Wednesday Morning, October 22, 2008

Thin Film
Room: 302 - Session TF-WeM

Chemical Vapor Deposition
Moderator: P.D. Rack, University of Tennessee

8:00am **TF-WeM1 Growth and Functional Properties of Thin Film Oxides Synthesized under Photon Irradiation**, ***S. Ramanathan***, Harvard University **INVITED**

Thin film oxides play a key role in several advanced electronics and energy technologies such as alternate gate dielectrics, memory devices and functional membranes in energy generation. Developing novel routes for synthesis of oxide thin films with controlled structure and stoichiometry is therefore of great importance. In this talk, we will present experimental and modeling results from our on-going work on synthesis of ultra-thin oxides under photon irradiation with particular emphasis on structure-property relations. Model systems that will be discussed include ultra-thin fluorite-strucutred zirconia dielectrics synthesized by low temperature ultra-violet ozone oxidation and yttria-doped zirconia films grown by physical vapor deposition methods. The role of photon irradiation during oxide formation will be discussed in depth along with their impact on functional properties. Examples of applications of the processing technique in advanced electronic devices as well as solid oxide fuel cells will be presented.

8:40am **TF-WeM3 A Zone Diagram for Conformal Film Growth by CVD**, ***J.R. Abelson***, *A. Yanguas-Gil, N. Kumar, Y. Yang*, University of Illinois at Urbana-Champaign

The field of thin film growth using physical vapor deposition has benefited enormously from the mechanistic insights provided by Thornton's zone diagram, which he introduced to this society in 1974. There has been no direct analogue for the case of chemical vapor deposition (CVD), presumably due to the multiplicity of chemical reactions and the wide range of experimental conditions associated with the use of different precursor molecules. One major advantage of CVD is the ability to deposit films with extremely good conformal (step) coverage, which is a requirement for the additive fabrication of many current and proposed nanoscale devices. We show that all conformal CVD processes share certain kinetic requirements and limitations. Each of these can be represented on a plot of precursor pressure vs. substrate temperature: threshold phenomena, such as the onset temperature for reaction, appear as a vertical or horizontal line; kinetic competitions, such as surface adsorption vs. desorption, appear as exponential slopes. The properties of the precursor molecule and the aspect ratio of the feature to be coated (represented by a trench) then define a polygonal figure on the (P,T) plot which may or may not allow for conformal growth. We further show that many of the kinetic coefficients can be represented in normalized form, which we present as a zone diagram for conformal growth by CVD. The usefulness of this construction is illustrated by analyzing well-known experimental systems, such as W or SiO_2 growth, and the recent results we have obtained for the low temperature CVD of HfB_2, CrB_2, TiB_2 and MgO. For all these systems, the underlying mechanism that affords good step-coverage is surface site-blocking due to adsorbed precursor molecules or reaction byproducts or co-reactants. The experimental results are consistent with the predictions of the zone diagram. We conclude by showing how the site-blocking processes, and thus the degree of conformal coverage, can be controlled through the addition of site-blocking agents, such that a precursor that normally does not afford conformal growth can be transformed into one that coats very deep features.

9:00am **TF-WeM4 Conformal Chemical Vapor Deposition of Metal Oxide Thin Films using Metal-Diboranamide Precursors**, ***A. Yanguas-Gil***, *N. Kumar, S.R. Daly, Y. Yang, G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana-Champaign

The N,N-dimethyldiboranamide (dmdba) ligand is used to synthesize a wide range of different alkaline earth, transition metal and rare earth metal compounds that have sufficient volatility to serve as precursors for the growth of complex materials by chemical vapor deposition (CVD). In this work, we report the successful growth of TiO_2, erbium-doped TiO_2, MgO, Y_2O_3, La_2O_3 and titanate complex oxides using water as a co-reactant at substrate temperatures as low as 225°C. The growth process is monitored in-situ using spectroscopic ellipsometry, and the films are characterized ex-situ by AES, RBS, SEM, XRD and AFM. The crystallinity of the films upon annealing is also studied. The results show that the metal center has a strong influence in the reactivity, surface chemistry and the vapor pressure of the precursor. The impurity concentrations in the films are below the AES and RBS detection limits, indicating that the dmdba ligand is efficiently released from the growth surface to the gas phase. Under suitable conditions the film growth is highly conformal, e.g. MgO films have been deposited onto trenches with 30:1 depth:width ratio with a step coverage (minimum to maximum thickness ratio) of 90%. The corresponding film growth rate is 5-100 times greater than that achievable using atomic layer deposition due to the uninterrupted nature of the CVD process. These results make the dmdba precursor family very attractive for the synthesis of complex oxide films by CVD.

9:20am **TF-WeM5 Chemical Vapor Deposition of WN_xC_y using Tungsten Piperidylhydrazido Complex: Deposition, Characterization and Diffusion Barrier Evaluation**, ***D.J. Kim***, *O.H. Kim, T.J. Anderson, J. Koller, L. McElwee-White, C.L. Leu, J.M. Tsai, D.P. Norton*, University of Florida

The tungsten piperidylhydrazido complex $Cl_4(CH_3CN)W(NN(CH_2)_5)$ (designated as 1) was deposited by metal organic chemical vapor deposition (MOCVD) for growth of tungsten carbonitride (WN_xC_y) thin films in the temperature range 300 to 700 °C in the absence and presence of ammonia (NH_3). The effect of deposition temperature and NH_3 on the film microstructure, chemical composition, bonding states, growth rate, electrical resistivity, lattice parameter, and grain size were studied. The microstructure of films deposited with NH_3 was amorphous below 500 °C and polycrystalline at and above this temperature. The chemical composition of films deposited with NH_3 increased the nitrogen levels and decreased the carbon levels over the entire deposition temperature range as compared to films deposited without NH_3. The XPS results indicate that W is primarily bonded to N and C for films deposited at 400 °C, but at lower deposition temperature the binding energy of the W-O bond becomes more evident. Growth rates of films deposited with NH_3 varied from 0.6 to 4.2 Å/min. Diffusion barrier properties were investigated from Cu/WN_xC_y/Si stacks consisting of 100 nm Cu deposited at room temperature by reactive sputtering on a WN_xC_y film deposited at 400 °C by CVD. XRD patterns, AES compositional depth profiling, and cross-sectional TEM imaging were used to determine the performance of the diffusion barrier. Cu/WN_xC_y/Si stacks annealed at 500 °C for 30 min maintained the integrity of both Cu/WN_xC_y and WN_xC_y/Si interfaces. Hence, WN_xC_y thin films deposited at 400 °C are a viable material to serve as a Cu diffusion barrier to prevent interdiffusion and intermixing between Cu and Si. The film properties of thin films deposited with 1 and tungsten imido complexes $Cl_4(CH_3CN)W(NR)$ (R = Ph, ^{i}Pr, and allyl)[1] were also compared to provide insight into the effect of hydrazido and imido ligands on film properties.

[1] O. J. Bchir, K. M. Green, H. M. Ajmera, E. A. Zapp, T. J. Anderson, B. C. Brooks, L. L. Reitfort, D. H. Powell, K. A. Abboud, L. McElwee-White, J. Am. Chem. Soc. 127 (2005) 7825-7833.

9:40am **TF-WeM6 Conformality of Chemical Vapor Deposited Copper Oxide Thin Films in High Aspect Ratio Features for ULSI/MEMS Applications**, ***Y. Shimogaki***, *Y. Susa*, The University of Tokyo, Japan

Kinetics of chemical vapor deposition of copper oxide (Cu_2O) thin film using Cu(tmvs)(hfac) and H_2O_2 as precursors were investigated. Cu_2O films could be deposited at relatively low temperature, as low as 80°C, on various kinds of under-layers including thermal silicon oxide and TaN. Cu_2O films can be easily reduced to metallic copper thin films using formic acid (HCOOH) as reducing agent. This reduction process can be performed at low temperature of around 100°C. Thus, Cu_2O deposition and its reduction process combination can be a novel chemical route to make metallic copper film at low temperature. In this work, we examined the source precursor partial pressure dependencies of Cu_2O growth rate (G.R.) using cold wall type CVD reactor. G.R. showed non-linear behavior, know as Langmuir-Hinshelwood mechanism, against partial pressure of Cu precursor (P_{Cu}), while G.R. showed linear dependence against the partial pressure of H_2O_2 (P_{H2O2}). These kinetics suggest Cu_2O is formed via direct reaction of gas-phase H_2O_2 and adsorbed Cu precursor. The extendibility of this Cu_2O-CVD process to make conformal deposition onto high aspect ratio (HAR) features was systematically investigated. The film thickness profile within HAR-feature, like as trench, was analyzed by solving diffusion equation for precursor molecules. The consumption of the precursors by surface reaction, whose rate had been obtained from the above mentioned kinetic studies, was taken into account. The analysis suggested that film thickness non-uniformity was mainly derived from the consumption of H_2O_2. The Cu precursor concentration profile does exist in the HAR-features, however, due to the non-linear kinetic behavior of G.R. against P_{Cu}, its non-uniformity will not affect to the film thickness uniformity. Existence of gas-phase reaction to decompose H_2O_2 was also confirmed from the growth rate profile analysis. These kinetic information were integrated and extendibility of this Cu_2O-CVD process for conformal deposition onto HAR features was estimated. We could conclude that this process is suitable for ULSI interconnect and TSV applications with nearly 100% step coverage, but for

MEMS applications, this process may have a limit. Step coverage of about 40% or less will be obtained for aspect ratio of 100, which may be sometimes required for MEMS applications.

10:40am **TF-WeM9 Structure and Morphology of Pentacene Film Grown on HOPG**, ***J. Götzen***, *D. Käfer, Ch. Wöll, G. Witte*, Ruhr-University, Germany

Previous studies have shown that the structure of organic semiconductor film depends sensitively on the interaction with the substrate. In this respect we have studied the film growth of pentacene onto highly oriented pyrolytic graphite which constitutes an interesting model system for a chemically rather inert but - in contrast to amorphous oxides – highly ordered crystalline substrate. Here we report a comprehensive characterization of the microstructure, morphology and thermal stability of pentacene films grown by OMBD onto freshly cleaved HOPG by employing STM, AFM, NEXAFS, XRD and TDS. Despite a rather weak, essentially van-der Waals-type substrate interaction pentacene molecules adsorb with their planes oriented parallel to the surface and form a commensurate monolayer due to the close match of the molecular carbon frame and the underlying graphite lattice. This packing motive, however, is not maintained in multilayer films where instead molecules in subsequent layers are tilted around their long axis. The multilayer growth is further characterized by the formation of individual crystalline islands exhibiting the Siegrist bulk polymorphism for rather different growth conditions (rate and temperature) and thus parallels the growth scenario observed previously for pentacene on Au(111)[1] In contrast films with upright oriented molecules were obtained if the graphite had been briefly sputtered before deposition and thus emphasizes the importance of micro-roughness on the resulting film growth.

[1]D. Käfer, L. Ruppel, G. Witte, Phys. Rev. B 75, 085309 (2007).

11:00am **TF-WeM10 Electrically Controllable Stationary Hadamard Shutter Exploiting the Semiconductor-To-Metallic Phase Transition of W-doped VO_2 Arrays**, ***M. Soltani***, *M. Chaker,* INRS-Énergie, Matériaux et Télécommunications, Canada*, E. Haddad, R.V. Kruzelecky, W. Jamroz,* MPB Communications Inc., Canada*, J. Margot,* Université de Montréal, Canada*, P. Laou, S. Paradis*, Defence R&D Canada-Valcartier

The well-known transmitting semiconductor (on) to the reflecting metallic (off) phase transition (SMT) of thermochromic VO_2 can be controlled by external parameters such as temperature, pressure, photo-carrier injection, photo-excitation, and an electric field. Also, the transition temperature (about 68 °C) of VO_2 can be controlled by metal doping such as W, Ti, Al, Mo, etc. Undoped and doped-VO_2 smart coatings are thus excellent materials for various switching applications such as IR uncooled bolometers, smart windows, all-optical, electro-optical and microwave switching devices. Here, we exploit the SMT characteristic of W(1.4 at. %)-doped VO_2 active layer in the fabrication of stationary Hadamard shutter arrays. The active layer was synthesized by reactive pulsed laser deposition. The micro-optical active slits were patterned by photolithography followed by plasma etching, while the lift-off process achieved the Au/NiCr electrodes onto the top of the individual micro-slit. This shutter consists of 16 active planar micro-optical slits for which both the infrared transmittance and reflectance switching can be controlled individually at room temperature by an external voltage. This allows performing any desirable on-off switching combinations. Both the electroreflectance and electrotransmittance switching of the individual slits were investigated at 1.55 µm. The transmittance switching was as high as 25 dB, while the reflectance switching was about 6 dB. In addition, the electrotransmittance switching modulation (on/off) was demonstrated at 1.55 µm by switching the individual slits by an external ac signal. This shutter can be used as individually programmable 16 multi-entrance slits (i.e., stationary Hadamard shutter) instead of the traditional single entrance slit of dispersive IR spectrometers. Thus, the role of the Hadamard shutter consists of multiplexing the incoming information into the output detector element arrays using binary coding. As results, enhancement of the signal-to-noise ratio and improvement of both the sensitivities and the resolutions of these spectrometers.

11:20am **TF-WeM11 Molecular Beams Tunable in Energy Yield Novel Growth Behavior in Small-Molecule Organic Semiconductors**, ***A. Amassian***, *S. Hong, T.V. Desai,* Cornell University*, S. Kowarik,* University of California at Berkeley*, J.E. Goose, A. Papadimitratos, V.A. Pozfin,* Cornell University*, A.R. Woll, D.M. Smilgies,* Cornell High Energy Synchrotron Source*, F. Schreiber,* Universität Tübingen, Germany*, P. Clancy, G.G. Malliaras, J.R. Engstrom*, Cornell University

The performance of organic electronic devices is closely tied to the packing structure and morphology of molecular semiconductors at the semiconductor-insulator interface, which in turn are intricately linked to molecular-scale processes operant during thin film growth. Tunable supersonic molecular beams have emerged as a versatile method to manipulate the state of incident molecules (e.g., kinetic energy, vibro-rotational states) and to promote novel growth behavior on the surface of the insulator (i.e., SiO_2). The growth of small-molecule thin films of pentacene and diindenoperylene from molecular beam sources tunable in kinetic energy (1 to 10eV) and flux was investigated in situ using synchrotron-based time-resolved X-ray reflectivity and grazing incidence X-ray diffraction techniques and ex situ by non-contact atomic force microscopy. Time-resolved X-ray scattering experiments reveal significant acceleration of the growth rate between the submonolayer and the multilayer thickness regimes. The acceleration of growth rate is not observed in thermal processes; it is operant when molecules are incident at hyperthermal kinetic energy and further enhanced by increasing the energy of molecules. Rate equation modeling of X-ray reflectivity data suggests that small-molecules incident at hyperthermal kinetic energy are trapped much more efficiently by a molecular monolayer formed on the surface of the "hard" insulator than by the bare insulator itself. Molecular dynamic simulations reveal that energetic molecules undergo a so-called "soft-landing" on molecular monolayers, during which can insert the molecular layer near step edges and transfer most of their kinetic energy to the "soft" molecular layer. Organic thin film transistors of pentacene and diindenoperylene fabricated from molecular beams tunable in energy exhibit significant increases – by a factor of five for pentacene and by an order of magnitude for diindenoperylene – of the field effect mobility in conditions of high kinetic energy. The relationship between the kinetics of growth and improved charge transport characteristics of conjugated small-molecule semiconducting thin films is discussed.

11:40am **TF-WeM12 Vanadium Oxide Thin Films for IR Imaging Bolometric Applications Deposited by Reactive Pulsed DC Sputtering**, ***N.M. Fieldhouse***, *S.S.N. Bharadwaja, M.W. Horn, S.M. Pursel, R. Carey*, Pennsylvania State University

Uncooled infrared focal plane arrays (IRFPAs) are the critical technology for night vision cameras needed for military and civilian applications. The two most widely used temperature sensitive imaging materials are vanadium oxide and amorphous silicon typically deposited by reactive ion beam sputtering and PECVD respectively. In this work, we report on vanadium oxide (VOx) films deposited by a reactive pulsed DC magnetron sputtering process using a pure vanadium metal target that are comparable to those presently used in commercial IRFPAs. The structural, microstructure and electrical properties were evaluated as a function of processing parameters such as substrate temperature, range of oxygen to argon ($Ar:O_2$) partial pressures ratio, and pulsed DC power. The VOx films deposited at various substrate temperatures between 30-400 °C over a range of $Ar:O_2$ partial pressure ratios exhibited distinct variations in their microstructure even though most of them appear amorphous using glancing angle X-ray diffraction. The critical electrical properties such as the temperature coefficient of resistance (TCR), resistivity and noise levels were found to be sensitive to film microstructure. Thin films of VOx (50-200 nm) were deposited with resistivity values between 0.1-100 ohm-cm and a TCR in the range of -1.1% to -2.4% K^{-1}. In particular, films grown at lower substrate temperatures with higher oxygen partial pressures have shown finer columnar grain structure and exhibited larger TCR and resistivity.

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