Thin Film
Room: 307 - Session TF+PS-ThM

Advanced CVD and Chemical Vapor Infiltration Methods

Moderator: Robert Davis, Brigham Young University

8:00am **TF+PS-ThM1 Industrializing Single Wall Carbon Nanotubes by Water-Assisted CVD**, ***Don Futaba***, AIST, Japan **INVITED**

Since the discovery of the carbon nanotube (CNT) 20 years ago, extensive effort has been made to utilize their exceptional intrinsic properties toward industrial applications. However, availability has significantly thwarted these endeavors. In one section of my presentation, I will describe our efforts toward the economical mass-production of single-walled carbon nanotubes (SWCNT) based on the water-assisted chemical vapor deposition technique, from which highly efficient synthesis of vertically aligned SWCNTs grow from substrates (SWCNT forests). These SWCNT forests form through the self-assembly of individual SWCNTs when grown in sufficient density and have been shown to be useful templates for various applications from energy device electrodes to MEMS materials due both the continuous nature and high porosity. Further, I will describe the forest, and present a few examples of how we have infiltrated these material to create a new material with enhanced properties.

8:40am **TF+PS-ThM3 Organoboranes as Single Precursors for Low Temperature CVD of Boron Carbide Thin Films for Neutron Detectors**, *M. Imam*, Linköping University, Sweden, *C. Höglund*, European Spallation Source (ESS AB), *J. Birch*, ***Henrik Pedersen***, Linköping University, Sweden

The world-wide shortage of the ^{3}He isotope has led to a need for novel designs of neutron detectors. A detector based on the isotope ^{10}B, in the form of thin films, has been suggested by the European Spallation Source (ESS). The detector design uses $^{10}B_4C$ films, ≥1 μm, deposited on both sides of neutron transparent substrates such as Al blades.[1] The melting point of Al (660 °C) sets a strict upper temperature limit for CVD of the $^{10}B_4C$ films. Also, metallic Al will be badly affected by corrosive by-products, like HCl. This means that traditional B_4C CVD routes based on BCl_3 and CH_4 cannot be used. An alternative CVD route is to use oragnoboranes, i.e. molecules with direct B-C bonds, as such molecules are very reactive and do not produce corrosive by-products.

We have demonstrated the synthesis of thin, X-ray amorphous, boron-carbon films at low temperature (400-600 °C), by thermally activated CVD using triethylboron, $B(C_2H_5)_3$, (TEB) as single precursor on both single crystalline Si (100) and Al substrates.[2] Films with B/C-ratio of 4.6 with density 2.42 g/cm^3 (bulk B_4C density 2.52 g/cm^3) and 3.6 with density 2.14 g/cm^3 were deposited at 600 °C in hydrogen and argon ambient respectively, the impurity levels in the films was about 4 at.% of H at 600 °C. Further studies of TEB as precursor at higher temperatures (700-1200 °C) on Si substrates show that films with a B/C ratio of 4.5 and 3 were obtained from films deposited at 700 °C in hydrogen and argon ambient respectively with < 0.24 at.% of H. A threshold temperature of 1000 °C for the deposition is identified above which the B content decreases dramatically. Based on our results, a chemical mechanism for boron-carbon films from TEB, where the TEB molecule is decomposed to BH_3 and hydrocarbons, is suggested.

Plasma Enhanced CVD using trimethylboron, $B(CH_3)_3$, (TMB) is also explored to further lower the deposition temperature. Results from CVD and PECVD will be compared with state of the art PVD of $^{10}B_4C$.

[1] R. Hall-Wilton et al. IEEE NSS/MIC conference record, 4283 (2012)

[2] H. Pedersen et al. *Chem. Vapor Deposition* 18, 221-224 (2012)

9:00am **TF+PS-ThM4 High-Quality ZnO Thin Films Grown by a New CVD Method using Catalytically-generated High-energy Precursors**, *T. Nakamura, Y. Ohashi, N. Yamaguchi, E. Nagatomi, T. Kato,* ***Kanji Yasui***, Nagaoka University of Technology, Japan

ZnO is useful for many applications, and various growth techniques, including MBE [1-2], PLD [3, 4], and MOCVD [5], have been used to prepare ZnO films. Despite the advantages of MOCVD in industry, ZnO deposition by conventional MOCVD consumes a lot of electric power to react the source gases and raise the substrate temperature. To overcome this, a more efficient means of reacting oxygen and metalorganic source gases is needed.

In this paper, a new CVD method for ZnO film growth using the reaction between dimethylzinc (DMZn) and high-temperature H_2O produced by a catalytic reaction on Pt nanoparticles is presented [6]. H_2 and O_2 gases were admitted into a catalyst cell containing a Pt-dispersed ZrO_2 catalyst, whose temperature increased rapidly to over 1300 K due to the exothermic reaction of H_2 and O_2 on the catalyst. The resulting high-temperature H_2O molecules were ejected from a fine nozzle into the reaction zone and allowed to collide with DMZn ejected from another fine nozzle. ZnO epitaxial films were grown directly on a-plane sapphire substrates at substrate temperatures of 773-873 K with no buffer layer. Growth rates were 0.02-0.13 μm min^{-1}, and film thicknesses were 2-8 μm. X-ray diffraction patterns exhibited intense (0002) and (0004) peaks. The smallest FWHM value of the ω-rocking curve of ZnO(0002) was less than 0.1º (194 arcsec). The Hall mobility and residual carrier concentration of the epilayers were in the ranges 140-197 cm^{2}V^{-1}s^{-1} and 5.8×10^{16}-6.0×10^{17} cm^{-3} at 300K, respectively. This Hall mobility is very large compared with ZnO films grown directly on sapphire by other deposition methods. PL spectra at 10 K showed a strong emission peak at 3.360 eV, attributed to the neutral donor-bound exciton D^o_x. The FWHM was as low as 0.9 meV, which is smaller than that previously reported for ZnO obtained by MBE (5.5 meV) [4], and by PLD on a sapphire(0001) substrate (1.7 meV at 2K) [3]. .

[1] M. Sano et al., *Jpn. J. Appl. Phys.*, **42** (2003) L1050. [2] H. Tampo et al., *Appl. Phys. Lett.*, **84** (2004) 4412. [3] E. M. Kaidashev et al., *Appl. Phys. Lett*., **82** (2003) 3901. [4] A. Ohtomo et al., *Semicond. Sci. Technol.*, **20** (2005) S1. [5] J. Dai et al., *J. Cryst. Growth*, **290** (2006) 426. [6] K. Yasui et al., *MRS Symp. Proc*., **1494** (2013) 127

9:20am **TF+PS-ThM5 Filling High Aspect Ratio Features: A Ballistic Transport Model**, ***Wenjiao Wang***, *J.R. Abelson*, University of Illinois at Urbana-Champaign

The ability to fill a high aspect ratio feature with a thin film material enables the fabrication of many nanoscale devices. Examples include shallow trench isolation or inter-metal dielectric in microelectronics. One approach is to use chemical vapor deposition under conformal coating conditions. However, as film builds up on the sidewalls the width of the feature shrinks and the aspect ratio increases sharply. This often results in incomplete filling, leaving a narrow void or 'seam' of low-density material along the central axis. One solution is to taper the feature into a 'V' shape, such that uniform deposition causes the apex of the V to move smoothly upwards.

To achieve complete filling, the flux of deposition precursor down the axis of the feature must be sufficient to maintain a uniform growth rate. Precursor transport is typically modeled using the diffusion equation under quasi-static conditions. We show that for high aspect ratio features, *the diffusion equation significantly under-estimates the flux of material that is deposited deep in the feature*. This occurs because the diffusion formalism assumes a mean transport distance between collisions that is proportional to the feature size. However, in molecular flow some of the transport events occur at glancing angles to the feature sidewall and afford very long flight paths. These events move precursor species to the bottom of the feature, an effect that enhances filling.

We have developed a ballistic transport model based on computing the emission/capture probability between all points on the surface and coding the result as a matrix. Species transport from a starting distribution is found by matrix multiplication to afford the distribution of final positions. We first show how the results of this model compare with the diffusion formalism: the bulk of the transport is similar, but the ballistic model predicts a 'tail' of long-range events. We then simulate the filling of V-shaped features as a function of the apex angle and sticking coefficient. The result is a prediction of regimes that can afford complete filling.

Finally, we consider the effect of growth rate saturation under high precursor flux, an effect that is physically significant and vastly improves conformal growth. We derive from the ballistic model the total flux arriving at each position, and self-consistently calculate the effective sticking probability. We simulate the coating profiles on rectangular and V-shaped features and determine that rate-saturated growth conditions, in combination with long-range precursor transport, greatly expand the regime that affords complete filling.

9:40am **TF+PS-ThM6 Ozone Pretreatment's Effect on Infiltration of Carbon Nanotube Forests**, ***Richard Vanfleet***, *L. Barrett, J. Rowley, K. Hinton, R.C. Davis, D.D. Allred*, Brigham Young University

Thin films deposited on carbon nanotubes (CNTs) appear to be enabling materials for a variety of applications including: capacitive and electrochemical energy storage, chromatography and filtration chemical separations media, chemical sensing, and MEMS. Using CNT forests as a

substrate creates new challenges to traditional thin film deposition techniques because of the need to penetrate into the forest and the chemical inertness of the CNT surface. We have explored the effect ozone pretreatment has on film morphology in two different deposition regimes: amorphous silicon deposited by low pressure chemical vapor deposition and nickel deposited by electroplating. TEM and SEM images of the forests after deposition show increased nucleation density on forests that were pretreated with ozone.

11:00am **TF+PS-ThM10 A Novel Gap Fill Technology to Address the Current and Future Scaling Challenges of the Semiconductor Industry**, *A. Mallick, **Jingmei Liang**, B. Underwood, K. Thadani, N. Ingle, T. Mandrekar*, Applied Materials Inc.

Gap fill has been a continuous challenge for the semiconductor industry driving innovation in the field of chemical vapor deposition. Applied Materials has continuously met this challenge by developing and refining CVD technologies to address the challenges of void-free gap fill in features of narrowing opening dimension and increasing aspect ratio. Technologies including Applied's HARP™ sub-atmospheric CVD and Ultima™ high density plasma established themselves as workhorses of the semiconductor industry. These technologies enabled dielectric materials including silicon dioxide, nitrides, carbides, and carbon in narrow gap. While these technologies see continued use in the manufacture of Logic and Memory device at <20nm node and below, gap fill of the narrowest and highest aspect ratio features required a new technical approach. As structure CD drops below 30nm, the sidewall angle approaches or exceeds 90° presenting a shape that promotes void or seam formation with conventional gap fill approaches including CVD and ALD.

To address these challenges Applied Materials has developed a new CVD technology we call FCVD™ to enable synthesis of high quality dielectric films including silicon oxides, silicon nitrides, silicon carbo-nitrides, silicon, low-k dielectrics, and carbon with a mechanism of film growth that promotes void-free fill irrespective of structure dimension and shape; this technology demonstrates capability to fill re-entrant structures with opening size <5nm and aspect ratio >20, flexibility to address multiple material systems and has been productized to address volume manufacturing requirements. In this paper we will demonstrate that we can achieve a void-free, profile-insensitive gap fill with multiple materials in a CVD reactor.

11:20am **TF+PS-ThM11 Comparison of Carbonaceous Thin Films Deposited on Ru-capped Multilayer Mirrors via Extreme-Ultraviolet Light and Electrons**, ***Michael Barclay***, Johns Hopkins University, *N.S. Faradzhev, S.B. Hill, T.B. Lucatorto,* National Institute of Standards and Technology (NIST), *D.H. Fairbrother*, Johns Hopkins University

This presentation focuses on comparing growth characteristics of carbonaceous thin films produced by irradiation of Ru-capped multilayer surfaces with either extreme-ultraviolet light or electrons in the presence of hydrocarbon vapors. This work is motivated by the likelihood that extreme-ultraviolet lithography (EUVL) will be the next step in improving chip production for the semiconductor industry. Using a shorter (13.5 nm) wavelength of light, manufacturers can mass-produce microchips with feature sizes (< 10nm) that are impossible to achieve with current lithographic techniques. Since all materials strongly absorb 13.5 nm light, EUVL must be carried out under vacuum. Ultimately, this makes certain that the delicate multilayer optics and chemical photoresists, used in the EUVL process, cannot be completely isolated from one another. As a corollary, volatile organics released from resist-outgassing have the ability to be deposited via EUV- induced reactions, resulting in degradation of the multilayer optics. To protect the delicate optics, industry has established a resist-outgas testing protocol to determine the outgas-contamination risk of each resist before introducing it to the EUVL tool. This qualification procedure determines a resist's rate of contamination as well as the cleanability of its outgas products. Unfortunately, a key component of this protocol is the use of a dedicated, bright, EUV source. To mitigate the large capital investment necessary for such a source, electron beams are often used as a proxy. It is therefore important to correlate the carbon deposition processes induced by electron and EUV irradiation. To this end, we have exposed Ru-capped multilayer optics to both electron and EUV irradiation in the presence of admitted hydrocarbon vapors of two model species: benzene and tetradecane. Multiple exposures were performed with varying doses of EUV and electron irradiation for various hydrocarbon partial pressures; then subsequently characterized using scanning X-Ray Photoelectron Spectroscopy and small-spot spectroscopic ellipsometry. Electron exposures utilized the electron beam from a Perkin-Elmer 10-155 Cylindrical-Auger Electron Optics System; calibrated and characterized using a ThorLabs DCC1645c camera in conjunction with a Ce:YAG scintillator. EUV exposures utilized the Synchrotron Ultraviolet Radiation Facility at NIST. We find that the carbon growth rates for both exposure methods have sub-linear pressure dependence at low irradiance which transitions to linear scaling at higher irradiance. The growth rates at which this transition occurs, however, are different for EUV and e-beam irradiation.

11:40am **TF+PS-ThM12 Production and Characterization of Thin Film Group IIIB, IVB and Rare Earth Hydrides by Reactive Evaporation**, ***James Provo***, J.L. Provo Consulting

A recent short history of reactive evaporation by Mattox (1) described various methods for producing oxides, nitrides, carbides, and some compound materials using this special process. However, no mention was made producing hydrides using this method. A study was performed in the mid 1970's at the General Electric Company (GE) Neutron Devices Department (GEND) in Largo, FL, by the author to study preparation of thin film hydrides using reactive evaporation and to determine their unique characteristics and properties.

Films were produced of scandium (Sc), yttrium (Y), titanium (Ti), zirconium (Zr), and the rare earth praseodymium (Pr), neodymium (Nd), gadolinium (Gd), dysprosium (Dy) and erbium(Er) hydrides by hot crucible filament evaporation in atmospheres of deuterium and tritium gas. All metal vacuum systems were used and dedicated for this special processing. Thin film test samples ~ 5,000Å thick were prepared on half-inch diameter molybdenum disk substrates for each occluder material.

Loading characteristics (i.e., gas –to-metal atomic ratios), oxidation characteristics, film structure, and stress properties were determined and showed near maximum gas-to-metal atomic ratios, variable oxidation properties, platelet type film structures and minimum film stress levels as determined by a double resonator technique. Also, stress aging characteristics were determined for some hydride films prepared in a radioactive tritium gas atmosphere.

The timeless data obtained showed gas-to-metal atomic ratios varied from 1.8 to 2.0, surface oxide levels varied from ~ 80Å to over 1,000Å, and initial normalized differential (tensile) stress levels were (1.0 to 4.0) x 10^8 dyne/cm^2 for tritium loaded samples and (1.0 to 2.0) x 10^9 dyne/cm^2 for deuterium loaded samples. Tritium loading, however, had the undesirable characteristic of having to dispose of the internal processing system fixtures, but the method generally produced desirable thin films.

† Formerly, Principal Member of the Technical Staff at Sandia National Laboratories,

Albuquerque, NM (Retired).

(1) Mattox, D.M., "History Corner- A Short History of Reactive Evaporation", SVC Bulletin, p.50 –

51, Spring 2014.

12:00pm **TF+PS-ThM13 Cathodic Cage Plasma Deposition of TiN and TiO_2 Thin Films on Silicon Substrate**, *R.R.M. de Sousa,* IFPI, Brazil, *P.S. Sato,* UFSCar, Brazil, *B.C. Viana,* UFPI, Brazil, *C. Alves Jr,* UFRSA, Brazil, *A. Nishimoto,* Kansai University, Japan, ***Pedro Nascente***, UFSCar, Brazil

A new technique called cathodic cage plasma deposition (CCPD) was used for growing TiN and TiO_2 films on silicon substrate. In this technique, the samples are positioned inside a cage having uniformly distributed round holes with fixed diameter, and onto an alumina insulator disk, so that the plasma acts on the cage and not on the sample surface, eliminating possible defects usually formed during the conventional plasma deposition. The CCPD technique produces films with high uniformity and permits a good control of roughness and crystallinity. The main advantages of this technique are the uniformity, tri-dimensionality, and high rate of deposition of the deposited films, as well as low cost of production.

TiN coatings increase the surface hardness and decrease the friction coefficient, thus enhancing the lifetime of components and tools employed in the metalworking industries. Thin films of TiO_2 have attracted considerable attention because of different applications on many fields due to their unique properties, such as chemical stability, no toxicity, low cost, high refraction index, high permittivity, wide valence band, etc. The TiO_2 main crystalline phases are: anatase, brookite, and rutile. The TiO_2 thin films can have a mixture of these phases showing hybrid properties. Many studies have focused on relationship of the different phases as dependent of the deposition method and parameters. Each one of these phases has its own characteristic properties, leading to different applications.

In this work, the influence of the parameters (temperature and gas atmosphere) in the characteristics of the deposited films was investigated. The TiN and TiO_2 thin films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy in order to identify their crystalline phases and estimate their thicknesses. The combination of XRD and Raman spectroscopy results indicates that only a TiN crystalline phase was detected for the TiN films, and mainly the anastase phase was detected for the TiO_2 film. High crystallinity and uniformity of the films were observed by XRD, Raman, and SEM,

confirming that this low cost technique is effective in producing high quality TiN and TiO_2 films.

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