

Monday Afternoon, October 31, 2011

Plasma Science and Technology Division

Room: 201 - Session PS+SE-MoA

Advanced FEOL / Gate Etching II

Moderator: A. Kadavanich, Mattson Technology

2:00pm **PS+SE-MoA1 Mechanical Analysis of the Line Edge Roughness in the sub-20nm Line Patterns**, *S.W. Park, K.H. Baek*, Samsung Electronics Co., Ltd, Republic of Korea, *S.H. Choi, J.S. Hong*, Lam Research Corporation, *K.S. Shin, Y.G. Shin, H.G. Kang*, Samsung Electronics Co., Ltd, Republic of Korea

In this study, the deterioration of line edge roughness during plasma etching process was analyzed to find possible control parameters. According to the aggressive design rule shrinkage of memory devices, the physical width of line patterns has become around 20nm. Controlling line edge and width roughness now became one of the biggest challenges in patterning process. Though a number of studies on this matter have done, the wiggling of line patterns is still making the migration slower. It is well known truth that the line edge and width roughness are mainly caused by the projection of poor photoresist patterns. However, the recent line patterns of around 20nm design rules experience severe wiggling added from the plasma etching process. This study focused on this etch-induced deformation that increased line edge roughness from the prior status. The final line edge roughness was assumed as the sum of the wiggling projected from that of mask pattern and the deformation during plasma process. The deformation part was explained with the equations of the mechanical beam theory assuming several stress sources originated from the plasma. This newly introduced approach could suggest the direction of process modification for more robust profile against deformation. Moreover, combining with the material properties of commonly used materials, this approach could estimate the extent of lateral deformation so that the ultimate size of line patterns could be expected in the aspect of line edge roughness.

2:20pm **PS+SE-MoA2 Dependence of ArF Photoresist Polymer Structure on Line-Edge-Roughness Formation during Plasma Etching Processes**, *T. Uesugi, A. Wada*, Tohoku University, Japan, *S. Maeda, K. Kato, A. Yasuda, S. Sakuma*, Mitsubishi Rayon, Japan, *S. Samukawa*, Tohoku University, Japan

ArF excimer laser (193nm) lithography technique is widely used in the fabrication of sub-50-nm devices. During plasma etching processes, however, the activated species radiated from plasma, such as ions, radicals, and photons, cause damages to ArF photoresist, resulting in low etching resistance and formation of line-edge roughness (LER). To solve these issues, we investigated the interaction between irradiated species from plasma and polymer structure of ArF photoresist. In our previous study, we found that improvement of stability of lactone group in side chain of ArF photoresist realized decrease in etching rate and reduction of the surface roughness of ArF photoresist.

In this study, to further improve the etching resistance and the surface roughness of ArF photoresist, we proposed a new polymer structure of ArF photoresist. Our newly developed ArF photoresist structure has acrylate group in main chain polymer structure, while usual ArF photoresist has methacrylate group in main chain polymer structure. We prepared silicon wafers coated by ArF photoresists with methacrylate group and acrylate group and etched them using chlorine plasma. As a result, these two types of photoresists had almost same etching rates. This result suggests that main chain structure of ArF photoresist does not affect its etching rate. On the other hands, the surface roughness of acrylate type photoresist after etching was drastically reduced in comparison with that of methacrylate type photoresist. It is considered to be due to stronger bonding energy of acrylate group than methacrylate group. From this result, it is concluded that the acrylate type ArF photoresist structure is very effective to suppress the roughness formation in ArF photoresist.

2:40pm **PS+SE-MoA3 193nm Photoresist Pre-Treatments Before Plasma Transfer to Improve LWR Transfer and CD Control**, *E. Pargon*, CNRS-LTM, France, *L. Azarnouche*, ST Microelectronics, France, *M. Fouchier, K. Menguelti, O. Joubert*, CNRS-LTM, France

Linewidth roughness (LWR) is today one of the main parameters that limits our ability to shrink the transistor gate dimension down to 20nm. Indeed, LWR needs to be controlled down to 2nm to ensure good electrical performance of the future CMOS device, while state of the art patterning techniques only allows 4-3 nm gate LWR at best. The major issue in decreasing the gate LWR comes from the fact that the significant LWR of the resist pattern printed after 193nm lithography (about 6nm measured by

CDAFM) is transferred into the gate stack materials during the subsequent plasma etching processes. One way to minimize the final gate LWR is to apply various pre-treatments to the resist patterns obtained right after lithography (before any plasma pattern transfer step).

In the present study, we have used CD-SEM and CD-AFM techniques to investigate the impact of different types of resist pre-treatments (combining plasma exposure (HBr, Ar, H₂ plasmas), vacuum ultra violet (VUV) light exposure, and annealing) on the photoresist LWR and profile. Many characterization techniques (FTIR and Raman spectrometries, ellipsometry, chromatography, DMA, TGA) have also been used to characterize the physico-chemical modifications of photoresist films responsible for the resist smoothing. We have also investigated the benefits of those resist pre-treatments on both LWR and CD control after pattern transfer in different stacks of materials.

We will show that all treatments generate resist chemical modifications that lead to a decrease in resist LWR while the etch resistance is not always improved. All treatments have in common the cleavage of the side groups (lactone group for plasma treatment and protecting group for annealing treatment) and a decrease of the glass transition temperature that seems to have a direct impact on the LWR decrease. But some other mechanisms compete according to the treatment used and its duration: main chain scission and crosslinking, leading to some different etch resistance improvement. Consequently even if some specific treatments (VUV light exposure, annealing) can improve the resist LWR before transfer, the subsequent plasma etching steps can degrade it and also induce a loss of CD control. We will show that by combining plasma exposure and annealing treatment the photoresist LWR could be decreased down to 2.6nm and that this LWR could be transferred into polysilicon gate without LWR and CD degradation.

3:00pm **PS+SE-MoA4 Plasma Smoothing of Extreme Ultraviolet Photoresist: LWR Reduction at 30nm Half Pitch**, *E. Altamirano-Sanchez*, *A. Pret Vaglio, R. Gronheid, D. Marc, W. Boullart*, IMEC, Belgium

Over the past years a tremendous amount of effort has been put on Extreme Ultraviolet lithography (EUVL) for printing the 16nm node. In 2010 imec's EUV alpha demo tool printed for the first time a 16nm node SRAM cell using state-of-the-art EUV photoresist (PR). In order to meet the line width roughness (LWR) requirements for the 16nm node, we have investigated plasma smoothing techniques on 30nm half pitch lines after exposure.

In this contribution we will report our findings on EUV PR plasma treatment (PT) using H₂, Ar and HBr for LWR reduction; and subsequent, in-situ PR encapsulation for preserving the improved LWR during subsequent pattern transfer. Currently we are investigating the vacuum UV role during the H₂ PT using MgF₂ windows. In parallel, we are characterizing a PR resist encapsulation carried out in-situ (in the etching chamber). The encapsulating layer is characterized through various analytical techniques, such as: XPS, Ellipsometry, mass metrology and TEM. These characterizations will provide understanding of how the H₂ plasma improves the LWR and of how the PR encapsulation preserves the PR pattern allowing a straight HM patterning profile.

This study was carried out on 300 mm silicon wafers with the following patterning stack, from top to bottom: 50 nm PR/20 nm under layer (UL)/15 nm SiOC/40 nm amorphous carbon layer (ACL). The dry etching was carried out in a ICP like reactor from Lam research (Kiyoo C reactor TCPTM)

Power spectral density (PSD) analyses have shown that Ar and HBr plasmas do not improve the LWR of EUV PR as they do on 193i PR. Using the correct conditions in the ICP reactor, H₂ plasmas can improve LWR by ~30% without CD bias; in other words no PR reflow was detected.

After the H₂ plasma treatment, the pattern was transferred into the UL using a CH₂F₂/CF₄/O₂ gas mixture. This chemistry provides on the one hand a high PR passivation but on the other hand induces a PR pattern degradation, which is translated into higher LWR. A novel alternative for maintaining the improved LWR after H₂ PT was to deposit in-situ (in the ICP reactor) a silicon containing layer that encapsulates the PR and preserves the improved LWR when the pattern is transferred into the UL, the SiOC and the ACL.

3:40pm **PS+SE-MoA6 Controlling Line Edge Roughness for Aggressively Scaled CMOS Devices by Reducing Organic Underlayer Deformation.** *H. Miyazoe, S.U. Engelman, M. Glodde, M.A. Guillorn, M. Brink, A. Banik, W.S. Graham, E.M. Sikorski, N.C.M. Fuller*, IBM T.J. Watson Research Center

As the feature size in CMOS technology continues to shrink, control over line edge roughness (LER) and line width roughness (LWR) is approaching atomic scale for the 14 nm node and beyond. When the line/space patterns are decreased, deformation of the organic underlayer material occurs during plasma processing, which adversely impacts pattern transfer into substrate material to fail. We previously reported that vacuum ultraviolet (VUV) “curing” (modification) of the organic under layer material by plasma discharges is a promising approach to extend the process window for obtaining high fidelity pattern structures [1]. To understand the details of this approach in more detail, we exposed VUV light at various wavelengths corresponding to the absorption energies of various underlayer materials by synchrotron radiation on “unopened” and “opened” samples comprising stacks inclusive of the underlayer material. We found that exposing underlayers to certain absorption maxima of the patterning material maximize the curing effect. Specifically, for the underlayer material trademarked as NFC, absorption maxima at 155 nm had relatively large effect, reducing LER by as much as 37%. Curing treatments on “unopened” (post lithography) samples comprising varying underlayer materials effectively reduced the pattern deformation, though much less effective than on previously “opened” samples comprising the same. Similarly, chemical and physical effects of the plasma on underlayer material deformation were investigated. To investigate the changes based on chemical modification by plasma, we have generally found that the non-selective pattern transfer plasmas are better than highly selective processes to minimize the deformation. In addition, we also noticed that the ion energy of the discharge plays an important role in the deformation and found that the extent of pattern deformation decreased for lower energies. In addition, many commercially available organic underlayer materials were tested with respect to their composition and hardness. We found that the relative hydrogen content of the underlayer material seemed to correlate with the deformation behavior, while little effect was seen for hardness. These initial findings show that a close interlock between patterning materials, lithography and plasma processes has to be executed to minimize effects such as LER for future technology nodes.

[1] N.C.M. Fuller *et al.*, AVS presentation (2007).

4:00pm **PS+SE-MoA7 Single Digit Nano Plasma Etching.** *D.L. Olynick*, Lawrence Berkeley National Laboratory **INVITED**

One of our themes at the Molecular Foundry at LBNL is “Single-Digit Nanofabrication” (SDN) which describes our efforts to pattern materials with resolution, precision, and control at the sub-10 nm scale. At this scale, we enable research and applications in areas such as nanoelectronics, nanomagnetism, nanofluidics and plasmonics. For instance, the Molecular Foundry’s work on graphene nanomeshes using SDN show a band gap opening with sub-bands.¹ However, the patterning and plasma pattern transfer for SDN present significant challenges and the question arises, “What are the limits?”

In this talk, I will survey nanoscale etching work from 30-3 nm to demonstrate the challenges and opportunities for plasma nanopatterning. High resolution patterns are made using a variety of materials and techniques including atomic layer deposition, directed self-assembly and electron beam and nanoimprint lithographies. Recent work with cryogenic etching and simulation in the SDN regime will be highlighted.

1.Liang, X.; Jung, Y.-S.; Wu, S.; Ismach, A.; Olynick, D. L.; Cabrini, S.; Bokor, J., *Nano Lett* **2010** 10, pp 2454-2460.

This work was performed at the Molecular Foundry, Lawrence Berkeley National Laboratory, and was supported in part by the U.S. Department of Energy under Contract No. DE-AC02—05CH11231

4:40pm **PS+SE-MoA9 Ar and He Plasma Pretreatments of Organic Masking Materials for Performance Improvements during Plasma Pattern Transfer.** *D. Metzler, F. Weillboeck, N. Kumar, G.S. Oehrlein*, University of Maryland, S. Engelmann, R.L. Bruce, N.C.M. Fuller, IBM T.J. Watson Research Center

Plasma based pretreatments (curing) of organic masking materials have been shown to offer significant potential for reduction of surface, line edge and line width roughness during the subsequent pattern transfer process. Since one of the underlying mechanism of roughness formation has been reported to be a synergistic effect of energetic ion bombardment, ultraviolet (UV) / vacuum ultraviolet (VUV) plasma radiation and increased temperature, a possible mechanism of organic mask curing may be the elimination of the above synergism by sequential exposures to VUV plasma radiation followed by ion bombardment dominated plasma etching. To examine this question, and establish the impact of pre-treatments on

roughness introduction, etch resistance and pattern transfer fidelity during the pattern transfer process, we have studied pretreatments of 193nm PR and other organic masking materials in Ar and He discharges with pronounced UV/VUV emission. The impact of pretreatments and subsequent pattern transfer processes on the organic materials were monitored in real-time by in-situ ellipsometry. Multilayer modeling of these data allows determination of optical material density and film thickness of various layers, i.e. the surface layer densified by ion bombardment, the UV/VUV modified layer in the material bulk, and the rough surface layer. Additionally, post plasma characterization by Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM) provides information on bulk material modifications and surface roughness improvements, respectively. UV/VUV spectroscopy combined with Langmuir probe characterization provides information on plasma parametric dependencies of photon and ion fluxes, respectively. Pretreatments in a He discharge reduced roughness introduction in a C₄F₈/Ar pattern transfer process by ~50% (RMS=4nm) while increasing film etch resistance by ~30% leading to only a slight increase in the total material removal when compared to the uncured material (pattern transfer only). Time resolved studies of this process allow detailed investigation of distinct stages and underlying mechanisms of materials modification, such as radiation induced changes in the materials bulk, ion crust formation at the film surface, and surface roughness development. Correlating these observations with post plasma characterization by AFM and FTIR allows a mechanistic understanding of plasma based pretreatments or organic materials and their impact on the subsequent pattern transfer process. The dependence of improvements in masking performance on Ar and He plasma based pretreatments and a description of the underlying mechanisms will be presented.

5:00pm **PS+SE-MoA10 Sub-32nm Node Mask Patterning for Deep Silicon Trench Etch.** *J. Yarmush, H. Haga, Y. Chiba, K. Kumar, P. Biolsi*, TEL Technology Center, America, LLC, J. An, H. Hichri, B. Dirahoui, X. Li, IBM Microelectronics, R. Wise, IBM Research

In the last several semiconductor device generations, one of the complexities in fabricating ever smaller feature sizes and increased density, has been the stringent requirements placed on photolithographic processes and mask scheme formation. The use of Immersion Lithography, reduced resist layer thicknesses and planarity requirements have driven the need for complex multilayer-multimaterial stacks that can be utilized for subsequent plasma Etching masks.

One requirement by manufacturers of Sub-32nm DRAM technology, utilizing deep silicon memory cells, is an extremely high aspect ratio mask that enables the anisotropic etch profile of the Silicon Trench. To meet both the needs of the photolithographic processes and the high aspect ratio mask requirements of the Silicon Trench etch, a complex Photo Resist, Silicon Anti-reflective coating, Optical Dispersive Layer, CVD Oxide layer is used. This deposited mask stack also sits on top of a Silicon-on-Insulator layer that must also be etched through anisotropically.

In this paper, we describe the unique requirements of etching each film stack in order to meet the overall physical requirements of this high aspect ratio mask patterning etch. It also describes the process capabilities of a commercially available Capacitively Coupled Plasma reactor that enables it to meet these advanced complex film stack requirements.

This work was performed by the Research and Development team at TEL Technology Center America in joint development with IBM Semiconductor Research & Development Center.

5:20pm **PS+SE-MoA11 Quantitative Determination of the Mechanism of Anisotropic Silicon Etching.** *M. Hines, M.F. Faggin, K. Bao, A. Gupta, B. Aldinger*, Cornell University

The production of atomically perfect surfaces by simple solutions is both intrinsically fascinating and technologically important. For over half a century scientists have known that many aqueous bases — so-called “anisotropic etchants” — selectively attack all silicon faces except Si{111}. As a result, a macroscopic silicon sphere placed into one of these solutions spontaneously transforms into a polyhedron. Twenty years ago, the surface science community was rocked when researchers at Bell Labs showed that, in some cases, the etched surfaces are not just smooth, they are atomically flat and passivated by a single monolayer of H atoms. This type of highly precise but inexpensive chemical machining is used in diverse applications ranging from the production of ink-jet nozzles to the fabrication of ultrasmall transistors to the cleaning and polishing of silicon wafers; however, the chemical reactions that govern this behavior remain a source of controversy. We resolve this controversy and give the first quantitative, atomic-scale understanding of anisotropic etching across all silicon surface — not just Si(111).

The reactivity of a wide variety of Si(100) surface sites towards a prototypical anisotropic etchant, ammonium fluoride, is quantitatively

determined from measurements of the atomic-scale morphology and chemical composition of etched surfaces. These measurements enable the effects of chemical strain, steric hindrance, and chemical structure to be separately determined. The high selectivity of the etchant is explained by the strain energy released during the chemical reaction; steric hindrance plays an important, but distinct, role. This pattern of reactivity is inconsistent with previously postulated mechanisms of aqueous silicon etching, which postulate insertion reactions across rigid, essentially immobile Si-Si backbonds. Instead, we propose that cleavage of the backbond occurs during the formation of a surface silanone which is driven by simultaneous interadsorbate strain release. On Si(100) surfaces, this hypothesis *quantitatively* explains the characteristic alternating-row etch morphology on both flat and vicinal surfaces, the observed site-specific reactivity, the unusual reaction kinetics, and the hydrogen termination of the etched surface without invoking an unreasonably strained reaction intermediate. This mechanism also explains the atomic-scale reactivity and relative etch rates of the three principal faces of silicon, thereby giving the first atomic-scale understanding of anisotropic silicon etching.

Tuesday Morning, November 1, 2011

Thin Film Division

Room: 104 - Session TF+SE-TuM

Glancing Angle Deposition (GLAD) I

Moderator: T. Karabacak, University of Arkansas at Little Rock

8:20am **TF+SE-TuM2 Progress in Glancing Angle Deposition Technology for Practical Applications**, M. Suzuki, Kyoto University, Japan **INVITED**

Recently, advanced top-down processes for the fabrication of nanostructures have been developed; however, these processes are long predated by the process of shadowing growth by glancing angle deposition (GLAD), which affords the fabrication of the self-assembled nanostructures over a much larger area at significantly lower costs. In the past two decades, significant progress has been made in the development of 3D nanomorphologies well-controlled by the GLAD such as the zigzag and helix morphologies. Much effort has also been expended to gain a theoretical and numerical understanding of the growth mechanism of nanostructures in order to improve their morphology. Many researches are being carried out in academia to investigate the useful properties of nanocolumnar thin films, such as magnetic anisotropy, birefringence, dichroism, and optical activity *induced by nanoshapes*; high-performance catalysis and electrodes *using large surface area*; and various *size effects*. On the other hand, most companies seem hesitant to introduce the GLAD technique in the factory because of the prejudice that obliquely deposited thin films are not durable and reproducible. However, some products of obliquely deposited thin films are already being manufactured, although their production processes have not necessarily been disclosed. In this presentation, we discuss the previous products and investigations of GLAD thin films and demonstrate that this prejudice can be overcome. In addition, we introduce our recently commercialized products manufactured by GLAD, namely, surface enhanced Raman substrate¹ and low-reflectivity wire-grid polarizers². Because GLAD films have the great potential of enabling humankind to overcome the energy and environmental problems it confronts, it is important to encourage the industry to adopt GLAD by removing the prejudice against GLAD films.

[1] M. Suzuki *et al.*, "Au Nanorod Arrays Tailored for Surface-Enhanced Raman Spectroscopy," *Analytical Sciences* **23**, 829 (2007).

[2] M. Suzuki *et al.*, "Low-Reflective Wire-Grid Polarizers with Absorptive Interference Overlayers," *Nanotechnology* **21**, 175604 (2010).

9:00am **TF+SE-TuM4 Engineering Columnar Nanostructures for Organic Photovoltaics**, R.T. Tucker, Univ. of Alberta, Canada, D.A. Rider, NRC-Nat. Inst. for Nanotech., Canada, J.G. Van Dijken, M. Thomas, B.J. Worfolk, A. Lalany, K.M. Krause, Univ. of Alberta, Canada, M.D. Fleischauer, NRC-Nat. Inst. for Nanotech., Canada, M.T. Taschuk, Univ. of Alberta, Canada, K.D. Harris, NRC-Nat. Inst. for Nanotech., Canada, J.M. Buriak, M.J. Brett, Univ. of Alberta, Canada

Organic photovoltaics (OPVs) represent one possible route to widespread adoption of solar energy production [1]. The most promising OPV technology to date has been the bulk heterojunction, a photoactive mixture which bridges the gap between exciton diffusion lengths (~15 nm) and typical device length scales (~200 nm). However, bulk heterojunctions are typically disordered, which can limit charge extraction and thereby reduce OPV performance. The ideal OPV bulk heterojunction structure has been identified as ordered interpenetrating columnar electron donor and acceptor layers [2]. The interface morphology of such structures may be fabricated with glancing angle deposition (GLAD), a well-developed, robust nanostructuring technique that has been demonstrated for numerous materials at the length scales required for high quality OPV devices.

Here we present a summary of organic solar cell research utilizing GLAD at the University of Alberta. GLAD's flexibility lends itself to structuring both the transparent conductor layer as well as the donor and acceptor photoactive layers. We have demonstrated GLAD structuring of indium tin oxide (ITO), copper (II) phthalocyanine (CuPc), and fullerene (C60). ITO nanopillars fabricated by GLAD have been incorporated as three dimensional high surface area electrodes in organic photovoltaic devices [3]. The nanostructured electrodes demonstrated 30% improved performance compared to planar ITO anodes, due to increased optical absorption and high surface area. Typical OPV donor and acceptor materials, CuPc and C60, have also been successfully structured by the GLAD technique [4,5]. Advanced motion control algorithms, designed to

form thinner columns, were used to optimize the material nanostructures and produce highly desirable ordered bulk heterojunctions when coupled with complementary polymers. In the case for GLAD C60 devices, the short-circuit current was double that of bulk heterojunction devices. The GLAD technique has proven to be an incredibly useful method for fabricating and tuning electrode and bulk heterojunction morphologies in OPVs.

[1] H. Spanggaard and F.C. Krebs, *Sol. Energy Mater. Sol. Cells* **83** 125-146 (2004)

[2] F. Yang and S.R. Forrest, *ACS Nano* **2** (5), 1022-1032 (2008)

[3] D.A. Rider *et al.*, *Nanotechnology* **22** (8), 085706 (2011)

[4] J.G. Van Dijken *et al.*, *J. Mater. Chem.* **21** (4), 1013-1019 (2011)

[5] M. Thomas *et al.*, *ACS Appl. Mater. Interfaces* (in press, 2011)

9:20am **TF+SE-TuM5 Enhanced Photoconductivity Response of Glancing Angle Deposited Indium Sulfide Nanorod Arrays for Photodetector Device Applications**, H. Is, M.F. Cansizoglu, T. Karabacak, University of Arkansas at Little Rock

Photoconductivity (PC) in semiconductors can be detected by measuring the change in electrical conductivity when the material is exposed to light. Photosensitive materials with high PC response can be useful especially for photodetector applications. Compared to conventional thin film geometry, semiconducting nanostructures can provide enhanced photoresponse due to their low dark conductivity and superior capability of absorbing light, which leads to an enhanced PC response even to the minimal changes in light intensity. Glancing angle deposition (GLAD) provides a unique capability of producing nanostructured arrays of various materials with controlled shapes, size, and separation. In this study, we fabricated semiconducting indium sulfide nanorod arrays by GLAD on ITO coated glass substrates in various lengths and capped them with a silver film as metal contact to form a proof-of-concept photodetector device. PC response of these devices was measured at different wavelengths with altered light intensities. We show that GLAD nanorods have a superior PC response than conventional thin film, which is believed to be mainly due to their enhanced light trapping and high optical absorption property.

10:40am **TF+SE-TuM9 Catalytic Nanomotor Control: Design Techniques Using Dynamic Shadowing Growth**, J.G. Gibbs, Y.P. Zhao, University of Georgia

Catalytic nanomotors with nanometer-to-micrometer dimensions convert chemical energy into mechanical work via catalysis allowing for autonomous self-propulsion. They are an emerging nanotechnology field and promise important technological advances in drug delivery, transport, assembly, and other processes at the nano-scale. Catalytic nanomotors are inorganic analogues of cellular motor proteins that convert chemical energy into work through stored energy. One of the greatest challenges in this field is the manipulation and direct control of motion and swimming behaviors.

We focus upon the geometric design of catalytic nanomotors to modulate motion behaviors. To achieve this goal, a dynamic growth technique must be implemented. Most research uses template-directed electroplating (TDEP) allowing only simple geometries. We use dynamic shadowing growth (DSG) for fabrication which is a dynamic process allowing for construction of a much wider range of structures and shapes.

Depositing different materials and controlling the overlapping area is the first method of motion modulation used. To alter the swimming speed of a spherical nanomotor, Au is overlapped with the Pt-catalyst to varying degrees; the Au surface area A is changed systematically. The average moving speed u is found to follow the scaling relationship, $u \propto A^{-1/2}$, which agrees with the self-electrophoresis mechanism.

Swimming behaviors can also be altered by geometrical design, easily implemented by DSG making the technique useful to engineer different types of motion. Various swimming behaviors are exhibited by altering the geometry, and/or changing the location of the Pt catalyst accomplishable. Two very similar structures were fabricated and move based upon the location of the catalyst. Multi-component rotational nanomotors consisting of Pt coated TiO₂ nanoarms grown upon ~ 2.01 μ m diameter silica microbeads are designed by dynamic shadowing growth. When exposed to hydrogen peroxide, H₂O₂, the structures rotate about an axis through the center of the microbead and perpendicular to the TiO₂ nanoarm at a rate of 0.15 Hz per % H₂O₂ concentration. The other nanomotors are tadpole-like structures that swim in large sweeping circular trajectories. The swimming trajectories are fine-tuned by altering the arm length and orientation

exploiting geometry-dependent hydrodynamic interactions at low Reynolds number. The curvature, angular frequency, and radius of curvature of the trajectories change as a function of arm length. Simulations based on the method of regularized Stokeslets are also described and correctly capture the trends observed in the experiments.

11:00am **TF+SE-TuM10 Fabrication of Cr-doped TiO₂ Nanorod Arrays by Oblique Angle Co-Deposition and Their Photocatalytic Properties**, *G.K. Larsen*, University of Georgia, *R. Fitzmorris, J.Z. Zhang*, University of California Santa Cruz, *Y.P. Zhao*, University of Georgia

In order to achieve efficient photocatalytic behavior in the visible light range, transition metal ions are often doped into TiO₂. Of these transition metal dopants, Cr appears superior in extending the photoresponse of TiO₂ into the visible range. However, different fabrication methods have produced mixed results regarding the effect of the Cr dopant on photocatalytic efficiency. In this study, a unique fabrication method, oblique angle co-deposition (OACD), is used to deposit a well-aligned array of Cr-doped TiO₂ nanorods that exhibit optical absorption in the visible region. These films are compared with TiO₂ nanorod arrays fabricated by oblique angle deposition (OAD). Due to the similarity of fabrication methods, the effect of the dopant on the structural, optical, and photocatalytic properties of TiO₂ can be isolated. The Cr dopant alters the TiO₂ lattice structure, with an increase in the crystallization temperature of the anatase phase and a decrease in the rutile crystallization temperature. Additionally, Cr is found to segregate out of the TiO₂ matrix and migrate to grain boundaries and the surface of the nanorods. The photocatalytic efficiency and IPCE of the Cr:TiO₂ films is reduced when compared to intrinsic TiO₂ due to changes in the photocatalyst's surface and charge transport properties as a result of the formation of intergranular Cr(VI) oxide clusters. The presence and the effects of the Cr(VI) phase is the result of exceeding the solubility limits of Cr within the TiO₂ lattice.

11:20am **TF+SE-TuM11 Optimal Conditions for Visualization of Fingerprints with the Conformal-Evaporated-Film-By-Rotation Technique**, *D.P. Pulsifer*, *S.A. Muhlberger*, *R.J. Martín-Palma*, *R.C. Shaler*, *A. Lakhtakia*, Pennsylvania State University

The conformal-evaporated-film-by-rotation (CEFR) technique was investigated for use as a development technique to visualize sebaceous fingerprints of forensic importance. A variation on oblique angle deposition, the CEFR technique requires the substrate holder to rapidly rotate about a perpendicular axis. The combination of an obliquely directed, collimated vapor flux and rapid rotation of the substrate gives rise to a conformal coating on the residue left behind on a substrate by the friction ridges of the finger. The coating has a closely packed nanocolumnar morphology. We conducted a systematic study of various deposition parameters in order to identify those conditions which are optimal for the development of fingerprints with the CEFR technique. We varied: base pressure during deposition, vapor flux angle with respect to the substrate plane, substrate rotation rate, deposition rate, and final film thickness. By qualitatively comparing fingerprints before and after development for various values of each deposition parameter, we were able to identify optimal conditions for development. For all depositions chalcogenide glass of nominal composition Ge₂₈Se₆₀Sb₁₂ was used to coat sebaceous fingerprints placed on glass microscope slides. We found the optimal conditions to be: a vapor flux angle of 10 deg as measured from the substrate plane, a rotation rate of 3 rps, a deposition rate of 1 nm/s, a final film thickness of 500 nm, and a deposition pressure of 0.1 mTorr. These values are close to those reported previously for CEFR coating of fingerprints with the exception of the base pressure. An optimal base pressure of 0.1 mTorr significantly relaxes the vacuum requirements of an evaporation chamber to be used for this purpose, making the technique very accessible to forensic scientists and law enforcement agencies. This work was supported by Grant No. 2010-DN-BX-K232 from the U.S. Department of Justice.

Advanced Surface Engineering Division

Room: 104 - Session SE+TF-TuA

Glancing Angle Deposition (GLAD) II

Moderator: N.A. Beckers, University of Alberta

2:00pm SE+TF-TuA1 Evolution of Crystal Orientation during Oblique Angle Deposition. G.-C. Wang, T.-M. Lu, Rensselaer Polytechnic Institute **INVITED**

The oblique angle deposition (OAD) has attracted attention due to the shadowing effect that results in interesting morphology of isolated nanostructures. These artificial nanostructures have rich textures depending on the growth conditions such as the angle of incidence, substrate temperature, deposition rate, and substrate rotation speed or mode. These OAD films often have biaxial textures even on amorphous substrates because the in-plane symmetry is broken under the off-normal incidence of the deposited atoms on the substrate. The most frequently used characterization technique for biaxial texture films is x-ray pole figure analysis. However, the texture obtained by x-ray is an average texture from the entire thickness of the film due to the x-ray's few micron penetration depth. As the texture of a film often changes during growth, information on the basic mechanisms that control the final texture is often lost. In this talk we will show how we can use our newly developed reflection high energy electron diffraction (RHEED) surface pole figure technique to probe the surface texture evolution of the growth front from the initial stage (a few nm thick) to the later stage of thick films [1] either *in situ* or *ex situ*. Examples of biaxial texture evolution of CaF₂ [2], Mg, W [3] and Mo nanostructures as a function of thickness, incident angle, and rotation schemes, will be presented. The surface sensitive RHEED pole figure technique reveals that biaxial texture can be formed at thickness as small as 20 nm. In some cases, surface texture at the growth front is seen to be quite different from the bulk texture measured by x-ray pole figures. We also show that these biaxial textured films can be used as buffer layers to grow near-single crystal semiconductor films which may find important applications in energy conversion devices.

Work was supported by NSF-0506738.

[1] F. Tang, T. Parker, G.-C. Wang, and T.-M. Lu, "Surface texture evolution of polycrystalline and nanostructured films: RHEED surface pole figure analysis", *Journal of Physics D: Applied Physics* 40, R427 (2007).

[2] C. Gaire, P. Snow, T.-L. Chan, W. Yuan, M. Riley, Y. Liu, S.B. Zhang, G.-C. Wang and T.-M. Lu, "Morphology and texture evolution of nanostructured CaF₂ films on amorphous substrates under oblique incidence flux", *Nanotechnology* 21, 445701 (2010).

[3] R. Krishnan, Y. Liu, C. Gaire, L. Chen, G.-C. Wang and T.-M. Lu, Texture evolution of vertically aligned biaxial tungsten nanorods using RHEED surface pole figure technique, *Nanotechnology* 21, 325704 (2010).

2:40pm SE+TF-TuA3 Vapor-Liquid-Solid Glancing Angle Deposition (VLS-GLAD): A New Way of Shaping Crystalline Nanowires, A.S. Alagoz, T. Karabacak, University of Arkansas at Little Rock

Vapor-liquid-solid (VLS) is a powerful method enabling fabrication of single crystalline semiconductor nanowires in feature sizes ranging from nano to micro scales. On the other hand, control of nanowire growth direction by using VLS technique is still challenging. In this presentation, we demonstrate a new approach, called vapor-liquid-solid glancing angle deposition (VLS-GLAD), of fabricating crystalline semiconductor nanowire arrays with controlled geometry. VLS-GLAD is a physical vapor deposition based nanowire fabrication technique which relies on selective deposition of source atoms onto metal catalyst nanoislands placed on a crystal wafer. In this technique, collimated obliquely incident flux of source atoms selectively deposit on catalyst islands by using "shadowing effect". Geometrical shadowing effect combined with VLS growth mechanism leads to the growth of crystalline semiconductor nanowire arrays. In this work, we show the morphological and structural properties of tilted single crystal semiconductor nanowire arrays fabricated by utilizing a conventional thermal evaporation system for VLS-GLAD.

3:00pm SE+TF-TuA4 Lithographic Processing of Nanostructured Thin Films Grown Using Oblique Angle Deposition Method, P. Shah, University of Dayton Research Institute, A. Sarangan, University of Dayton
It is known that exposing structured thin films (STF) grown using oblique angle deposition (OAD) to liquids such as DI water or any common solvents permanently deforms the physical structure of the thin films and alters their properties. This is a severe limitation of STFs because the films

cannot be patterned into useful devices using conventional wet lithographic processes. In this work, we overcome this challenge and propose to demonstrate conventional i-line lithography technique for patterning STF's grown using OAD. The ability to selectively fabricate STF in chosen areas of the active devices will be beneficial for numerous applications. It is shown that the structure of these thin films is preserved after lithographic processing. Processing limits in terms of dimensions of the devices or patterns that may possibly be fabricated are discussed.

4:00pm SE+TF-TuA7 Automated Measurement Technique for Growth Scaling in Glancing-Angle Deposited Films, J.M. Siewert, J.M. LaForge, M.T. Taschuk, M.J. Brett, University of Alberta, Canada

With growing application of glancing-angle deposition (GLAD) thin films, there is increasing need to understand and engineer GLAD growth mechanics. Devices that make use of GLAD films, such as RH sensors, optical filters, and solar cells require precise knowledge and control of GLAD nanostructure. Typically, GLAD vertical post diameters are described by a power law, $d = w_0 h^p$, where d is column diameter, h is height, and w_0 and p are material dependent constants which describe column diameter and broadening, respectively [1, 2]. Based on theoretical growth models, p is expected to range from 5/16 to 1/2. While many GLAD materials have been characterized for p , reliable trends have not yet been obtained [2,3,4,5].

Most groups measure p from cross-sectional SEM images, recording diameters of clearly distinct posts as a function of height. This technique is labour-intensive and large scatter in the data has been observed [4]. One alternative, focused ion-beam cross sections of GLAD films [5], produces very precise measurements but is impractical for characterizing the ensemble properties of a GLAD film. In both cases, the limited number of measurements restricts what can be learned about GLAD films.

To eliminate this limitation, we have been developing an automated characterization method for GLAD posts that enables effective measurement of thousands of posts. Using this technique, we have measured p and w_0 as a function of pitch for 1500 nm TiO₂, 81° deposition angle, vertical post films. We examine post growth for "extinct" and full height posts, discovering markedly different growth scaling behaviors. Characterization of phi-sweep slanted post structures is underway. We will present the optimized technique, current experimental results, and comparisons of automated measurements with existing measurement methodologies.

[1] T. Karabacak, J. Singh, Y.-P. Zhao, G.-C. Wang, and T.-M. Lu, *Phys. Rev. B*, vol. 68, Sep. 2003.

[2] C.M. Zhou and D. Gall, *J. Appl. Phys.*, vol. 103, Jan. 2008, p. 014307.

[3] C. Buzea, G. Beydaghyan, C. Elliott, and K. Robbie, *Nanotechnology*, vol. 16, Oct. 2005, pp. 1986-92.

[4] M.T. Taschuk, K.M. Krause, J.J. Steele, M.A. Summers, and M.J. Brett, *J. Vac. Sci. Technol. B*, vol. 27, 2009, p. 2106.

[5] K.M. Krause, D.W. Vick, M. Malac, and M.J. Brett, *Langmuir*, vol. 26, Nov. 2010, pp. 17558-67.

4:20pm SE+TF-TuA8 Heterogeneous Nanorod Arrays Fabrication by a Two-Source Dynamic Shadowing Growth System, Y.P. He, Y.P. Zhao, University of Georgia

There are increasing interests in designing and engineering nanostructured materials to improve their performances in various applications. Among many nanostructure fabrication and synthesis techniques, the dynamic shadowing growth can offer an unique advantage by sculpturing nanorod-based structures through computer programming using the self-shadowing effect. The geometry shadowing effect is the dominant growth mechanism resulting in the formation of topologically engineered nanostructure arrays, such as tilted, C-shape, S-shape, L-shape, zigzag, matchstick, helical, and vertical nanorods, by programming the substrate rotation in polar and/or azimuthal directions. Such a topological design can be further advanced through compositional engineering. A co-deposition provides a way to evaporate two or more materials simultaneously to form homogeneous composite/doped nanostructures by controlling the relative ratio of the deposition rates of two or more sources. Recently, we have constructed a two-source dynamic shadowing growth (DSG) and demonstrated that various topologically and compositionally engineered nanostructures can be designed by multilayer glancing angle deposition (GLAD) and/or glancing angle co-deposition (GLACD) techniques. Here, we will highlight some of the recent progress in designing heterostructured nanorod arrays through a two-source dynamics shadowing growth system. In particular, Vanadium catalyst doped Mg nanorod arrays fabricated through the oblique angle co-deposition show very different morphology compared to the Mg nanoblades

formed by oblique angle deposition. The kinetics of the hydrogen storage performance of the doped Mg nanostructures can be greatly improved compared to that of the Mg nanoblades. The composition-graded CuSi nanorod array can be designed through dynamically changing the deposition rates of the two sources. The Li⁺ battery performance of these nanostructures compared to that of pure Si nanorods will be discussed.

Tuesday Afternoon Poster Sessions

Advanced Surface Engineering Division
Room: East Exhibit Hall - Session SE-TuP

Advanced Surface Engineering Poster Session

SE-TuP2 Fabrication of Multilayer X-ray Gratings on Staircase Substrates, C. Liu, Argonne National Laboratory, S. Lynch, National Heart, Lung, and Blood Institute, L. Assoufid, Argonne National Laboratory, H. Wen, National Heart, Lung, and Blood Institute

Classical hard x-ray transmission gratings fabricated using lithography are limited by a small aspect ratio of less than 20 when the grating periods are smaller than 2 microns. State of the art X-ray phase contrast imaging techniques require high density transmission gratings with smaller periods and higher aspect ratio to cover larger energy range for thicker samples. This problem may be addressed with a sliced multilayer technique, similar to that used in multilayer Laue lenses and multilayer transmission mask gratings. To increase the acceptance area of the grating, it was proposed [1] to use a thin Si substrate that is asymmetrically etched to a staircase with each stair supporting a multilayer parallel to its surface. Using an X-ray beam shining through the layers at an oblique angle to the substrate and parallel to the layer surfaces, one hopes to have a large-area transmission grating with small multilayer periods. The first fabrication test is completed using W/Si multilayers with dc magnetron sputtering deposition. The layer thickness d is designed to be (stair height)/ $2N$, where $2N$ is the total number of layers. Preliminary results and challenges are presented.

[1] S. K. Lynch and H. H. Wen et al. "Multilayer-Coated Micro-Grating Array for X-Ray Phase-Contrast Imaging," SPIE Proceedings 2011, submitted.

* This work is supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. SKL and HHW are supported by Division of Intramural Research, National Heart, Lung and Blood Institute, National Institutes of Health.

SE-TuP3 Investigations on Physical Processes for Low Temperature Plasma Activated Wafer Bonding, T. Thomas Plach, K. Hingerl, Johannes Kepler University, Austria, V. Dragoi, M. Wimplinger, EV Group, Austria

Direct wafer bonding is a straightforward method of directly connecting wafers, with suitable (in terms of micro-roughness, flatness and cleanliness) surfaces, permanently to each other, by bringing them into contact and subsequently annealing them or simply storing them. The conventional process for hydrophilic oxidized Silicon surfaces (native as well as thermal oxide) is well understood, and explained the following way [1]:

Up to 100°C the substrate surfaces are held together via van der Waals interaction which is mediated by a few monolayers of water. In the range of 100-200°C the water diffuses away from the interface both along the interface and through the oxide into the crystalline bulk, where it reacts with the silicon and forms oxide. The increase of the bond strength from 50% to 100% of Si bulk strength is usually attributed to a closing of gaps at the interface, which starts at the softening temperature of the thermal oxide at around 900-1000°C, depending on whether dry or wet oxide was used.

Low temperature plasma activated direct wafer bonding is a process that lowers the required annealing temperatures necessary for reaching high bond strength. One example for such an improvement is a pair of native oxide – thermal oxide wafers, where bulk strength can be realized by plasma activation with subsequent annealing at temperatures below 200°C. At this temperature conventional wafer bonding reaches half of Si bulk strength, and is limited by gaps at the bonding interface. The mechanism behind this improvement compared to the non activated process is still under discussion.

To clarify the mechanism for this commercially available process, different bonding experiments were performed to evaluate the lifetime of the surface activation and the achievable bond strength when varying some of the boundary conditions of the process (substrates with different orientations, various plasmas, and lowering the annealing temperature).

By partly covering wafers during plasma activation, comparisons between the activated and non-activated regions could be made on single wafers. Therefore the influence of the slightly different substrates could be eliminated. Such wafers were then analyzed by atomic force microscopy, by spectroscopic ellipsometry, by Auger analysis and by X-ray photoelectron spectroscopy.

Finally a model for the mechanism, which was derived from the model for the conventional bonding process, and which explains the experimental results will be presented.

[1] Q.-Y. Tong, U. Gösele, Semiconductor Wafer Bonding: Science and Technology, Wiley, (1998)

SE-TuP4 Crystalline Thin Film Materials with Ultra-Low Thermal Conductivity, C. Muratore, V. Varshney, A. Reed, J. Hu, J. Bultman, T. Smith, A.A. Voevodin, Air Force Research Laboratory

Transition metal dichalcogenide (TMD) crystals are characterized by their distinct layered atomic structures, with strong covalent bonds comprising each layer, but weak van der Waals forces holding the layers together. The relationship between chemical bonding in a material and its thermal conductivity (k) is well-known, however the thermal properties of TMD thin films with such highly anisotropic chemical bonds have only recently been investigated with remarkable results, such as ultra-low k_z . Materials with very low thermal conductivity in the z-axis, but higher k_x and k_y have potential as next-generation thermal barrier or heat spreading materials. Molecular dynamics (MD) simulations predicted $k_x=k_y=4k_z$ for perfect TMD crystals (MoS₂ in this case). Experiments to determine $k_{x,y}$ and k_z were conducted by developing processes to grow crystalline TMD thin film materials with strong (002) (basal planes parallel to surface) or (100) (perpendicular basal planes) preferred orientation. Initially, no correlation between structure and thermal conductivity was apparent, as water intercalation and reactivity to ambient air resulted in a thermal "short-circuit" across basal planes, such that the time between deposition and k measurement had a stronger impact on thermal conductivity than film orientation. Experiments to measure intrinsic thermal conductivity of MoS₂ revealed values approximately one order of magnitude lower than those predicted using MD simulations, however, measurement of $k_x=k_y=4k_z$ was consistent with simulation results. Simulations to evaluate the dependence of thermal conductivity on grain size were evaluated, which correlated well to measured values. Comparison of measured k values for MoS₂, WS₂, WSe₂ and other materials with analogous crystal structures are discussed in the context of the Slack Law, which accounts for intrinsic physical properties of the crystal, but not film microstructure. Alternatives to TMDs, with less environmental sensitivity, will also be illustrated.

SE-TuP5 Investigation on the Nanoindentation Research Trend in the Surfacing and Joining Technologies, H.T. Kim, S.C. Kil, Korea Institute of Science and Technology Information, Republic of Korea

The research trend on the nanoindentation testing in the surfacing and joining/welding technologies has been reviewed. The increasing interest in the mechanical properties of modern surfacing and joining/ welding structures is placing stringent demands on the manufacturing techniques and performance requirements, and the manufacture employs the high quality and efficiency testing devices to produce best quality products. Nanoindentation testing which enables to evaluate hardness, yield/tensile strength, and residual stress plays an important role in measuring the mechanical properties for relatively small and local volumes, so that it is very useful in obtaining profiles or maps of mechanical properties in the narrow zone of coating and HAZ of weldment. This has led to an increasing attention to the field of surfacing and joining/welding structures. This paper covers recent technical trends of nanoindentation testing technologies of surfacing and joining/welding including the COMPENDEX DB analysis of published papers, research subject and research institutes.

Wednesday Morning, November 2, 2011

Advanced Surface Engineering Division

Room: 104 - Session SE+SS-WeM

Surface Engineering for Thermal Management

Moderator: A.A. Voevodin, Air Force Research

Laboratory, H. Barankova, Uppsala University, Sweden

8:20am **SE+SS-WeM2 Near-Field Radiation Heat Transfer**, A. Mavrokefalos, P. Sambegoro, K. Esfarjani, G. Chen, Massachusetts Institute of Technology **INVITED**

Radiation heat transfer in nanostructures can differ significantly from that in macrostructures due to wave effects. Max Planck himself realized that the blackbody radiation law that now bears his name was limited to geometries much larger than wavelength of thermal radiation. Theory has predicted that thermal radiation heat transfer between two surfaces separated by tens of nanometers can exceed that of Planck's blackbody radiation law by several orders of magnitude. We have designed an experiment measuring near-field radiation heat transfer between a sphere and a flat plate using bi-layer atomic force microscope cantilevers as a heat flux and a temperature sensor. We demonstrated experimentally that near-field radiation heat transfer can exceed Planck's law prediction by four orders of magnitude, mediated by surface phonon polaritons. We will also show that existing fluctuating electrodynamics theory cannot predict experimental results in the extreme limit of small separation between two surfaces. Our experiments raise interesting question on the convergence of radiation heat transfer mechanism and interfacial heat conduction mechanism. Theoretical approaches bridging these two regimes will be discussed.

9:00am **SE+SS-WeM4 Atomic Level Temperature Measurements and Nearfield Thermal Energy Tunneling**, A.A. Voevodin, I. Altfeder, J. Hu, V. Varshney, A. Roy, Air Force Research Laboratory

An atomic level thermometer was developed to study interfacial thermal conductivity using a scanning tunneling microscope with inelastic electron tunneling spectroscopy (STM-IETS), where inelastic peak broadening was used to measure temperature of the CO molecular group at the platinum probe apex, while Au substrate with (111) surface was cryogenically cooled. The experiments led to a discovery of vacuum phonon tunneling across nanometer contact gaps. This discovery showed that contact thermal transport can exceed by 10 orders of magnitude Planck's radiation Law for heat transfer in vacuum [1]. This indicated that there should be an alternative mechanism for thermal energy transfer, where near field effects support energy tunneling across such small vacuum gaps. A hypothesis about mirror charge coupling at the interfaces was formulated and tested in the experiments with varied tip-sample temperature gradients. Based on these developments, the STM-IETS experimental approach was further extended to study interfaces made of the surfaces with different Debye temperatures. The second derivative of the tunneling current was used to obtain information on the interfacial thermal coupling and energy transfer. This paper reports on the experimental set-up for atomic scale thermometry, corresponding first principle calculation approaches for small gap interfacial thermal coupling, and discusses experimental and modeling results for different tip-surface combinations toward understanding near-field effects for thermal energy transfer.

1. "Vacuum phonon tunneling", I. Altfeder, A. A. Voevodin, A. K. Roy, Physical Review Letters, 105, 166101 (2010).

9:20am **SE+SS-WeM5 Two-Color Time-Domain Thermoreflectance with an Optical Parametric Oscillator**, J. Gengler, Spectral Energies, LLC, C. Muratore, Air Force Research Laboratory, S. Roy, Spectral Energies, LLC, J.R. Gord, Air Force Research Laboratory

Conventional single-color laser pump-probe methods for measuring thermal properties are limited by sample requirements that arise from considerations of surface roughness and compatible thermoreflectance transducers. Here we describe a new experimental arrangement for performing two-color time-domain thermoreflectance (TDTR). The technique is a variation of traditional pump-probe spectroscopy that is based on a femtosecond Ti:sapphire oscillator of fixed wavelength and an optical parametric oscillator (OPO), with the goal being to create an independently tunable probe wavelength. This method offers two advantages: 1) spectral filtering of diffusely scattered pump light (to prevent it from reaching the detector), and 2) generation of thermoreflectance signal from different metal thin films. The wavelength tunability of the system allows enhancement of TDTR signal generation for multiple thermoreflectance transducer materials. This wavelength-adjustable feature, in turn, facilitates direct measurement of the thermal transport properties of various thin films and

substrates, which would be difficult with single-color femtosecond pump-probe systems. Demonstrated results include optimization of the probe wavelength for different metals, measurement of metal-graphite interfacial conductances on relatively rough samples, and two orders-of-magnitude calibration of thermal conductivity measurements using copper as a thermoreflectance transducer.

9:40am **SE+SS-WeM6 Low-Friction V-alloyed ZrO₂ Thin Films with Temperature Homogenization Functions for High Temperature Sliding Interfaces**, O. Jantschner, C. Walter, C. Mitterer, University of Leoben, Austria, C. Muratore, A.A. Voevodin, Air Force Research Laboratory

The effect of vanadium on reactively magnetron-sputtered zirconia coatings was investigated with respect to its structural and mechanical properties as well as its thermal management abilities for high temperature sliding interfaces. ZrO₂ coatings with different V-content (0, 2.2, 5.8 and 17.4 at%) were co-sputtered from Zr and V targets using an Ar/O₂ discharge. The X-ray diffraction pattern of the as-deposited coatings show a change in crystal structure from monoclinic (0-2.2 at% V) to cubic/tetragonal (5.8 at% V) and finally X-ray amorphous structure at even higher V content (17.4 at% V). Hardness and Young's modulus were evaluated by nanoindentation showing a decrease beyond 2.2 at% V from 17.4 to 7.5 GPa and from 230 to 150 GPa, respectively. The tribological investigations by ball-on-disc tests against alumina balls were carried out at three different temperature levels (25, 600 and 800°C). Additional in-situ Raman analyses have been done to study the formation of tribolayers in the sliding contact. At 25°C, the coefficient of friction (COF) is about 0.2 for low V contents (≤ 2.2 at%). For higher V contents, the COF increases up to 0.5 and higher. At 600°C, the COF measured was between 0.4 and 0.8. At the even higher temperature of 800°C, the COF decreased to below 0.2 for V contents of 17.4 at%, where a self-lubricating film was formed in the sliding contact. Differential scanning calorimetry (DSC) measurements of virgin powder samples showed a characteristic exothermic peak at $\sim 600^\circ\text{C}$ which is due to the formation of a stoichiometric ZrV₂O₇ phase. This phase was found to decompose at $\sim 800^\circ\text{C}$ by an endothermic reaction in ZrO₂ and V₂O₅. The re-runs of the DSC measurements indicated melting of V₂O₅ at 670°C.

In summary, alloying of V to ZrO₂ coatings has on the one hand been proven to result in self-lubricious properties at temperatures above 700°C. On the other hand, the endothermic reactions needed for formation of the self-lubricious phase have the potential to reduce high local temperatures in the sliding contact, enabling thermal management abilities of these coatings.

10:40am **SE+SS-WeM9 Thermal Characterization of Metal/Carbon Interfaces: Comparison of Metallized Nanotubes and Graphite**, C. Muratore, S. Shenogin, A. Waite, A. Reed, J. Gengler, T. Smith, J. Hu, J. Bultman, A.A. Voevodin, Air Force Research Laboratory

Most applications of carbon nanotubes require contact with more ordinary materials, such as metals or polymers. Unfortunately, the extraordinary thermo-electro-mechanical properties of nanotubes are often negated at the interface between the nanotubes and whatever they touch, resulting in a major shortfall between the measured and predicted performance of nanotube-based materials. One of the most troubling discrepancies in projected versus measured properties is found in thermal conductivity measurements of nanotube-containing composite materials. For example, a continuous network of thermally conductive nanotubes (or about 1 percent, by volume) within an organic matrix ($k = 0.3 \text{ W m}^{-1} \text{ K}^{-1}$) should yield a 30-fold increase in thermal conductivity over the pure matrix phase alone, based on simple effective medium theory. Despite this potential increase, experimental results typically show an increase of only a factor of 2 at best in composites with nanotube additives. To better understand the nature of interfacial resistance in carbon nanotubes, modeling and experimental studies investigating engineered interfaces on highly oriented pyrolytic graphite (HOPG) samples were conducted. This substrate was selected as a practical 2-dimensional analog for nanotube sidewalls to facilitate modeling and experimentation. Molecular dynamics simulations of heat transfer through metal carbon interfaces were conducted, and measurements of thermal conductance at these interfaces were made by analysis of the two-color time domain thermoreflectance (TDTR) data from the samples. The TDTR analysis of the different metals on HOPG was made possible by having an optical parametric oscillator on the probe beam which allows for tuning the wavelength to match absorption bands for each metal studied. Comparison of simulation and experimental results between graphite and nanotubes is highlighted. Metal films were selected to identify effects of atomic mass, chemical interactions and mechanical properties. For example, metals known to exhibit in situ formation of an interfacial carbide layer when in contact with a carbon source and heated, such as titanium and boron, were investigated, and the effect of this carbide layer formation on

interfacial conductance was examined. Graded and sharp interfaces were also considered with computational and experimental efforts.

11:00am **SE+SS-WeM10 The Experiment of Surface Tension Driven Flow with Various Parameters on JEM/ISS**, *S. Yoda*, Japanese Aerospace Exploration Agency, *S. Matsumoto*, JAXA, Japan, *A. Komiya*, Tohoku University, Japan

The surface tension driven flow (Marangoni) experiments were carried out by using 50mm diam. with liquid bridge of Silicones oil under microgravity condition on Japanese Experiment Module on International Space Station. The parameters in these experiments were liquid bridge length being corresponded to aspect ratio which is defined as liquid length/liquid diam., and temperature difference between hot and cold disks which sustains the liquid bridge. The particles coated by gold to fit with the density of the liquid silicones were inserted into the liquid bridge. Observing the movement of the particles by three CCD camera, we can determine the flow behavior of Marangoni with different temperature as 3 dimension observation of the flow. Moreover, two ultrasonic transducers were attached in the cold disk to measure the particles velocity. The number of experiments done on JEM were more than 40 times with around 6 hr for all each experiment. The Marangoni number was changed with aspect ratio. The smaller aspect ratio around showed smaller critical Marangoni numbers, whereas the larger those were larger the numbers.

11:20am **SE+SS-WeM11 Enhanced Thermal Transport at Covalently Functionalized Carbon Nanotube Interfaces**, *S. Kaur*, Lawrence Berkeley National Lab, *N. Ravivikar*, Intel Corporation, *D.F. Ogletree*, Lawrence Berkeley National Lab

Thermal transport is restricted in systems including carbon nanotubes (CNT) due to high thermal interface resistance. We have substantially improved thermal transport at CNT-metal interfaces by functionalizing the contacting surfaces with amino-propyl silane to form covalent chemical bonds bridging the CNT-metal gap. This strategy was suggested by molecular dynamics calculations of Hu *et al.* (1)

We have characterized the resulting interface using multi-frequency and multi-wavelength time-domain thermo-reflectance (TDTR) measurements, which are able to independently determine interface and bulk CNT contributions to thermal transport. TDTR analysis showed that thermal contacts were made between a functionalized Al surface and 4-5% of the CNTs in an array grown on silicon. The intrinsic CNT interface conductivity exceeded 300 MW/m²-K, resulting in an effective thermal interface resistance of less than 0.8 mm²-K/W. Successful interface functionalization was independently verified by mechanical adhesion testing, which showed a correlation between interface strength and thermal transport, as discussed by Prashar. (2).

(1) Ming Hu, Pawel Keblinski, Jian-Sheng Wang, Nachiket Ravivikar, J. Appl. Phys. 104 083503 (2008).

(2) Ravi Prashar, Appl. Phys. Lett. 94 041905 (2009).

Wednesday Afternoon, November 2, 2011

Advanced Surface Engineering Division

Room: 104 - Session SE+PS-WeA

Atmospheric Pressure Plasmas

Moderator: H. Barankova, Uppsala University, Sweden

2:00pm **SE+PS-WeA1 An Investigation of the Influence of Hybrid Current Modes on the Plasma Behavior during Plasma Electrolytic Oxidation (PEO) Coating Process on Mg and Mg-Alloys**, *R.O. Hussein, D.O. Northwood, X. Nie*, University of Windsor, Canada

The increased use of magnesium alloys is considered one of the more promising methods for light-weighting in the automotive industry since, for a given strength level, Mg represents a 57% weight reduction over steel and 8% weight reduction over aluminum. However, due to its high chemical and electrochemical activity, magnesium has poor corrosion resistance in aqueous and other environments. In order for Mg and its alloys to find increased usage, there is a need to surface engineer these materials for improved corrosion and wear resistance. Plasma Electrolytic Oxidation (PEO) is an electrochemical process working at atmospheric pressure that uses an environmentally-friendly aqueous electrolyte to oxidize the metal surfaces to form ceramic oxide coatings which impart a high corrosion and wear resistance. The properties and structure of PEO coatings are dependent on parameters such as substrate metallurgy, composition of the electrolyte and the process conditions including current density, current mode and processing time. In this study we investigated the effect of current mode on plasma temperature and coating properties of PEO coatings formed on pure magnesium and an AM60B magnesium alloy (mass fraction: Al 5.6–6.4%, Mn 0.26–0.4%, Zn \leq 0.2%, balance Mg). Unipolar, bipolar and hybrid (combination of both) current modes were used in this work. Optical Emission Spectroscopy (OES) was employed to study the plasma species, and electron temperature of the plasma. The morphology and microstructure of the coatings were investigated using Scanning Electron Microscopy (SEM). Potentiodynamic polarization in a 3.5% NaCl solution was used for the corrosion investigations.

2:20pm **SE+PS-WeA2 Aging Mechanism of the Hydrophilic Silicon (100) Native Oxide Surface**, *T.S. Williams, R.F. Hicks*, University of California Los Angeles

The wetting behavior of surfaces is important in many applications, such as for example, microfluidic devices that are fabricated on silicon wafers. In this study, silicon native oxide surfaces were cleaned with a radio frequency, atmospheric pressure helium and oxygen plasma and with ammonium hydroxide, hydrogen peroxide, and deionized water in a 1:1:5 ratio (RCA SC-1). Both processes created a hydrophilic state with water contact angles of $<5^\circ$ and $16.2 \pm 1.7^\circ$, respectively. During subsequent storage in a chamber purged with boil off from a liquid nitrogen tank, the water contact angle increased over several days at a rate dependant on the cleaning method used. Internal reflection infrared spectroscopy revealed that the change in water contact angle was due to the adsorption of organic molecules with an average hydrocarbon chain length of 10 ± 2 . The rate of the adsorption process decreased with the fraction of hydrogen-bonded hydroxyl groups on the surface relative to those groups that were isolated. On Si (100) surfaces that were cleaned by RCA SC-1 and the plasma, 96% of the silanol groups were hydrogen bonded. The first-order rate constant for adsorption of the organic contaminant on this surface was $0.182 \pm 0.008 \text{ hr}^{-1}$. Several methods have been explored for keeping the silicon dioxide surface in a hydrophilic state for extended periods of time, and these will be presented at the meeting.

2:40pm **SE+PS-WeA3 Polyimide Surface Treatment to Hydrophobic Surface with Self Assembled Mask Layer for Direct Inkjet Patterning Process**, *J.B. Park, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

The inkjet printing technology is emerging as one of the important process technologies for electronics, because it can significantly reduce the manufacturing process cost, materials waste, and number of process steps. Especially, many researchers investigating the inkjet-printed process have focused their attention on the printing of conductive films on a polymer film. The technique is not suitable for applying to organic transistors yet, because its pattern width is limited to several dozens μm by statistical variations of the flight direction of droplets and their spreading on the substrate.

In this study, polyimide film was treated to hydrophobic surface using modified atmospheric pressure plasma system (double discharge system). Especially, for keeping the surface characteristics permanently, surface of

the polymer film was etch/textured with self assembled mask layer to form the textured polymer surface. The texturing process is progressed for 4 process step. The mask layer (HMDS) is deposited and agglomeration/oxidation by using atmospheric discharge of HMDS/He/O₂ gas mixture through 1st step and 2nd step. And Etch and texturing process is progressed with atmospheric discharge of He/O₂/Ar gas mixture in 3rd step. And the mask layer is removed in 4th step using NF₃/N₂ gas mixture of remote atmospheric plasma. In the 2nd process, the HMDSO mask layer is formed specific tissue layer as the input power was increased. And the morphology is also varied with the whole size of the HMDSO mask layer. And this whole process is possible because of perfect etch selectivity between the polyimide film and HMDSO layer. The contact angle of textured polyimide film was measured over the 100 degree and varied with textured surface morphology. And keeping the pattern width of inkjet printing was clearly improved compare with normal polymer surface.

3:00pm **SE+PS-WeA4 In Situ Fabricating Blue Ceramic Coatings on Al Alloy by Plasma Electrolytic Oxidation**, *Z.J. Wang, R.O. Hussein, X. Nie, H. Hu*, University of Windsor, Canada

In-situ formation of novel blue ceramic coatings on Al alloy with a controllable blue color was successfully achieved using a plasma electrolytic oxidation (PEO) process working at atmospheric pressure. This novel blue ceramic coating overcomes the shortcomings of surface treatments resulting from traditional dyeing process by depositing organic dyes into the porous structure of anodic film, such as poor resistance of abrasion and rapid fading when exposed to light. X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy were employed to characterize the microstructure of the blue ceramic coating. The main compositions of the coating are CoAl₂O₄ and Al₂O₃. This work shows that the working current density plays significant roles on CoAl₂O₄ phase in the ceramic coating which has a controllable influence on the coating color. Low current density reduces the percentage of CoAl₂O₄ component in the coating, and light blue ceramic is produced. On the other hand, higher current density increases CoAl₂O₄ component in the coating, hence deep blue ceramic is fabricated. Electrochemical test, ball-on-plate sliding wear tester and thermal shock method were utilized for the corrosion, wear and thermal shock resistance analysis of the fabricated ceramic coatings. The results indicate that the developed blue coating via PEO process superiorly improves the tribological property, anti-corrosion property and thermal shock resistance. The fabricated blue ceramic coating tends to be applied to colored light cast alloys for applications used in relatively harsh and severe working environments.

4:00pm **SE+PS-WeA7 Cold Atmospheric Plasma Sources for Treatment of Cell-Containing Surfaces**, *M.G. Kong*, Loughborough University, UK

INVITED

Low-temperature gas discharges generated at atmospheric pressure, commonly known as cold atmospheric plasmas, are a relatively new member of the processing plasma family. Without the need for a vacuum chamber, they offer a much more cost-effective route to material processing and open up opportunities for chamber-less processes and vacuum-incompatible materials such as moist objects. With a mean electron energy at a few eV and a gas temperature close to room temperature, cold atmospheric plasmas are ideally placed for effective chemical dissociation and hence for a wide range of materials processing applications. In this contribution, a review of the current cold atmospheric plasma sources will be presented in terms of their underpinning science and their current technology capability. These include the traditional dielectric barrier discharges, radio-frequency glow discharges, and cold atmospheric plasma jets and jet arrays. Through discussion of their plasma characteristics, their applications are exemplified through treatment of cell-containing surfaces, including living tissues. The interaction of cold atmospheric plasmas with individual microorganisms and indeed microbial communities will be discussed, and its implications to treatment of skin diseases and wounds will be presented. This will also be supported with data of plasma interaction with mammalian cells.

4:40pm **SE+PS-WeA9 High Performance of 60-Hz Atmospheric Pressure Plasma: Basic Characteristics and Applications**, *F. Jia, K. Takeda, K. Ishikawa, H. Inui, S. Iseki*, Nagoya University, Japan, *H. Kano*, NU Eco-Engineering Co., Ltd., Japan, *H. Kondo, M. Sekine, M. Hori*, Nagoya University, Japan

In this paper, the spatial distribution of atomic oxygen density in a 60-Hz non-equilibrium atmospheric pressure plasma[1] is diagnosed by two-photon absorption laser induced fluorescence (TALIF)[2]. The plasma unit is made of ceramics comprised three regions: gas diffusion region, main discharge region, and plasma jet in the open air. The discharge gases were

Ar and a small amount of O₂. The plasma could offer electron density as high as 10¹⁵ cm⁻³ with a low gas temperature[1,3], and have been successfully used to clean glass surface[1]and inactivate the spores of *Penicillium digitatum*[4]. In the above applications, we find that atomic oxygen plays an important role[1,4], and the samples are usually treated in the open air; therefore it is necessary to investigate the behavior of atomic oxygen, especially in the open air, in order to achieve high performance. A dye laser pumped by an excimer laser is used to generate nanosecond UV laser pulses at around $\lambda = 226$ nm for the two-photon excitation of atomic oxygen ($2p\ 3P-3p\ 3P$). The laser power is adjusted to 0.1 mJ/pulse to make sure that the effect of photo dissociation of ozone can be negligible in the experiment. The results showed that the effect of O₂ admixture variation on the atomic oxygen density is totally different in the main discharge region and in the plasma jet. In the main discharge region where the discharge gas are only Ar and O₂, the density of atomic oxygen increased quickly with adding only 0.25% O₂, became saturated with adding 1% O₂, and reduced quickly when adding 1.5% O₂. The discharge was stable until adding 2.5% O₂. However, in the plasma jet that was in the open air, the density of atomic oxygen remained almost same while adding O₂ from 0% to 2.5%. This is because the mechanisms of generation and recombination of atomic oxygen are different in the main discharge region and plasma jet. More work will be done to study the behavior of atomic oxygen in the plasma jet, the data and results will be very useful to understand the behavior of atomic oxygen and improve the applications of non-equilibrium atmospheric pressure plasma. [1] M. Iwasaki, H. Inui, Y. Matsudaira, H. Kano, N. Yoshida, M. Ito, and M. Hori, *Appl. Phys. Lett.* **92**, 081503 (2008). [2] K. Niemi, V. Schulz-von der Gathen, and H. F. Dobeles, *Plasma Sources Sci. Technol.* **14**, 375 (2005). [3] Fengdong Jia, Naoya Sumi, Kenji Ishikawa, Hiroyuki Kano, Hirotoshi Inui, Jagath Kularatne, Keigo Takeda, Hiroki Kondo, Makoto Sekine, Akihiro Kono, and Masaru Hori, *Appl. Phys. Express*, **4**, 026101 (2011). [4] S. Iseki, T. Ohta, A. Aomatsu, M. Ito, H. Kano, Y. Higashijima, and M. Hori, *Appl. Phys. Lett.* **96**, 153704 (2010).

5:00pm **SE+PS-WeA10 Dense Atmospheric Pressure Discharges for Surface and Gas Treatment**, *M.J. Kelly, B.D. Schultz, W.M. Hooke*, International Technology Center

Dielectric barrier discharge (DBD) plasmas have been formed in atmospheric pressure gases exhibiting peak currents in excess of 100 amperes. Power densities during the pulse routinely exceed 100 kilowatts per cubic centimeter for moderately sized electrodes (>100 square centimeters) with ionization densities of 10¹⁴ per cubic centimeter. Charge transfer of 100 microcoulombs per pulse has been repeatedly generated at frequencies up to 100 hertz, and the charge delivery is found to scale in proportion to the electrode area for a given dielectric consistent with a homogeneous discharge. Diffuse discharges have been formed over larger areas (exceeding 1 meter in length and 500 square centimeters) as well. These results were obtained using a custom high voltage driving source and in the absence of helium, argon, or any other easily ionized gas. The source readily achieves an overvoltage in excess of the DC breakdown voltage prior to the onset of breakdown in which 20-30 kV is delivered with rise times shorter than the lag time between the pulse crossing the threshold voltage and the onset of a discharge. Electrical modeling of the discharge characteristics has produced correlations relating power and charge transfer to various electrical and geometrical parameters of the system which will be discussed in this paper.

5:20pm **SE+PS-WeA11 Investigation of Discharge Modes of Cylindrical Dielectric Barrier Discharge Configuration for Surface Treatment at Atmospheric-Pressure**, *T.S. Cho, Y.L. Wu, J.M. Hong, Z. Ouyang, D.N. Ruzic*, University of Illinois at Urbana Champaign

To date, various structural concepts of atmospheric-pressure dielectric barrier discharge had been studied and some of the concepts have already been commercialized for surface treatment processes because of its simplicity and scalability. In this study, cylindrical dielectric barrier discharge configurations for treating the powder particles or controlling the air pollutants at atmospheric-pressure have been investigated. The electrical characteristics of the cylindrical dielectric barrier discharge structure as a capacitive load have been experimentally measured for the mixture of helium and nitrogen and its flow rate with voltage-charge lissajous analysis method. Also, it has been compared with remote plasmas from the commercial planar dielectric barrier discharge system of which capacitance has been 280pF for driving conditions of 5kV and 30 kHz. Emissions from the atmospheric-pressure dielectric barrier discharge plasma have been analyzed for varied gas conditions with the optical emission spectroscopy. For comparison purposes, the glass substrates treated with commercial planar and cylindrical dielectric barrier discharge plasmas have been analyzed. In addition, the sugar-alcohol particles have been treated with atmospheric-pressure plasma from the cylindrical dielectric barrier discharge system, and compared with the untreated particles.

Thursday Morning, November 3, 2011

Advanced Surface Engineering Division
Room: 104 - Session SE-ThM

Nanostructured Thin Films and Coatings

Moderator: C. Mitterer, University of Leoben, Austria

8:00am **SE-ThM1 Characterization of Solution-Processed HfO₂, HfSiO₄, and ZrSiO₄ Thin Films on Rigid and Flexible Substrates for Memristive Applications.** *J.L. Tedesco, W. Zheng, O.A. Kirillov, S. Pookpanratana, A.A. Herzing, H.-J. Jang, P.P. Kavuri, N.V. Nguyen, C.A. Richter*, National Institute of Standards and Technology

Memristors, nonvolatile bipolar resistive switching devices first intentionally fabricated in 2008 [1], have attracted attention for use in a wide range of applications. To date, most memristors have been fabricated from either TiO_x [1] or TaO_x [2]. However, it is necessary to explore other dielectric materials, because the memristive properties of these dielectrics have not yet been explored.

In this study, memristors were fabricated on both silicon and flexible polyethylene terephthalate (PET) substrates by using HfO₂, HfSiO₄, and ZrSiO₄ thin films and thermally evaporated aluminum contacts. The dielectric films were formed from sol-gel precursors synthesized based on the recipe of Meena et al. [3]. Following synthesis, the precursors were spun on to substrates, exposed to an oxygen plasma, and annealed in air at 150°C for 24 hours. Memristors with cross sectional areas ranging from 2×2 mm² to 0.5×0.5 mm² were fabricated.

The dielectric films were extensively characterized by using optical profilometry and microscopy, x-ray photoelectron spectroscopy (XPS), and deep ultraviolet spectroscopic ellipsometry (SE). The optical profilometry measurements demonstrate that the films show no evidence of significant inhomogeneities due to the solvent-based sol-gel synthesis methods. According to the XPS measurements, the films are ≈50% carbon. Such high levels of carbon are reasonable given the synthesis approach employed, and similarly high levels of carbon have been observed previously in TiO₂ films synthesized from sol-gels [4]. From the SE measurements, it is evident that the bandgaps of the HfO₂, HfSiO₄, and ZrSiO₄ films are similar to their predicted values, but the densities of the films are ≈0.5 due to the high amounts of excess carbon. Transmission electron microscopy measurements of the films will also be discussed.

Current-voltage (I-V), capacitance-voltage (C-V), capacitance-frequency (C-f), and conductance-frequency (G-f) measurements were performed at room temperature in a commercial probe station. The I-V measurements indicate that devices fabricated from these films exhibit bipolar resistive switching. Furthermore, optical microscopy images indicate that the switching events are often accompanied by significant changes to the morphology of the active region of the device, particularly when the switching occurs at high voltages. These changes suggest the formation of localized conduction pathways through the dielectric. The C-f and G-f measurements indicate that the capacitive properties of the devices also change following switching events. Additionally, after 24 days, retention tests show the devices are still in the ON state, thus, they may be considered nonvolatile.

References

- [1] D.B. Strukov et al., *Nature* **438**, 80 (2008).
- [2] J.J. Yang et al., *Appl. Phys. Lett.* **97**, 232102 (2010).
- [3] J.S. Meena et al., 2010 3rd International Nanoelectronics Conference (INEC), **1-2**, 992, 2010.
- [4] J.L. Tedesco et al., *ECS Trans.* **35**, 107 (2011).

8:20am **SE-ThM2 Tensile Testing of Substrate for Fracture Toughness of Thin Films.** *S. Zhang, X. Zhang*, Nanyang Technological University, Singapore **INVITED**

Measurement of fracture toughness for bulk materials is a routine but extremely difficult and still not standardized for thin films (or coatings). The difficulties in clamping a freestanding thin film and the requirement of a critical dedicate loading system are the main obstacles. In this talk, a method is proposed to carry out tensile loading of the substrate to avoid both problems. The film is deposited on a rectangular silicon wafer on which an edge crack is fabricated beforehand. The film is then "micromachined" into microbridges perpendicular to and ahead of the initial substrate crack. A displacement controlled tensile force is applied to propagate the substrate crack and fracture the "microbridges". The critical fracture strain of the microbridge is measured through measuring the strain of the substrate at the respective location of the microbridge. The fracture

toughness of the film is thus obtained in between the un-fractured and the last fractured bridge. A case study is also presented.

9:00am **SE-ThM4 Structure and Properties of TaN-(Ag,Cu) Nanocomposite Thin Films.** *J.H. Hsieh, S.Y. Hung*, Ming Chi University of Technology, Taiwan, Republic of China, *S.Y. Chang*, National Chung Hsing University, Taiwan, Republic of China, *C. Li*, National Central University, Taiwan, Republic of China

TaN-(Ag,Cu) nanocomposite thin films with various Ag/Ti ratios were deposited by reactive co-sputtering on Si(001) substrates. The samples were then annealed using RTP (Rapid Thermal Processing) at 400 °C to induce the nucleation and growth of Ag/Cu nano-particles in TaN matrix and on film surface. One set of TaN-(Ag₆₀Cu₄₀) were annealed at various temperatures. The structure and morphologies were examined using XRD, FESEM, and HRTEM. Nano-indenter was used to study the variation of mechanical properties. The results reveal that the mechanical properties were affected by the annealing temperature rather than the atomic ratios of Ag/Cu. However, the anti-bacterial behaviors against *E. coli* and *S. aureus* were significantly affected by the Ag/Cu ratios.

9:20am **SE-ThM5 Nanoporous Osmium-Ruthenium Thin Film Coatings for Dispenser Cathodes.** *P. Swartzentruber, T.J. Balk*, University of Kentucky

Nanoporous osmium-ruthenium may be applicable as an improved coating for dispenser cathodes used in travelling wave tubes and other various vacuum tube devices. Osmium-Ruthenium (OsRu) was co-deposited with either magnesium (Mg) or scandium (Sc) as a sacrificial element to form an intermetallic thin film. The sacrificial element was then selectively etched away, which dealloyed the film and left behind a nanoporous structure. Electron microscopy, x-ray diffraction, and x-ray photoelectron spectroscopy were used to characterize the morphology, structure, and composition of the films in both the as-deposited and dealloyed states. Various film compositions and dealloying conditions were studied to determine the optimal conditions for creating a nanoporous film structure.

9:40am **SE-ThM6 Influence of Chemistry and Structure on the Thermal Stability and Oxidation Resistance of Ti-Al-N.** *P.H. Mayrhofer, L. Chen, J. Paulitsch*, Montanuniversität Leoben, Austria, *Y. Du*, Central South University, China

The excellent hardness, good abrasive and sliding wear resistance and high thermal stability and oxidation resistance favor Ti_{1-x}Al_xN to be used as hard protective coating in a variety of industrial applications such as advanced machining and forming tools, automobile and aerospace industry or for semiconductor electronics. Although, thin films based on this material system are investigated in detail, only little is known on the sequential relations between deposition conditions, chemistry, structure and physical and mechanical properties.

Here we show that Ti_{1-x}Al_xN coatings can be synthesized by magnetron-sputtering in single-phase cubic (NaCl, c) structure for x = Al/(Ti+Al) ratios up to 0.62 and single-phase hexagonal (ZnS-wurtzite, w) structure for x ≥ 0.75. These critical values for the individual favored structures strongly depend on the deposition conditions used such as N₂-partial pressure and resulting growth rate. Generally, a low N₂-partial pressure and a high growth rate favor the cubic structure. Increasing Al content of the single-phase cubic coatings results in increased hardness (to ~35 GPa for c-Ti_{0.38}Al_{0.62}N), earlier onset of the decomposition towards the stable phases c-TiN and w-AlN (across the formation of Ti-rich and Al-rich cubic nm-sized domains) and increased oxidation resistance. The single-phase wurtzite-structure coatings exhibit a high thermal stability and better oxidation resistance as compared to the single-phase cubic structure coatings. Even after 40h at 800 °C in ambient atmosphere the w-Ti_{0.25}Al_{0.75}N coating exhibits only an ~1 μm thin dense oxide layer on top of the ~2 μm remaining nitride, whereas the other coatings are already fully oxidized.

The coatings with a dual-phase or mixed-phase structure in the as deposited state show a reduced thermal stability and oxidation resistance as compared to the single-phase cubic or wurtzite structure coatings.

Furthermore, we show that a post-deposition annealing treatment of c-Ti_{0.48}Al_{0.52}N to 900 °C results in a hardness increase from 29 to 32 GPa (due to the formation of cubic nm-sized domains) as well as an increased oxidation resistance. Hence, our results provide insight in designing-strategies for coatings with increased mechanical, thermal stability and oxidation resistance.

10:40am **SE-ThM9 Design of Catalytically Active Nanostructured Coatings for Severe Tribological Applications**, A. Erdemir, O.L. Eryilmaz, Argonne National Laboratory

Nanostructured and composite coatings are very unique in the field and offer many attractive properties for a wide range of demanding applications. They can also provide the kind of flexibility that is needed for achieving highly protective, super-slippery boundary films on lubricated tribological surfaces. In this study, we explored the possibility of nano-scale designing of a new class of catalytically active super-hard nitride coatings which when used under boundary lubricated sliding conditions can produce a carbon-rich boundary film. The Raman spectra of the carbon film are similar to that of the diamondlike carbon coatings typically produced by CVD and PVD methods. In a wide range of tribological test systems, such carbon-rich boundary films were shown to provide extreme resistance to scuffing and provide very low friction and wear even under the harshest tribological conditions. In this paper, we will mainly concentrate on the structural and chemical nature of these films and present a hypothetical model to explain their unusual tribological properties under severe contact conditions.

11:00am **SE-ThM10 Structure and Electrical Properties of Nb-Ge-C Nanocomposite Coatings**, O. Tengstrand, Linköping University, Sweden, N. Nedfors, Uppsala University, Sweden, L. Fast, SP Tech. Res. Inst. of Sweden, A. Flink, Impact Coatings AB, Sweden, A.M. Andersson, ABB AB, Corporate Research, Sweden, U. Jansson, Uppsala University, Sweden, P. Eklund, L. Hultman, Linköping University, Sweden

Nanocomposite ceramic coatings are being explored based on their good tribological and electrical properties, which can be tailored by changing e.g. the composition, microstructure, and surface morphology. For example, the nc-TiC/a-SiC nanocomposite system has shown promising properties for electrical contact applications [1, 2]. The tendency to form oxides and carbides greatly influences these properties. For instance, NbC has similar electrical properties as TiC, but has a lower tendency to form oxides. Especially for low force electrical contact applications, this makes NbC a suitable choice as replacement for TiC. Ge is in the same group as Si, but does, as a more noble element, not form carbides or oxides as easily. Here, we investigate the Nb-Ge-C material system with respect to nanostructure and electrical properties.

Nb-Ge-C thin films were deposited onto Si(001) and Ni-electroplated bronze substrates using dc magnetron sputtering in an Ar discharge at a low temperature (200 °C). By use of three elemental targets in current-regulating mode both the Nb/C ratio and the Ge content was varied to study the effect of composition. XRD, TEM, and SEM showed that the NbC films are columnar and exhibit a preferred 111 crystallographic orientation. With increasing Ge content up to 10 at.%, the NbC grain size was reduced to ~5 nm with a random orientation. While the nc-NbC/Ge nanocomposites have no discernable amorphous tissue phase, XPS showed predominantly Ge-Ge with only little Ge-C bonds. In contact resistance measurements the films performed well (1.7-3.7 mΩ) in comparison to Ag reference (1.2 mΩ) at a contact force of 10 N.

[1] Eklund,P., Surface Engineering, 23, (2007), 406

[2] Lauridsen,J.; et al. Surf. Coat. Technol., 205, (2010), 299

11:20am **SE-ThM11 Tuning the Properties of Chromium Oxynitride Coatings**, L. Castaldi, Oerlikon Balzers AG, Liechtenstein, J. Patscheider, EMPA, Switzerland, V. Shklover, ETH Zurich, Switzerland, D. Kurapov, A. Reiter, Oerlikon Balzers AG, Liechtenstein

CrO_xN_{1-x} coatings deposited by reactive cathodic arc evaporation were investigated for concentration levels oxygen between 0 and 1. The present study shows some of the possibilities for tuning the crystallographic and electronic properties of chromium oxynitride films by progressively increasing the oxygen concentration. Upon oxygen addition the CrO_xN_{1-x} films remain in the face-centered cubic B1 structure of CrN for oxygen fractions of up to x = 0.70. At higher oxygen contents the properties of the films approach those of Cr₂O₃ and crystallize in the corundum structure. The gradual decrease of the stress-free lattice parameter of the films with the B1 structure at higher oxygen concentrations is consistent with oxygen substituting progressively nitrogen atoms. The almost random orientation of oxygen-free CrN films transforms to a distinct (001) preferred orientation with the increase of oxygen concentration in the films. XPS investigations prove enhanced charge transfer from Cr to O 1s with increasing x with respect to N by changes in the core-level binding energies (BE) of the Cr 2p_{3/2} and N. A shift of the valence band edge toward higher BE indicates a decrease of electrical conductivity of the films with increasing oxygen content.

11:40am **SE-ThM12 Synthesis of Al-Cr-O and Al-Cr-O-N Thin Films in Corundum-Type Structure by Reactive r.f. Magnetron Sputtering**, M. Stueber, Karlsruhe Institute of Technology (KIT), Germany, D. Diechle, Walter AG, Germany, H. Leiste, S. Ulrich, Karlsruhe Institute of Technology (KIT), Germany

The PVD synthesis of wear and oxidation resistant aluminum oxide and derivative coatings is currently attracting large scientific and technical interest. Ternary Al-Cr-O thin films with mechanical properties comparable or superior to binary Al-O thin films can be deposited at moderate deposition temperatures. New coatings from the quaternary Al-Cr-O-N system could even offer increased strength, hardness and toughness. A combinatorial approach to the growth of Al-Cr-O-N thin films by means of reactive r.f. magnetron sputtering will be presented. For specific deposition conditions well adherent, nanocrystalline Al-Cr-O-N thin films with high Vickers hardness and elastic modulus values were grown at non-equilibrium conditions on cemented carbide and silicon substrates. Detailed results on the coatings composition, constitution, microstructure and properties will be presented and discussed in comparison to ternary Al-Cr-O thin films deposited under identical conditions.

Thursday Afternoon, November 3, 2011

Advanced Surface Engineering Division

Room: 104 - Session SE+PS-ThA

Pulsed Plasmas in Surface Engineering

Moderator: J. Patscheider, EMPA, Switzerland

2:00pm **SE+PS-ThA1 High-Power Impulse Magnetron Sputtering of WO₃ - Influence of the Pulse Parameters on the Discharge**, A. Hemberg, F. Renaux, J.P. Dauchot, Matera Nova, Belgium, R. Snyders, S. Konstantinidis, UMons, Belgium

Metal oxides as WO₃, SnO₂ and TiO₂ are widely used as active layers in gas sensor applications. The sensor performances (sensitivity, selectivity, and ageing) are strongly dependent grain size, phase constitution, and material microstructure. It is accepted that in magnetron sputtering, these properties can be modified by controlling the energy and the flux of ions impinging the growing films. The ion bombardment allows modifying the nucleation process, increasing the film density, and changing texture, stress and microstructure of the coating, and ultimately improving its performances. Compared to other techniques used for thin films deposition, HiPIMS (High Power Impulse Magnetron Sputtering) enables the sputtered material to be strongly ionized. Therefore, using HiPIMS, the film properties can be altered to a larger extent as compared to conventional DC magnetron.

In this study, WO₃ films have been synthesized using reactive HiPIMS of a metallic tungsten target in Ar/O₂ mixtures. A comparison is made between results obtained in HiPIMS with those obtained with a conventional DC reactive magnetron discharge (RDCMS) at identical mean power (*PD*). We discuss the influence of the pulse duration (*t*) and the target voltage (*VD*) on both the film deposition rate (*RD*) and the hysteresis behaviour. During the HiPIMS experiments, *t* is varied between 10 and 50 μ s and *VD* between 800 and 1500 V. *PD* is kept constant by adjusting the frequency. In reactive mode, for a given value of *PD*, *RD* increases as *t* and *VD* are increased. Comparing the HiPIMS data with those recorded during the RDCMS process, it is found that for *t* = 50 μ s and *VD* = 1500 V, *RD* in HiPIMS is larger than for the RDCMS discharge. In order to understand this behaviour, the target current waveforms associated with these working conditions have been studied. For this particular condition (*t* = 50 μ s, *VD* = 1500 V), the discharge current waveforms in metallic and reactive mode are similar. This observation would reveal that the target surface chemistry is identical, although the discharge is ignited either in a pure Ar or in an Ar/O₂ mixture.

The ion flux composition was also studied with a mass spectrometer located in front of the magnetron target. Time-resolved and time-averaged measurements were carried out.

2:20pm **SE+PS-ThA2 A Versatile Magnetized Pulsed Cascaded Arc Source for Surface Modifications and Efficient Material Deposition**, G. De Temmerman, J.J. Zielinski, FOM Institute for Plasma Physics Rijnhuizen, Netherlands, L. Marot, D. Mathys, University of Basel, Switzerland, W. Melissen, FOM Institute for Plasma Physics Rijnhuizen, Netherlands, M.C.M. van de Sanden, FOM-Instituut for Plasma Physics Rijnhuizen & Eindhoven University of Technology, Netherlands

The interaction of low-temperature plasmas with solid surfaces is at the core of numerous applications such as thin film deposition or materials processing. On the other hand, the interaction of the confined plasma with the plasma-facing materials in a nuclear fusion device can have a serious impact on the operations of a fusion device. This is especially true during plasma instabilities where surfaces are exposed to high transient heat and particle fluxes (several MJ.m⁻² for 0.2-1ms). A pulsed cascaded arc source has been developed [1] to produce fusion-relevant plasmas and study the surface modifications induced by simultaneous continuous and pulsed plasma exposure.

The cascaded arc source, extensively used for thin film deposition by PECVD is used, in the Pilot-PSI linear plasma device to reproduce the plasma conditions expected in a fusion reactor with particle and heat fluxes of 1024.m⁻²s⁻¹ ~10 MW.m⁻² respectively. Magnetic field of up to 1.6T is used to confine the plasma. The plasma source has been modified to allow for combined pulsed/continuous operations [1]. Parallel to the DC power supply, the plasma source is connected to a capacitor bank (5kV, 8.4mF, 100kJ), which is discharged in the source to transiently increase the input power. Peak surface heat fluxes in excess of 1 GW.m⁻² have been generated

with pulse duration of about 1 ms (up to 1MJ.m⁻²). To provide more flexibility, the shape and the duration of the pulse can be adapted to the needs. The plasma conditions during the continuous and pulsed phases can be varied independently. The source can be operated in a variety of gases (Ar, H, He, N) as well as with mixed gases. Plasma properties are studied using Thomson scattering, fast visible and infrared imaging.

We will describe how synergistic effects arising from the simultaneous exposure to continuous and pulsed plasma affect the surface of a polycrystalline tungsten surface. The field of applications of the pulsed cascaded source is however not restricted to fusion-related research. Using a slightly altered configuration, the pulsed plasma source system has also opened a new route for the efficient deposition of metallic nano-particles and nano-structured thin films. Complete coverage of the surface by 10-15nm diameter nano-particles can be obtained with only a few pulses (5-10). Under different conditions, deposition rates as high as 50nm per pulse (1ms duration) have been achieved for copper and aluminium films. With a possible repetition rate of 10Hz, the system combines unprecedented deposition rates and the possibility of in-situ surface processing in between pulses.

[1] G. De Temmerman et al., Appl. Phys. Lett. 97 (2010) 081502

2:40pm **SE+PS-ThA3 Pulsed Magnetron Sputtering Systems for Reactive Deposition of Oxide and Nitride Films**, J. Vlcek, J. Rezek, P. Steidl, University of West Bohemia, Czech Republic **INVITED**

In recent years, novel high-power pulsed dc magnetron systems have been used for sputtering of films[1].

In the presentation, we report on discharge and deposition characteristics, and on film structure and properties for two different pulsed magnetron sputtering techniques.

High power impulse magnetron sputtering of zirconium target in argon-oxygen gas mixtures was investigated at a high average target power density in a pulse, being up to 2kWcm⁻². The repetition frequency was 500Hz at duty cycles ranging from 2.5 to 10%. The total pressure of the argon-oxygen gas mixture was around 2 Pa. An effective reactive gas flow control, developed by us, was used for high-rate reactive deposition of insulating, highly optically transparent ZrO₂ films. In addition to the ZrO₂ films, high power impulse magnetron sputtering was also successfully used for high-rate reactive deposition of highly optically transparent Al₂O₃ and Ta₂O₅ films. Details of the process and measured properties of the films will be presented.

Pulsed dc magnetron sputtering of B₄C-Si (25:75%) target in an argon-nitrogen (50:50%) gas mixture at the total pressure of 0.5Pa was used for deposition of Si-B-C-N films with extremely high thermal stability (even above 1500°C). The repetition frequency was 10kHz at an 85% duty cycle to avoid microarcs at the target and thus, to produce high-quality defect-free films. Prior to the deposition, target atoms were subplanted into various substrates, being at a high negative rf potential, during their etching using pulsed magnetron sputtering of the B₄C-Si target in argon gas (the same repetition frequency and the duty cycle of 20%) to enhance adhesion of the Si-B-C-N films.

[1] K. Sarakinos, J. Alami, S. Konstantinidis, Surf. Coat. Technol. 204 (2010) 1661.

3:40pm **SE+PS-ThA6 Structure Evolution and Wear Mechanism in TiAlCN/VCN Nanoscale Multilayer Coatings Deposited by Reactive High Power Impulse Magnetron Sputtering Technology**, P. Hovsepian, A.P. Ehiasarian, G.K. Kamath, Sheffield Hallam University, UK, R. Haasch, I. Petrov, University of Illinois at Urbana Champaign

2.5 μ m thick TiAlCN/VCN coatings were deposited by reactive HiPIMS process. XTEM showed gradual evolution of the structure of the coating with thickness. The initial structure is nanoscale multilayer with sharp interlayer interfaces. This transforms to nanocomposite of TiAlCN and VCN nanocrystalline grains surrounded by C-rich tissue phase and finally changes to an amorphous carbon rich Me-C phase. In contrast deposition in similar conditions using standard magnetron sputtering produces a well defined nanoscale multilayer structure. Depth profiling by AES showed that the carbon content in the HiPIMS coating gradually increased from 25% at the coating substrate interface to 70% at the top thus supporting the TEM observations.

Energy-resolved mass spectrometry revealed that HiPIMS plasma is a factor of 10 richer in C¹⁺ ions, and therefore more reactive, as compared to the plasma generated by standard magnetron discharge at the same

conditions. The peculiar structure evolution in HIPIMS is discussed in relation to target poisoning effect and carbon outward diffusion during coating growth.

Highly abrasive AlSi9Cu1 alloy was dry machined using TiAlCN/VCN coated 25 mm diameter end mills to investigate the coating-work piece material interaction. Green (532 nm excitation) and UV (325 nm excitation) Raman spectroscopy was employed to identify the phase composition of the built up material on the cutting edge and swarf surfaces produced during machining. These analyses revealed formation of lubricious Magnèli phases namely V_2O_5 and graphitic carbon as well as highly abrasive SiO_2 and Al_2O_3 thus shedding light on the wear processes and coating tribological behaviour during machining.

4:00pm SE+PS-ThA7 Plasma Study and Interconnect Metallization using a Modulated Pulse Power (MPP) Hollow Cathode Magnetron, L. Meng, H. Yu, T.S. Cho, S. Jung, D.N. Ruzic, University of Illinois at Urbana Champaign

Modulated pulse power (MPP) magnetron sputtering, as a derivative of high power pulsed magnetron sputtering (HPPMS), was applied to a 200 mm hollow cathode magnetron (HCM) with a Cu target. The aim was to develop a more advanced ionized physical vapor deposition (IPVD) tool for applications such as interconnect metallization for sub-32 nm technologies. The MPP plasma generator, featured with 1000 V maximum pulse voltage and 550 A maximum pulse current, has a unique advantage of flexibly adjusting on- and off-time for each individual pulse, so that a long pulse packet of several milliseconds with desired waveform shapes can be generated. Distinct discharge stages were normally observed in one MPP pulse packet. Time-dependent plasma parameters were investigated using a triple Langmuir probe to help understand the MPP discharge characteristics and its performances. Plasma behaviors were shown to closely depend on the pulse waveforms and various other parameters including pulse current, repetition frequency, pressure, and distance from the target. A high electron density (n_e) of $3 \times 10^{18} \text{ m}^{-3}$ and an electron temperature (T_e) of 5 eV during the pulse were obtained at the substrate level, with an average power less than 8 kW. Compared with the DC magnetron sputtering at the same average power, the pulsed plasma density was an order of magnitude higher, which resulted in an enhanced ionization of the sputtered flux. As measured by an electrostatic gridded energy analyzer combined with a quartz crystal microbalance, the Cu ionization fractions above 30% were easily achieved by the MPP sputtering on the substrate level, twice higher than those by the DC sputtering. Increasing the pulse duty ratio or reducing the pressure resulted in a stronger ionization. The performance of Cu deposition in narrow trenches (70-100 nm) using the MPP sputtering was further studied, which exhibited an improvement over the DC sputtering. Stronger pulses with higher duty ratios and a lower gas pressure were preferred to reduce the overhang and achieve better step coverage and bottom coverage.

4:20pm SE+PS-ThA8 Structural and Optical Properties of Ultra-Thin Silver Films Deposited via High Power Impulse Magnetron Sputtering (HIPIMS) on Various Adhesion Layers, R. Jakubiak, Air Force Research Laboratory, L. Sun, General Dynamics Information Technology, N. Murphy, Air Force Research Laboratory, A. Waite, Universal Technology Corporation, J. Jones, Air Force Research Laboratory

Multilayer metal-dielectric stacks containing noble metals such as gold, silver, and copper have myriad applications in the areas of linear and nonlinear optics and photonics. The optical dispersion of Ag makes it particularly attractive for optical interference filters and metamaterials applications. In this regard, it is essential for the Ag layers be sufficiently thin as to not inhibit transparency in the visible spectral region yet still exhibit the favorable optical dispersion of bulk Ag. This can prove difficult due to the Volmer-Weber island growth process noble metals exhibit on dielectric materials. Island formation occurs at the initial growth stages, followed by nucleation and coalescence with increasing material deposition. Below the coalescence threshold the optical dispersion does not follow that of bulk Ag and that has a detrimental effect on the optical performance of the coating. In order to lower the thickness at which coalescence occurs we've explored highly energetic deposition techniques such as high power impulse magnetron sputtering (HiPIMS) alone or in conjunction with deposition on adhesion layers of Ti, Ge or transition metal nitrides. The adhesion layers also act as barriers to oxidation of the Ag from dielectric materials incorporated in the interference coatings. Using *in-situ* spectroscopic ellipsometry the coalescence threshold of the Ag was easily monitored by noting when during the growth process the optical dispersion of the film matched that of bulk Ag. A systematic study of the how the adhesion layers and deposition parameters affected the optical properties of the Ag films was achieved by correlating structural and compositional data gather from XPS and X-ray diffraction (XRD) to the optical transmission and optical dispersion obtained by UV-Vis spectroscopy and spectroscopic ellipsometry, respectively.

4:40pm SE+PS-ThA9 Inductively Coupled Impulse Sputtering (ICIS): A Novel Technique for Ionised PVD, A.P. Ehasarian, D. Loch, Sheffield Hallam University, UK

One limitation of magnetrons is their use of inhomogeneous magnetic fields which constrains deposition of magnetic materials to thin targets, complex (magnetic) alloys by erosion-dependent stoichiometry, and oxides by build-up of arc-prone insulating layers on the target edge. Inductively Coupled Impulse Sputtering (ICIS) is a new technology for physical vapour deposition based on sputtering without magnetic fields. A plasma is generated in front of the target via an inductively coupled coil driven with a 13.56 MHz radio frequency (RF) power supply. The target is then biased to a high voltage to initiate sputtering. In order to ionise significant fractions of the sputtered flux, the RF power density is pulsed with peak values in excess of 30 Wcm^{-2} to produce plasma density of the order of 10^{12} cm^{-3} . A low duty cycle of < 25% is used to achieve high peak powers and plasma densities at low average power. The degree of ionisation of ICIS of Cu and Ti in Ar atmosphere were evaluated using optical emission spectroscopy and atomic absorption spectroscopy and the film microstructure and coverage of vias was studied with cross sectional SEM. The effect of peak RF power density (P) was to increase metal ionisation degree hyperbolically. The rate of production of Ti^{1+} metal ions was proportional to $\sim P^{1.1 \pm 0.2}$ and was significantly faster than that of metal neutrals of $\sim P^{0.66 \pm 0.08}$ indicating enhanced ionisation of the vapour with power. The mechanisms of ionisation will be discussed. The influence of pressure on the process was studied at a constant peak RF power density of $P = 30 \text{ Wcm}^{-2}$. The intensity of copper and argon neutral emission rose linearly for pressures of $2.95 \times 10^{-2} - 1.2 \times 10^{-1} \text{ mbar}$ and saturated at higher pressures. The deposition rate was 2 nm min^{-1} for RF-power density of 30 Wcm^{-2} , average target power of 67 W and a pressure of $1.2 \times 10^{-1} \text{ mbar}$. The microstructure of Cu films was globular at $2.95 \times 10^{-2} \text{ mbar}$ and large-grain columnar at $1.2 \times 10^{-1} \text{ mbar}$. Bottom coverage of unbiased vias with width $0.36 \mu\text{m}$ and aspect ratio of 2.5:1 increased from 15 % to 20 % as pressure increased from 2.95×10^{-2} to $1.2 \times 10^{-1} \text{ mbar}$. The current work has shown that the concept of combining a high powered RF coil with a magnet-free cathode is feasible and produces very stable plasma and uniform target erosion. The experiments have shown a significant influence of power and pressure on the plasma and coating microstructure. The process is suitable for Fe, Ni and FeCo alloy deposition.

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