Wednesday Afternoon, November 11, 2009

Thin Film
Room: B4 - Session TF-WeA

ALD/CVD: Novel Applications, Mechanical Properties
Moderator: N.P. Guisinger, Argonne National Laboratory

2:00pm **TF-WeA1 ALD Applications to DNA Sequencing, Electrolytic Junctions and Nanofluidics**, ***S.M. Rossnagel***, *S.-W. Nam*, IBM T.J. Watson Research Center

One approach to sequencing DNA electrostatically pulls single-stranded DNA through a small, 2-3nm diameter aperture, also known as a nanopore. We have built and configured this electrolytic device with three 3 nm-scale electrodes and nanopores ranging from 15 to 1 nm with the goal of measuring the impedance of each nucleotide (C,G,A,T) as it passes through the nanopore. ALD films are critical to the fabrication at this dimension, and we have focused mostly on dielectric layers where conformality and pinhole-free deposition are critical. A related structure uses an ALD gate dielectric in a single electrode electrolytic device which functions as a pfet at sub 5nm range. (The source and drain are the upper and lower electrolte reservoirs). Electrical results show a modest gain (10x) in the range where debye shielding of the electrolyte is similar to the nanopore dimensions. This opens the ability to electrically switch conducting biological fluids at the nanoscale, and we have built devices to this end. The ALD-based approach can fabricate trench-based horizontal nanochannels down to 8nm diameter. These devices are fabricated using ALD of both metals and oxides in a keyhole structure based on trenches patterned by e-beam lithography.

2:20pm **TF-WeA2 Fabrication and Characterization of Point Contact Metal-Insulator-Metal Diodes for Potential Applications in Energy Harvesting**, ***P. Periasamy***, Colorado School of Mines, *A. Dameron, J. Bergeson, J. Berry, P. Parilla, D.S. Ginley*, National Renewable Energy Laboratory, *R. O'Hayre*, Colorado School of Mines

A **rectenna** is a device that can convert electromagnetic radiation such as **visible light to DC power** using a rectifier and an antenna component. Our focus in this paper is on fabrication and characterization of the rectifier component. **Metal-Insulator-Metal (MIM) diodes** are an excellent choice for the rectifier, since MIM diodes rectify via tunneling. Thus, a properly optimized MIM may be able to rectify signals in femto seconds (10^{-15} s), which enables rectification of visible light (400-790 THz). A **point contact MIM diode (PCD) configuration** is adopted in order to achieve the small diode capacitance necessary for high-frequency rectification. In the PCD, a planar metal/insulator bilayer "sandwich" is contacted by a second metal in the form of a sharp tip, resulting in a diode contact area as small as μm^2 – nm^2. For our initial studies we are using blunt wire tips, since our initial objectives are to optimize the planar metal/insulator layers. PCD devices with **different metal 1, insulator and metal 2 (wire tip) combinations were fabricated** and characterized for the desired I-V characteristics.

The PCD diodes were fabricated as follows. First, 100nm films of metal 1 candidates such as **Ni, Nb, Sm, Hf** were deposited by **DC sputtering**. The insulator layer (**NiO_X, NbO_X, SmO_X, HfO_X**) was grown by **anodization** of the metal films and by **atomic layer deposition**. Devices were characterized as a function of thickness of the insulator layer. In addition, dual insulators (MIIM) were grown and compared with single insulator (MIM) devices. TiO_2 and Al_2O_3 were used for the second insulator layer. The deposition parameters of the metal and the insulator films were optimized to obtain films that are pinhole free and have low surface roughness. The films were characterized using scanning electron microscopy, atomic force microscopy, x-ray reflectivity and x-ray photoelectron spectroscopy. Pt, Au and Ag wire tips were used for Metal 2. PCD IV characteristics were analyzed in terms of **non-linearity** (NL) [(dI/dV)*(V/I)], **asymmetry** (AS), **responsivity** (RY) [(d^2I/dV^2)*(dI/dV)] and **turn-on voltage** (TOV) [based on positive current]. From the matrix of different material combinations and the fabricated MIM devices, an attempt was made to identify critical parameters that influence the desired I-V curve characteristics.

The NL, RY and TOV values for the Nb-NbO_X (5.2 nm thick)-Pt system were 2.3, 3.8 A/W and 0.1 V respectively. But the AS value was not as good as found in Nb-NbO_X (22.81 nm thick)-Pt system. At the same time, however, the turn-on voltage was relatively higher (1.7 V) in the latter system. Such results would help us fabricate a diode suitable for solar energy harvesting.

2:40pm **TF-WeA3 Tungsten Oxide (WO_3) Thin Films for Application in Advanced Energy Systems**, ***S.K. Gullapalli***, *C.V. Ramana*, University of Texas at El Paso

Coal gasification plants are advanced energy production systems. Inherent processes in these plants produce a lot of hazardous gases, such as hydrogen sulfide (H_2S), which must be continuously and efficiently detected and removed before the syngas is used for power generation. The objective of the present work is to develop stable and reliable H_2S sensors based on nanostructured tungsten oxide (WO_3) thin films. The chemical sensing ability and high-temperature stability of WO_3 is the motivation for the work. WO_3 thin films have been fabricated by RF reactive magnetron-sputter deposition. A W-target has been employed for all the depositions and to investigate the effect of processing conditions on the growth and structure of resulting WO_3 films. The fabrication has been made under varying substrate temperatures (T_s), in the range 30(RT)-400 ^oC. The argon to oxygen flow ratio is kept constant at 1:6 for reactive deposition and oxide formation. Investigations made using x-ray diffraction (XRD) and scanning electron microscopy (SEM) indicate that the effect of T_s is significant on the microstructure of WO_3 films. XRD and SEM results indicate that the WO_3-films grown RT are amorphous, whereas films grown at higher temperatures are nanocrystalline. Thermally activated growth process of WO_3 films is evident in the data. The average grain size increases with increasing T_s. WO_3 films exhibit smooth morphology at lower temperatures (< 200 ^oC) while relatively rough at 400 ^oC. The optical measurements indicate that the films exhibit relatively high transmittance and the band gap is dependent on the grain-size. The analyses indicate that the nanocrystalline WO_3 films grown at 100-200 ^oC could be the potential candidates for H_2S sensor development for application in coal gasification systems.

3:00pm **TF-WeA4 Growth Kinetics in a Large-Bore Vertically-Aligned Carbon Nanotube Film CVD Process**, ***K. Bosnick***, *L. Dai*, National Research Council Canada

We installed and developed a large-bore CVD reactor for the growth of carbon nanotube materials on device substrates. The reactor was custom built by Tystar, Inc. and is capable of processing batches of up to fifty 150-mm wafers with industry-standard process controls. We synthesize vertically-aligned films of multi-walled carbon nanotubes by employing a Cr-Ni-Fe thin film catalyst stack pre-deposited on substrates. The kinetics of the growth process is studied by measuring the film thickness, the resistivity (indicative of the density), and the distribution of CNT diameters as a function of pre-growth catalyst treatment time, growth time, and growth temperature. It is found that pre-growth treatment times of about 200 min are needed before reaching steady-state catalyst conditions. Shorter pre-growth treatment times produce a more thick but less dense film. The CNT diameters are only weakly affected by the pre-growth treatment time (for at least greater than 30 min). A model is proposed to explain these results whereby the catalyst film quickly breaks up into catalyst particles but further treatment is needed to activate these particles. More activated particles leads to a more dense film but due to increased demand on feedstock also produces a less thick film. The kinetics of the film growth are studied as function of growth time and temperature under steady-state catalyst conditions.

4:00pm **TF-WeA7 Study of Silicon Strain in Shallow Trench Isolation**, ***M. Belyansky***, *N. Klymko, D. Chidambarrao, R. Conti, F. Liu*, IBM

Generation of strain in a silicon channel has been successfully used to increase performance of state of the art CMOS devices. The most studied methods are embedded silicon germanium, stress liners and stress memorization techniques. However, there have been relatively few studies of the effect of thin film dielectric materials in the Shallow Trench Isolation (STI) area on silicon strain.

Raman spectroscopy has been used as a primary tool to measure silicon strain on a variety of STI structures. Different STI dielectric gap fill materials have been evaluated including high density plasma CVD, sub-atmospheric CVD and spin-on glass based oxide thin films. It has been shown that both intrinsic stress of thin film dielectric material and STI structure type affect strain in silicon. Ways of introducing new dielectric gap fill materials and generating high stress in STI are discussed including the effect of the STI CVD liner material on Si strain.

Advantages and limitations of Raman based strain metrology in the semiconductor industry are delineated. Raman spectroscopy showed much better sensitivity to Si strain compared to TEM based strain measurement techniques.

The findings have been confirmed electrically on CMOS devices with tensile and compressive strain in STI region. Substantial improvement in pFET transistor performance has been demonstrated for devices with tensile dielectric in STI.

4:20pm **TF-WeA8 Critical Compressive Stress for Cracking of Al_2O_3 ALD Films**, ***S.H. Jen***, *J.A. Bertrand, S.M. George*, University of Colorado

Flexible displays require various thin films that must withstand stress without cracking. Very little is known about the critical stress for cracking for ALD films for either tensile or compressive stress. The critical stress for cracking is particularly important for the design of gas diffusion barrier films on polymer substrates. Flexible organic light emitting diodes (OLEDs) require barriers with extremely low water vapor transmission rates of < 1 x 10-6 g/m2/day. Film cracking will severely impair the gas diffusion barrier.

Compressive stress can be applied by depositing films at elevated temperature on a high thermal expansion substrate and then letting the sample cool to room temperature. The critical compressive stress for cracking of Al2O3 ALD films was determined using Teflon FEP which is a polymer with a high thermal expansion coefficient. Different compressive stresses were defined using different deposition temperatures. Crack densities were visualized using scanning electron microscopy (SEM) images. The critical stress for cracking was determined for various Al2O3 ALD film thicknesses.

Al2O3 ALD film thicknesses were examined from 19-48 nm. The SEM images showed that the films buckled and then cracked with increasing compressive stress. The critical stress for cracking was constant at ~2 GPa for the thicker films with thicknesses >30 nm. The critical stress for cracking increased dramatically to >4 GPa for film thicknesses < 20 nm. These results indicate that thinner Al2O3 ALD films are more flexible and able to withstand higher compressive stresses without cracking. Enhanced multilayer gas diffusion barriers should employ thin Al2O3 ALD layers for optimum flexibility.

4:40pm **TF-WeA9 Elaboration of Dichroic Filters on Shape Memory Substrate**, ***O. Carton***, *M. Lejeune, A. Zeinert*, Laboratoire de Physique de la Matière Condensée, France, *S. Zaidi, F. Lamarque*, Laboratoire Roberval, France

The aim of this work is the elaboration of thin films for optical filtering under mechanical constrains. Our dichroic filters (transmission of one wavelength and reflection of another one) had to be deposited on shape memory substrates, with respect to several conditions:

- low thickness of the filter in order to minimize the weight supported by the substrate

- low internal stress in the structure to limit the mechanical action of the filter on the substrate

- high elasticity in order to preserve a good adhesion when the substrate is strongly deformed

- low light absorption in order to transmit the maximum of energy

The realised structures were made up of the stack of two couples of materials: amorphous hydrogenated silicon (a-Si:H) / silicon dioxide (SiO_2), and a-Si:H / amorphous polyacid methacrylic (a-pAM), using the Bragg reflector structure with seven layers only. These materials have been elaborated using two plasma techniques: a-Si:H and SiO_2 were deposited by magnetron sputtering and the polymeric layers were deposited by inductive plasma enhanced chemical vapor deposition (PECVD). A brief study of the optical properties as a function of the deposition parameters has been performed for each material, and the chemical structure of the polymer was investigated with FTIR as a function of the RF power forwarded to the plasma. The internal stress of the optical filters has been calculated using the Stoney formula, and structures made up with polymeric layers have shown better mechanical properties than structures with silicon dioxide, with a lower value of residual stress. The elasticity of the realized optical filters has been tested on plastic substrate with a repeatedly deformation applied to the structure, and a good stability has been observed with no significant change in the optical filtering properties before and after the deformations.

The aimed application of these filters is to achieve a chromatic wireless control of shape memory alloy (SMA) micro-actuators. The actuation is performed by the use of two laser sources in order to heat and distort pieces of SMA (Nitinol). This chromatic response was first realised with optical filters on glass substrate, the Nitinol pieces were placed under this glass substrate and the selective response for the different laser wavelengths was observed. Then the optical filters were directly deposited on Nitinol sheet and the selective response was also visualized.

5:00pm **TF-WeA10 Single-Stage Deposition of Organic/Inorganic Multilayer by Plasma Enhanced and Initiated Chemical Vapor Deposition**, ***A.M. Coclite***, University of Bari, Italy, *G. Ozaydin-Ince*, Massachusetts Institute of Technology, *F. Palumbo, R. d'Agostino*, University of Bari, Italy, *K. Gleason*, Massachusetts Institute of Technology

Deposition techniques of multiple dense, inorganic layers alternated with soft, organic ones are widely investigated for several technological applications. Generally, a combination of two different deposition techniques is employed for deposition of organic/inorganic multilayered coatings. The possibility of a single-chamber vacuum-deposited system may greatly simplify the production and allows the quicker and cheaper roll-to-roll deposition. Here we propose a new technique for multilayer deposition, consisting of coupling initiated and plasma enhanced CVD, maintaining the same organosilicon precursor and the same reactor configuration.

Multilayer coatings comprised of alternating inorganic (silica-like) and organic (organosilicon polymer) layers were deposited using hexavinyldisiloxane (HVDSO) as precursor. The organosilicon polymers were deposited by initiated CVD (iCVD) at filament temperature of 280°C. The silica-like layers were obtained by Plasma Enhanced CVD (PECVD) applying RF power to the same filament used in the iCVD process. The multilayers were obtained through layer by layer deposition, switching from one technique to the other without venting the system.

Chemical and morphological characterization of the organic single layer showed that the iCVD of poly-HVDSO resulted in a very crosslinked film with high deposition rate, high Carbon content (79 % from XPS analysis) and very low roughness (0.7 nm). PECVD of the same monomer, when highly diluted in Oxygen, gave inorganic coating with a low content of OH terminal groups and high deposition rate. X-ray photoelectron spectroscopy (XPS) depth profile, ellipsometric characterization and Secondary electron microscopical imaging of multilayer coatings clearly showed that the various layers do not mix or interdiffuse, but maintain the same chemical composition and refractive indices as in single layers deposition. When the inorganic layer was deposited over the organic layer a graded interphase (around 40 nm thick) was detected, due to plasma ion bombardment of the underlayer.

The advantage of coupling iCVD and PECVD consists in the possibility of having dense inorganic coatings alternated with organic interlayers characterized by high crosslinking and high C content. Moreover the high smoothness of the iCVD layer is important to reduce the roughness of the under-layers in order to limit the formation of defects in the successive inorganic up-layer. Hence, all this properties make this kind of multilayer coatings promising as ultrahigh barriers (UHB) against the transmission of water vapor and oxygen through polymer substrates.

5:20pm **TF-WeA11 The Role of Ammonia as an Inhibitor Species in Low Temperature CVD to Reduce Film Growth Rate and Enhance Conformal Coverage**, ***S. Babar***, *P. Zhang, W. Wang, N. Kumar, J.R. Abelson*, University of Illinois, Urbana-Champaign

Our group recently demonstrated the phenomenon of growth inhibition in low temperature chemical vapor deposition of TiB_2: a neutral molecule is added to the flow of precursor in order to reduce the growth rate and enhance the degree of conformal coverage; the atoms contained in the inhibitor are not incorporated into the film [JACS **130**, 52 (2008)]. Here, we demonstrate the inhibition behavior of ammonia on HfB_2 growth using $Hf(BH_4)_4$. The growth rate and surface roughness are measured in-situ by spectroscopic ellipsometry. At substrate temperatures below 350^{o}C, ammonia reduces the growth rate of HfB_2, down to zero at an ammonia pressure of ~ 1 mTorr. Upon cessation of the ammonia injection, growth resumes after 1-2 minutes. When ammonia is delivered as short pulses, the surface roughness appears to increase, then declines again after the ammonia is pumped out. We explore the origins of this phenomenon, which may involve the formation of a dielectric surface layer or re-nucleation of HfB_2 growth. We explain the role of ammonia using a site-blocking model in which ammonia adsorbs reversibly on the surface sites and reduces the rate of precursor adsorption. This simple rate model fits the data well. We show that growth inhibition by ammonia can be used to greatly enhance the degree of conformal coverage in a deep trench.

5:40pm **TF-WeA12 Nanoscale Engineering of Ceramic Supports for High Permeance Ultrafiltration Membranes**, ***R. Nahm***, *P.C. Rowlette, C.A. Wolden*, Colorado School of Mines

Anodized aluminum oxide (AAO) membranes are commercially available supports that offer a high pore density and a narrow pore size distribution. In this talk, we describe the use of pulsed plasma-enhanced chemical vapor deposition (PECVD) to modify AAO supports for arbitrarily designed molecular weight size cutoffs. Pulsed PECVD is a self-limiting deposition technique that provides digital control over the amount of deposited material (i.e. 1 Å/pulse). Specifically, we use pulsed PECVD to deposit SiO2 at room temperature to affect arbitrary pore size control. For this

work, pulsed PECVD is operated in a nonconformal mode, meaning that only the very pore opening is modified with no deposition occurring throughout the majority of the structure. Modified membranes are characterized by atomic force and electron microscopies. An advantage of this approach is that the modifications can be done very quickly. In addition, we demonstrate that the nominal pore size may be significantly reduced without any impact on the permeance. Moreover, these membranes provide a well-defined geometry that provides a unique experimental platform for studying hindered transport and nanofluidics. The modified membranes are characterized by gas permeance, water permeance, and measurements of solute rejection. SiO2 is the material of choice since it may be readily modified through addition of self-assembled monolayers to control the hydrophilicity of the surface and enhance biocompatibility. We will present preliminary work in this regard as well.

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