Thursday Morning, October 31, 2013

Advanced Surface Engineering
Room: 203 C - Session SE+PS-ThM

Pulsed Plasmas in Surface Engineering (8:00-10:00 am)/Atmospheric Pressure Plasmas (10:40 am-12:00 pm)
Moderator: H. Barankova, Uppsala University, Sweden, J. Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada

8:00am **SE+PS-ThM1 A 60 Year Perspective on Developments in Plasma Assisted PVD Processes for Enhanced Surface Engineered Performance**, ***A. Matthews***, University of Sheffield, UK **INVITED**

Over the past 60 years there have been many developments in PVD technology which have contributed to the successful emergence of the technological discipline which we now know as Surface Engineering. There now exist many products which could not even function without these developments, and other products whose performance so far-exceeds what was previously possible that they can offer improvements in measures such as productivity which are many hundreds (if not thousands) of times better than previously achievable. We can see these benefits in all major industrial sectors, especially aerospace, automotive, energy and healthcare. This paper highlights how these product enhancements have been achieved through a combination of plasma process developments and materials systems developments. The plasma processes have included ionisation enhancing systems such as thermionic assistance, magnetic confinement and pulsed-plasmas, and the materials developments have included multi-layered and nanocomposite combinations of phases which have allowed the creation of surfaces with mechanical and chemical properties which were previously unachievable. We can now even create "duplex" engineered surfaces which combine plasma assisted diffusion treatments with optimised coatings, which allow the use of substrate materials (such as titanium and aluminium alloys) which were previously considered unsuitable for heavily-loaded tribological contacts in arduous conditions. The progress in process and performance enhancements is charted with examples from each decade over the past 60 years.

8:40am **SE+PS-ThM3 Optimized Magnetic Field Configuration for High Power Impulse Magnetron Sputtering**, ***P. Raman***, *L. Meng, H. Yu, D.N. Ruzic*, University of Illinois at Urbana Champaign, *M. Schilling*, Dexter Magnetic Technologies, Inc, *S. Amstrong*, Kurt J. Lesker Company

Magnetic field design is critical in magnetron sputtering systems at it affects the plasma parameters and film quality. Most magnetic field configurations are designed for DC sputtering and they suffer from low target utilization, non-uniform ionized metal atoms, etc. High Power Pulsed Magnetron Sputtering (HIPIMS) discharge has high degree of ionization of the sputtered material with very high peak power on the target [1]. Therefore HIPIMS is an ideal candidate for the next generation magnetron sputtering systems. There are no magnetic field configurations that are optimized for HIPIMS discharge. It has been confirmed from our previous work on HIPIMS that a spiral-shaped magnetic field design on 36 cm diameter copper target was able to produce superior plasma uniformity on the substrate in addition to improved target utilization without the need for magnet rotation [2]. Commercial 4 inch sputter cathodes are very popular as they function with a wide variety of target materials and they can be operated with DC, RF and Pulsed-DC power supplies. These 4 inch cathode guns typically have a conventional circular magnetic field design (old). To optimize the magnet field configuration in HIPIMS for the 4 inch cathode gun, the spiral design (new) from the 36mm target was shrunk in size to produce the same magnetic field on the 4 inch target surface. In order to understand the effects of new magnet field configuration, the old and new magnet field configurations were tested in HIPIMS, Z-pulser and DC power supplies side by side using two 4 inch guns for deposition rate, film density, film uniformity and film stress. Plasmas from each power supply were diagnosed (ne, Te, ionization fraction) for the new and old magnet filed configuration in order to understand the pulsing parameters for better plasma control.

References

1. J. Bohlmark, J. Alami, C. Christou, A. P. Ehiasarian and U. Helmersson, J. Vac. Sci. Technol. A, 23, 18 (2005).

2. He Yu, Liang Meng, Matthew M. Szott, Jake T. McLain, Tae S. Cho and David. N. Ruzic, Investigation and Optimization of Magnetic Field Configuration in High Power Impulse Magnetron Sputtering, Plasma Sources Sci. Technol (Submitted).

9:20am **SE+PS-ThM5 HiPIMS Deposition of Semiconducting ZnO Thin Films**, *A.N. Reed, P.J. Shamberger*, Air Force Research Laboratory, Wright Patterson Air Force Base, *C. Muratore*, University of Dayton, *J.E. Bultman*, University of Dayton Research Institute, ***A.A. Voevodin***, Air Force Research Laboratory, Wright Patterson Air Force Base

High power impulse magnetron sputtering (HiPIMS) was demonstrated for the first time on semiconducting zinc oxide thin films for use as a transistor channel material. Nanocrystalline ZnO thin film transistors are of interest for integrated RF devices due to their high mobilities (110 $cm^2V^{-1}s^{-1}$) and high on-off ratios (up to 10^{12}) [1]. These electrical transport properties are critically dependent on film microstructure, defect densities, crystal orientation, surface roughness and grain size. Due to a highly ionized flux, HiPIMS allows for control of thin film microstructure, while simultaneously producing high quality crystalline films on unheated substrates. However the use of HiPIMS for the growth of oxide semiconductors and their resulting electrical transport properties remain largely unexplored.

In this study, we investigate the interrelationship between the plasma characteristics, resulting film microstructure, and the electrical transport properties of nanocrystalline ZnO thin films. HiPIMS was used to deposit thin (~100 nm) ZnO films from ceramic ZnO and metallic Zn targets onto substrates heated to 150 ^oC. In both non-reactive and reactive cases, the resulting films had stronger crystallinity, more highly aligned (002) texture and lower surface roughness than films grown with pulsed DC sputtering, as determined by XRD, SEM and AFM measurements. The degree of alignment in the films was strongly dependent on the target potential, gas pressure and pulsing parameters. Film I-V characteristics were compared alongside microstructures to correlate electrical transport properties with specific aspects of microstructure (grain size, crystallinity, texture). Similarly, time-resolved current measurements of the target and ion energy distributions, determined using energy resolved mass spectrometry, were correlated to film microstructure in order to investigate the effect of plasma conditions on film nucleation and growth. Finally, we will compare ZnO films grown by HiPIMS against those grown by other techniques (pulsed DC sputtering, pulsed laser deposition) and will critically evaluate the capability of HiPIMS for the deposition of electronic oxide films.

[1] B. Bayraktaroglu, K. Leedy, R. Neidhard. Microwave ZnO Thin Film Transistors. IEEE Electronic Device Letters V 29 Iss. 9, 1024-1026 2008

9:40am **SE+PS-ThM6 Si_3N_4 Spacers Etching in Synchronized Pulsed $CH_3F/O_2/He/SiF_4$ Plasmas**, ***R. Blanc***, STMicroelectronics, France, *M. Darnon, G. Cunge, O. Joubert*, LTM – MINATEC – CEA/Leti, France

Gate spacers are used in submicron metal oxide semiconductor field effect transistor (MOSFET) in order to precisely define the channel length with abrupt junction geometry and eventually to tailor the electrical characteristics of the MOSFET transistors. Therefore, spacer etch process is considered to be one of the most critical processes of CMOS technologies.The Si_3N_4 spacer etching process requires a high etch selectivity to Si so that Si_3N_4 etching can be stopped on the Si surface without silicon substrate consumption in source/drain (S/D) regions of the MOSFET transistor. Silicon loss in S/D regions during spacer etching causes substrate bias dependent leakage and etch induced damage in the silicon surface raises the resistance of ultra-shallow junctions. More recently, the introduction of an ultra-thin Si channel in 28 nm FDSOI technology brought more aggressive requirements in terms of Si consumption. At the same time, plasma etch processes are reaching their limits regarding etch selectivity and profile control at the nanometer scale. In this study, we investigate the combination of synchronized pulsed plasma technologies and the addition of a Si-containing gas, SiF_4, with the objective to improve spacer etch process performance.

The experiments are performed in a 300mm AdvantEdge^{TM} etch tool from Applied Materials. The inductively coupled plasma is sustained by two RF generators (13.56 MHz) to create the plasma and to polarize the wafer, using synchronous pulsing at different frequencies and duty cycles. Moreover, a Theta300 angle resolved XPS system from Thermo Scientific is connected under vacuum, allowing quasi in-situ analysis of etched samples.

In this work, we investigate the effect of SiF_4 addition in a synchronized pulsed $CH_3F/O_2/He$ plasma. In a previous study, we have already shown that high Si_3N_4/Si selectivity is obtained by oxidizing the silicon surface during the landing of the nitride etching process on the silicon surface. When the plasma is pulsed at 1 kHz with a duty cycle of 10%, spacer profiles are improved and the oxidized thickness is significantly reduced but still generates a Silicon recess of 0.5 nm. With 5sccm SiF_4 added to the plasma gas phase, we observe a SiO_x deposition at the Si surface without

any Si consumption, showing that the etch stop is obtained by the deposition of a SiO_x layer originated from the plasma gas phase.

10:40am **SE+PS-ThM9 CO_2 Conversion to CO and O_2 by DBD Plasma at Atmospheric Pressure**, ***G. Arnoult***, *T. Bierber, A. Ozkan, P. De Keyzer, F.A.B. Reniers*, Université Libre de Bruxelles, Belgium

Because of its high thermodynamical stability, carbon dioxide is usually considered as a waste, unavoidable end-product of many industrial processes. It is therefore necessary to develop technologies able to reuse it. In this objective, dry reforming of carbon dioxide by plasma has attracted significant interest to generate carbon monoxide which has an interesting energetic value [1], [2].

We present here a study of the plasma assisted conversion of CO_2 into CO and O_2 in a Dielectric Barrier Discharge plasma device operating at atmospheric pressure. We focus on determining the influence of several parameters on the conversion efficiency: the input power, the flow rate and finally the use or not of an additional plasmagen gas (argon or helium) in the mixture. Gas chromatography and mass spectrometry at atmospheric pressure are used to determine the composition of the gas after plasma treatment. Conversion rates for CO_2 can then be extracted.

The conversion rate increases with the power, suggesting an effect of the electron density (Fig.1 and Fig.2). On the other hand, the conversion rate drops with increasing flow rate from 0.1 L/min to 10 L/min. Indeed since the flow rate is inversely proportional to the residence time of the gas in the reactor, increasing it means that the gas spends less time in the plasma. Furthermore the addition of a plasmagen gas increases the conversion rate.

Optical emission spectroscopy and electrical measurements are also performed in order to have a better comprehension of the physical and chemical processes leading to the observed results.

[1] R. Li, Q. Tang, S. Yin, et T. Sato, « Plasma catalysis for CO_2 decomposition by using different dielectric materials », *Fuel Processing Technology*, vol. 87, n° 7, p. 617–622, 2006.

[2] S. Paulussen, B. Verheyde, X. Tu, C. De Bie, T. Martens, D. Petrovic, A. Bogaerts, et B. Sels, « Conversion of carbon dioxide to value-added chemicals in atmospheric pressure dielectric barrier discharges », *Plasma Sources Science and Technology*, vol. 19, p. 034015, 2010.

11:00am **SE+PS-ThM10 Cold Atmospheric Plasma Assisted Production of Hydrogen**, ***L. Bardos***, *H. Baránková*, Uppsala University, Sweden

Experimental study of submerged cold atmospheric plasma generated in water and in water-based mixtures has been carried out. A hermetic stainless steel reactor with an originally designed coaxial plasma source immersed in the tested liquid has been used both with and without additional gas transported into the plasma zone. The reactor has been equipped with a pH meter, conductivity meter, thermometer, a simple pressure gauge, and a quartz fiber optics for optical emission spectroscopy of the submerged plasma. A sensor measuring the hydrogen content has been installed at the outlet of the reactor after rotameter tube measuring the outlet gas flow. The gas outlet has been provided also by a simple jet for gas flammability tests. Several types of the power generators have been tested for ignition and maintenance of the submerged plasma in the water and in water mixtures with ethanol. Preliminary experiments have confirmed production of the hydrogen containing synthesis gas that can be enhanced by adding ethanol admixtures. Very short dc pulses with average power of less than 50 W led to spontaneous formation of gas bubbles and flammable outlet gas with more than 50 % H2.

11:20am **SE+PS-ThM11 Optical Emission Spectroscopy of He Dielectric Barrier Discharges at Atmospheric-Pressure Applied to the Functionalization of Wood Surfaces**, ***L. Stafford***, *R.K. Gangwar, O. Levasseur*, Universite de Montreal, Canada, *N. Gherardi*, CNRS-LAPLACE, France, *N. Naudé*, Universite Paul-Sabatier, France

Application of dielectric barrier discharges (DBD) to the modification of "novel" materials such as nanostructured polymers is much more challenging than for conventional substrates such as Si or SiO2. This can be attributed not only to the highly anisotropic nature of this polymer which can introduce spatial inhomogeneities of the electric field near the substrate surface, but also to its highly porous microstructure which can release impurities either from plasma-substrate chemical reactions or from sample outgassing. In this work, a porous wood sample (sugar maple, acer saccharum) was placed on the bottom electrode of a DBD operated in nominally pure helium to examine the influence of plasma-wood interactions and substrate outgassing on the evolution of the plasma properties. Optical emission spectroscopy revealed strong emission from N2, N2+, O and OH impurities. While the nitrogen and oxygen emission can be attributed to air outgassing, the OH emission was ascribed to etching of the weak boundary layer and humidity desorption from wood. We have calculated various line ratios from the time-resolved optical emission spectra. The He-588 nm-to-He-707 nm line ratio, I588/707, was found to decrease from when going from right after ignition of the first few discharges where substrate outgassing is important to longer treatment times where "pumping" of the wood samples is nearly complete. Assuming that the He 3D and 3S levels (L•S coupling) giving rise to the emission at 588 and 707 nm are populated by stepwise excitation through the most populated metastable He 3S1 level and are lost by spontaneous emission, the I588/707 line ratio becomes link to the ratio of the rate for stepwise excitation of the He 3D and 3S levels, which is only a function of the electron temperature Te. Accounting for collisional energy transfer reactions between the He 3D, 3P, and 3S states in atmospheric-pressure plasmas and using the set of cross sections reported in literature for stepwise excitation, energy transfer reactions, and collisional quenching, it was found that the observed decrease of I588/707 can be ascribed to an decrease of the electron temperature. Further analysis of the time evolution of the emission spectra and of the current-voltage characteristics indicated that the release of products from the wood substrate also yields to a significant quenching of He metastables. This method was further used to examine the detailed influence of hexamethyldisiloxane (HMDSO) and titatnium isoproxyde (TTIP) injection on the plasma characteristics during plasma enhanced chemical vapor deposition of functional, nanostructured coatings on wood.

11:40am **SE+PS-ThM12 Substitution of ThO_2 by La_2O_3 for Tungsten Electrodes used in Atmospheric Plasma Spraying**, *M. Heissl*, ***C. Mitterer***, Montanuniversitaet Leoben, Austria, *T. Granzer, J. Schroeder, M. Kathrein*, PLANSEE Composite Materials GmbH, Germany

ThO_2 additions are commonly used in tungsten-based electrodes for plasma spraying due to the excellent electron emissivity, improved arcing behavior, higher strength, and better machinability. Because of their radioactive potential, which makes handling, use, recycling, and disposal more difficult, alternative additives are required that provide the same advantages as thoriated tungsten, but without environmental hazards. Within this work, tungsten cathodes with 2 wt.% ThO_2 and 1 wt.% La_2O_3 were compared with respect to their arc ignition behavior, plasma stability and arc erosion. Both, cyclic and continuous plasma spraying experiments were carried out. In addition, structure and mechanical properties of Al_2O_3 coatings sprayed on Mo substrates were evaluated. La_2O_3 is characterized by a similar plasma ignition and operation behavior as well as a comparable coating quality with respect to ThO_2 additions. Further, La_2O_3 additions caused a reduced degradation of the cathode material, which is attributed to the lower cathode temperature, giving rise to an expected longer lifetime.

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