin films of tetravinylsilane in a mixture with oxygen gas employing an RF (13.56 MHz) helical coupling pulsed-plasma system. Plasma polymer films of the thickness from 0.02 to 1 µm were deposited on silicon substrates at different powers (0.1 – 10 W) and oxygen content (0 – 79%) in mixture. When an appropriate on-time and off-time is selected for pulsed plasma, the physical and chemical properties of hydrogenated amorphous carbon-silicon oxide alloy (a-SiOC:H) may be controlled by the effective power. We will demonstrate that the mechanical properties (Young's modulus 9 – 24 GPa, hardness 0.9 – 4.1 GPa), optical properties (refractive index 1.58 – 1.68 (633 nm), extinction coefficient 0.05 – 0.19 (250 nm), band gap 1.9 – 2.9 eV), and wettability (water contact angle 50 – 83 deg, surface free energy 35 – 58 mJ/m^2) of the film may be well tuned in correlation with chemical properties (elemental composition, organic/inorganic character C/Si = 2.5 – 8.6, chemical structure) to prepare tailored materials not only for functional interlayer in polymer composites. The construction of multilayers from individual films of tunable properties will be discussed as well.

5:20pm **PS2-ThA11 Plasma Deposited Films Containing Platinum Nanoclusters as Catalysts for Fuel Cells**, *A. Milella,* ***E. Dilonardo****, F. Palumbo, R. d'Agostino, F. Fracassi*, Università degli Studi di Bari, Italy

Today, the development of fuel cells is a promising solution to the "energy crisis" and the necessity to provide "clean energy" with virtually zero emission. Fuel cells offer the possibility of abundant energy with negligible emission and high efficiency for converting chemical energy into electricity and heat; however, one of the major disadvantage is their high production cost. Extensive studies are currently addressed to the development of new materials with the aim of improving fuel cell efficiencies and decrease production costs. As far as the catalyst is concerned, nanocomposites films consisting of metal nanoparticles embedded in polymeric matrix are very attractive materials because they allow to decrease the overall amount of Pt while providing high surface area. In literature various approaches have been used to incorporate metal nanoparticles into polymers. In this contribution a one-step plasma deposition process is described to obtain an uniform dispersion of small platinum nanoclusters throughout a thin hydrocarbon matrix. These composite films have been deposited by simultaneous plasma-enhanced chemical vapour deposition (PECVD) of ethylene (C_2H_4) and argon (Ar) gas mixtures and RF sputtering of a platinum target. Characterization of platinum-containing plasma-polymerized ethylene films has been realized using X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infra-Red spectroscopy (FT-IR), UV-Vis spectroscopy, Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Optical Emission Spectroscopy (OES) has been used to correlate

the chemical composition of the plasma with the amount of metal embedded in the deposited film. The electrochemical active area of the samples was determined from ex-situ cyclic voltammetry analyses. A comprehensive study on the effect of different plasma parameters (RF power, deposition time, flow rate of gasses) on the chemical composition and structure of the film will be presented. Results show that the platinum content in the coating can be finely controlled by changing the RF power and the monomer flow rate. In particular TEM images confirm that platinum aggregates in crystalline nanoclusters in distributed uniformly in the material. Furthermore the porosity due to the columnar film growth, together with the nanodispersion of the metal clusters, can be advantageously used for catalytic applications.

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