

Thin Film Division

Room: 109 - Session TF1-ThM

Post-Deposition Processing and Characterization of Thin Films

Moderator: C. Vallée, LTM/CNRS-UJF, France

8:00am **TF1-ThM1 Protrusions, Surface Grains and Extended Single-Crystalline Plates**, A. González González, Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Spain, G.M. Alonzo Medina, A.I. Oliva, Centro de Investigaciones y de Estudios Avanzados del IPN, CINVESTAV Unidad de Mérida, Mexico, C. Polop, Universidad Autónoma de Madrid, Facultad de Ciencias, Spain, E. Rodríguez Cañas, J.L. Sacedón, E. Vasco, Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Spain

The processes controlling shape transformations during post-deposition treatments attract great interest due to their technological implications. As an example, residual stress relaxation during thermal annealing could influence component lifetime and performance in applications ranging from microelectronics to mechanical coatings, affecting their functional properties [1]. In this work, we investigate the morphology evolution during thermal annealing at $0.2 T_{\text{melting}}$ in polycrystalline Au(111) films using atomic force [scanning electron] (AFM [SEM]) microscopies and x-ray diffraction in order to follow both shape and structural transformations of surface features for different annealing times. Before annealing, a high density of round-like surface grains—which are surface components of an underlying competitive columnar microstructure—is observed. During annealing, surface grains merge together into “multigrain” structures that expand laterally up to a saturation size, suggesting a size-dependent phenomenon controlling surface recrystallization. By comparison with Au polycrystalline growth fronts for the same temperature range [2] (T zone of the zone models [1]), we can relate the annealing-generated multigrain structures to the incipient formation of extended sub-micrometric-sized plates that are observed for thinner films. They contain many small surface grains with low-angle or no inner grain boundaries [2]. The small amount of material to be recrystallized for each component favors the multi-component extension of recrystallized zone. Interestingly, results here reported concerning the recrystallization phenomenon are discussed on the basis of local interactions between surface grains triggering plausible elastic/plastic mechanisms of stress accommodation (grain zipping and shear strain) and relaxation by surface diffusion processes [1,3], which in principle seems not to be very different from those expected in the coalescence stage at the T zone.

[1] L. B. Freund and S. Suresh, *Thin Film Materials: Stress, Defect Formation and Surface Evolution* (Cambridge University Press, Cambridge, England, 2003) and references therein.

[2] C. Munuera *et al.*, *J. Vac. Sci. Technol. A* **22**, 1767 (2004)

[3] A. González-González *et al.*, “*Morphology evolution of thermally annealed polycrystalline thin films*” (submitted)

8:20am **TF1-ThM2 Characterization of Mg Acceptors in GaN:Mg Grown by Metal Modulated Epitaxy and MOCVD**, J.E. Lowder, M.W. Moseley, B. Gunning, W.A. Doolittle, Georgia Institute of Technology, M.E. Zvanut, J. Dashdorj, University of Alabama

Acceptor doping of III-Nitrides has been the subject of many studies due to the relatively low hole concentration ($\sim 10^{17}$ - 10^{18} cm⁻³) material commonly grown in contemporary devices. This limitation is thought to be one of the contributing factors to efficiency droop in LED's. Recently, extremely high hole concentration ($p > 4 \times 10^{19}$ cm⁻³) material with very high (>50%) ionization efficiency (see Fig. 1) has been demonstrated by metal modulated epitaxy (MME), an application of MBE where surface chemistry is controlled via shuttering of the source material [J. Appl. Phys. 106, 014905]. The samples in this study are characterized by temperature dependent Hall measurement to elucidate the reduction in the acceptor activation energy. Electron paramagnetic resonance spectroscopy (EPR) was used to show the microscopic view of the Mg acceptor without influence of the surrounding crystal as well as the effect of annealing temperature on the EPR signal. It is found that the primary transport mechanism is likely due to impurity band conduction, consistent with a distributed acceptor band as opposed to an isolated acceptor energy level as is generally observed in p-type GaN. Likewise, the interaction of the Mg with hydrogen shows different annealing behavior when compared to MOCVD p-type GaN.

The samples analyzed by EPR were annealed at various temperatures in forming gas (H₂:N₂). Fig. 2 shows the relative intensity from the EPR signal of the neutral Mg acceptor as a function of forming gas anneal temperature. It is clear that there is a sharp decrease in signal for the MME grown samples (doped $> 10^{20}$ Mg as seen in fig. 1) at 525 °C as compared to the drop observed at 750 °C for the MOCVD grown samples (doped $\sim 10^{19}$ Mg). The exact nature of this temperature dependent decrease in signal is not fully understood, however it is suggested the different growth kinetics and resulting surface leads to a change in H₂ transport. A second mechanism may be the formation of Mg-H complexes with varying activation energies.

Preliminary temperature dependent Hall results (Fig. 3) show an as-grown activation energy of 70 meV in the MME samples as well as 5×10^{18} cm⁻³ holes remaining at cryogenic temperatures. This extremely low activation energy and lack of carrier freeze out is evidence of impurity band conduction and shows the degenerative nature of the material. The full effect of the annealing temperature on this degenerative material will be presented in further detail as it pertains to device processing.

8:40am **TF1-ThM3 Post Deposition Annealing Effects on Thin Film Material, Process, and Device Properties**, Y. Kuo, Texas A&M University **INVITED**

Thermal annealing is a critical but often neglected step in semiconductor production. It has been routinely used to activate the ion implanted dopant and at the same time, to restore the single crystal structure. However, it is also a powerful tool in repairing damages in bulk films as well as at film-film interfaces, which are caused by the plasma-related deposition or etching process. In addition, the thermal annealing step can change film characteristics, which affects the subsequent process result. In this talk, the author will review some of his recent work related to thermal annealing, which involves three types of solid-state devices and thin films. First, an example on repairing the RIE damaged a-Si:H TFT with a low temperature thermal annealing process will be given. This step reduced defects in the bulk a-Si:H and SiNx layers as well as at the gate-dielectric interface. This result has been interpreted in all TFT LCD productions around the world. In the second example, it will be shown that the thermal annealing step changed the grain size of the sputter deposited copper thin film. It resulted in the change of the copper-Cl reaction mechanism and therefore, the copper consumption rate. This is critical to a new plasma-based copper etch process that has been interpreted in large-area TFT LCDs and BiCMOS chips. In the third example, it will be shown that the post deposition annealing (PDA) condition is the key to the realization of a new type of nonvolatile memory device, i.e., the nanocrystals embedded high-k capacitors or MOSFETs. Furthermore, an additional low temperature annealing step removed the defects generated in the gate and back-contact sputtering processes. In summary, the thermal annealing effects are non-negligible because they are directly involved in product reliability and yield.

(1) Y. Kuo, “TFT and ULSIC – Competition or Collaboration,” *Jpn. J. Appl. Phys.*, **47**(3), 1845-1852 (2007).

(2) G. Liu, Y. Kuo, S. Ahmed, D. N. Buckley, and T. Tanaka-Ahmed, “Grain Size Effect on Plasma-based Copper Etch Process,” *J. Electrochem. Soc.*, **155**(6) H432-H437 (2008).

(3) Y. Kuo, “Status Review of Nanocrystals Embedded High-K Nonvolatile Memories,” *ECS Trans.* **35**(3), 13-31(2011).

9:20am **TF1-ThM5 Semiconductor Thin Film Metrology using Coherent Acoustic Phonon Spectroscopy**, A.D. Steigerwald, K. Varga, A.B. Hmelo, Vanderbilt University, L. Feldman, Rutgers University, N.H. Tolk, Vanderbilt University

Here we discuss the use of coherent acoustic phonon spectroscopy as a noninvasive and nondestructive measurement tool for semiconductor thin films. Specifically we emphasize its usefulness in studying the optoelectronic structure of materials with various types of structural defects. We discuss in-depth studies of ion-implanted GaAs, demonstrating that the technique may be used to quantitatively determine depth profiles of lattice disorder. Our optoacoustic measurements are shown to be 2-3 orders of magnitude more sensitive in defect concentration than channeling techniques, and establish a quantitative dependence between the change in optical response and defect concentration between 10^{18} - 10^{21} defects/cm³. Further, we demonstrate the entire range over which the coherent acoustic phonon technique is applicable in defect studies, and show results ranging from no noticeable change in optical response to complete damping of the phonon wave. We also discuss the electronic nature of the CAP response, which can provide insight into the interplay between lattice disorder and electronic structure.

9:40am **TF1-ThM6 On the Phase Formation of Reactively Sputtered ZrO₂ Thin Films**, *R. Snyders, G. Geumez, S. Konstantinidis*, UMons, Belgium

ZrO₂ is a material used as thin films in numerous applications. One of the applications with the highest added value is its use as ionic conductor in, for example, fuel cell devices. Nevertheless, only the tetragonal and cubic polymorphs of ZrO₂ exhibit these ionic conduction properties. Therefore, effort have to be made in order to synthesis phase pure tetragonal or, ideally, cubic ZrO₂ thin films. It has been demonstrated that these polymorphs are generated when about 10% of oxygen vacancies are introduced in the material lattice. Recently, some works have demonstrated that it was possible to synthesize, by reactive high power impulse magnetron sputtering, cubic HfO₂ (a compound very close to ZrO₂) containing, as for cubic ZrO₂, 5% of oxygen vacancies when working in the transition region of the poisoning curve. This implementation of this strategy was possible thanks to the smoothness of this transition using this peculiar sputtering technology.

In this work, we aim to apply such a strategy to grow tetragonal (or cubic) ZrO₂ by reactive DC magnetron sputtering. Due to the very sharp metallic-to-poisoned mode transition, we used a plasma monitoring system (PEM) to work in stable conditions in that region.

A pure Zr metallic target is sputtered at constant current (0.2 A) at 10 mTorr in Ar/O₂ mixtures using a DC magnetron sputtering source with an unbalanced magnetic field configuration. A PEM system is implemented in order to grow films in the transition region. The Zr line at 340 nm is monitored in real time. The deposited films were characterized by grazing angle X-Ray diffraction (GAXRD) and X-Ray photoelectron spectroscopy (XPS).

Discharge parameters (voltage, current) and XPS data reveal that the transition occurs for 4% < %O₂ < 6%. For %O₂ < 4%, the films are under-stoichiometric with a metallic character. In the transition, we measure a stoichiometry of about ZrO_{1.8}. Finally, %O₂ > 6%, the films are stoichiometric. In term of phase constitution, it has been demonstrated that working in the poisoned mode, the monoclinic phase is synthesized while in the transition, for which the compound is under-stoichiometric, the tetragonal (and maybe cubic) phase is grown. These data support, for the first time, the theoretical assumption about the oxygen vacancies-generated tetragonal (or cubic) phase of ZrO₂. Finally, the thermal stability of the coatings has been studied: the as-grown samples have been annealed up to 1200°C. For annealing temperature up to 600°C, no modification of the phase constitution is observed while for an annealing temperature of 1200°C, the films experience a phase transition towards the monoclinic structure.

10:40am **TF1-ThM9 Effect of 10 keV X-rays on Silicon Oxidation**, *S. Bhandaru, S.M. Weiss, E.X. Zhang, D.M. Fleetwood, R.A. Reed, R.A. Weller, B.R. Rogers, R.R. Harl*, Vanderbilt University

In the past few decades, studies have been conducted to investigate photon assisted oxidation of silicon substrates. Most of these efforts have focused on understanding and modeling the oxide growth mechanism using photon energies spanning the visible (1.55 eV – 3.0 eV) to the UV range (3.0 eV – 6.5 eV). In this work, we study the influence of higher energy x-rays (10 keV) on silicon oxidation. We found that x-ray irradiation of silicon substrates, performed at ambient temperature and atmospheric pressure conditions, can significantly affect the formation of silicon oxide. The oxide formation is influenced by the dose rate and total dose of x-ray irradiation, as well as the initial silicon surface preparation.

Boron doped silicon samples (0.01 Ω-cm - 0.02 Ω-cm) were irradiated at dose rates ranging from 5.8 krad(SiO₂)/min to 31.5 krad(SiO₂)/min using a 10 keV x-ray source (ARACOR Model 4100). The samples were cleaned in dilute HF acid to remove the initial native oxide and obtain a clean surface prior to irradiation. The resulting silicon oxide thickness was estimated using spectroscopic ellipsometry (J. A. Woolam M-2000). Different models for the optical properties of the surface layer were evaluated. Oxide growth on the irradiated samples was compared to oxide growth on control samples, which were placed in ambient air at room temperature. The ellipsometry analyses suggest that the oxide growth on the irradiated samples was greater than that on the control samples. Initial XPS analysis showed that the oxide layers on the irradiated and control samples were chemically different, suggesting that differences observed in the ellipsometry analyses may be due, in part, to differences in the optical properties of the oxide layers and not purely due to a change in thickness.

We will present the results of the oxidation study in addition to XPS and AES characterization of the resulting oxide films. The impact of heating the silicon substrate up to 150°C during x-ray irradiation will also be discussed. A mechanism to explain the experimental observations is proposed based

on ozone concentration measurements performed during irradiation. The possible generation of atomic oxygen, due to dissociation of molecular oxygen, by the high energy x-rays is suggested as a key factor in the observed x-ray irradiation induced silicon oxidation.

Acknowledgement: This work was supported in part by the DTRA Basic Research Program (Grant No. HDTRA1-10-0041).

11:00am **TF1-ThM10 Investigating the Local Physical Structure of Amorphous Hydrogenated Boron Carbide**, *M.M. Paquette, W. Li, M.S. Driver, S. Karki, N.A. Olyer, A.N. Caruso*, University of Missouri - Kansas City

The unique physical structure of boron-rich carbides, based on an extended molecular network of covalently bound icosahedral cages, has distinguished this material with an exceptional set of thermal, electrical, and mechanical properties. Technologically, boron carbide has generated interest for applications in solid-state neutron detectors, interlayer low-*k* dielectrics for ultra-large-scale integrated circuits, and high-temperature thermoelectric power converters. A method that has proven amenable to thin-film heterostructure device fabrication is the plasma-enhanced chemical vapor deposition (PECVD) of high-resistivity amorphous hydrogenated boron carbide (a-B_xC:H_y; *x* ≈ 2–5) from the single-source precursor orthocarbonane (C₂B₁₀H₁₂). However, although the physical structure of bulk crystalline boron carbide (e.g., B₄3C) is nowadays well-understood, the short-range physical structure of the hydrogenated material (e.g., the number and types of atoms/bonds) has remained unsatisfactorily characterized, likewise for the intermediate-range physical structure of the amorphous lattice (e.g., how molecular subunits are bound together and arranged on a short sub-nm length scale)—structural modifications which have important consequences on the properties of the a-B_xC:H_y films. Herein, we investigate the short- and intermediate-range physical structure of a-B_xC:H_y films using solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) and Fourier transform infrared (FTIR) spectroscopies, backed by density functional theory (DFT) molecular structure calculations. The comparison of experimentally observed spectral features with theoretical predictions for model molecular compounds provides valuable insight into the different local chemical environments and intermediate-range networks that make up the a-B_xC:H_y films. We demonstrate how applying these combined analyses provides an important stepping stone to understanding and optimizing the chemical, electrical, and mechanical properties of a-B_xC:H_y films for next-generation device fabrication.

11:20am **TF1-ThM11 Characterization of Amorphous and Nanocomposite Nb-Si-C Thin Films Deposited by dc-Magnetron Sputtering**, *N. Nedfors*, Uppsala University, Sweden, *O. Tengstrand*, Linköping University, Sweden, *A. Flink*, Impact Coatings AB, Sweden, *A.M. Andersson*, ABB AB, Corporate Research, Sweden, *P. Eklund, L. Hultman*, Linköping University, Sweden, *U. Jansson*, Uppsala University, Sweden

Thin films of Me-Si-C (Me = early transition metal) have interesting multifunctional properties, see, e.g., [1]. We have in the present study investigated thin films in the Nb-Si-C system deposited by dc-magnetron sputtering using elemental targets. The microstructure and composition of the films have been characterized with x-ray diffraction, x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy. Nanoindentation and atomic force microscopy were used to investigate the mechanical properties of the thin films while the electrical contact resistance was measured using a four wire set-up with an Au-coated probe pressed against the film surface.

Our results show that films with a silicon content less than 20 at.% exhibit a nanocomposite (nc-NbC/a-SiC) structure with nanocrystalline NbC grains embedded in an amorphous matrix phase. The size of the carbide grains decrease with the carbon content increase. A transition to a completely amorphous structure occurs with a Si content above 20 at.%. The transition in microstructure is reflected in the properties of the films with an abrupt increase in contact resistance (from 30 mΩ to 200 mΩ at 1 N) and a change in the mechanical behavior of the thin films. The XPS spectra show a change of chemical bonding from mainly C-Nb to a significant amount C-Si bonds as the Si and C content increase in the films. This results in harder films and an increase in the electrical resistivity. The amorphous films can be described as a metal carbide-based glass and the formation of this type of structures in sputtered Me-Si-C films will be discussed.

[1] J. Lauridsen et al., *Surf. Coat. Technol.*, 205, 299-305, 2010

11:40am **TF1-ThM12 Evaluation of Mn-based Cu Barriers for Interconnect Applications**, *E. Van Besien, N. Jourdan*, IMEC, Belgium, *L. Zhao*, Intel assignee at IMEC, Belgium, *K. Croes, Y.K. Siew, S. Van Elshocht, Zs. Tökei*, IMEC, Belgium

Diffusion barrier layers with a uniform thickness and good step coverage in narrow lines are needed to enable the continuing scaling of Cu interconnects. Since physical vapor deposition (PVD) processes have limitations in respect of conformality, atomic layer deposition (ALD) and chemical vapor deposition (CVD) might become the preferred alternatives. Among others, Mn-based CVD barriers have been proposed [1], but up to now, Cu barrier properties for such films have not been proven electrically.

In this study, MnOx layers were deposited by CVD, on top of an O3/TEOS SiO2 layer. Deposition was done at two different temperatures: 200 °C and 350 °C. The effect of a post-plating anneal of one hour at 300 °C or 430 °C was studied. A test structure based on planar capacitors was used, in which first wide areas were patterned, followed by the deposition of the oxide and CVD MnOx layers, metallization, and CMP, respectively [2]. After passivation, voltage ramp (at 25 °C and 100 °C) and TDDB measurements (at 100 °C) were conducted. The electrical data were compared with those from a known good TaN/Ta-barrier reference system.

Voltage ramp measurements at 25 °C show a similar behaviour for all Mn-based films under study, except for the one deposited at 350 °C, with a post-plating anneal at 430 °C. For the latter a leakage current of about 1 order of magnitude lower is found, comparable to the leakage current of our TaN/Ta reference. For the film deposited at 200 °C, and annealed at 430 °C, voltage ramp measurements only showed shorts.

TDDB lifetimes were in all cases higher than for a reference without barrier, but lower than for a TaN/Ta reference. For the Mn-based films deposited at 350 °C, a post-plating anneal at 430 °C clearly improved the reliability properties. In this case, the extrapolated lifetime at user conditions (using the E-model), is above 10 years. A γ value of -3.4 cm/MV was found. However, for the films deposited at 200 °C, an anneal at 300 °C already degraded the reliability properties.

In conclusion, voltage ramp and TDDB measurements on planar capacitors structures show that, with optimised processing, CVD Mn-based barriers are promising candidates as Cu barriers in advanced interconnects.

[1] K. Neishi, S. Aki, K. Matsumoto, H. Sato, H. Itoh, S. Hosaka, J. Koike, *Appl. Phys. Lett.* 93 (2008) 032106

[2] L. Zhao, Zs. Tökei, G. Giari Gischia, M. Pantouvaki, K. Croes, G. Beyer, *IEEE International Reliability Physics Symposium*, 2009, 848-850

Authors Index

Bold page numbers indicate the presenter

— A —

Alonzo Medina, G.M.: TF1-ThM1, 1
Andersson, A.M.: TF1-ThM11, 2

— B —

Bhandaru, S.: TF1-ThM9, 2

— C —

Caruso, A.N.: TF1-ThM10, 2
Croes, K.: TF1-ThM12, 3

— D —

Dashdorj, J.: TF1-ThM2, 1
Doolittle, W.A.: TF1-ThM2, 1
Driver, M.S.: TF1-ThM10, 2

— E —

Eklund, P.: TF1-ThM11, 2

— F —

Feldman, L.: TF1-ThM5, 1
Fleetwood, D.M.: TF1-ThM9, 2
Flink, A.: TF1-ThM11, 2

— G —

Geumez, G.: TF1-ThM6, 2
González González, A.: TF1-ThM1, 1
Gunning, B.: TF1-ThM2, 1

— H —

Harl, R.R.: TF1-ThM9, 2

Hmelo, A.B.: TF1-ThM5, 1
Hultman, L.: TF1-ThM11, 2

— J —

Jansson, U.: TF1-ThM11, 2
Jourdan, N.: TF1-ThM12, 3

— K —

Karki, S.: TF1-ThM10, 2
Konstantinidis, S.: TF1-ThM6, 2
Kuo, Y.: TF1-ThM3, 1

— L —

Li, W.: TF1-ThM10, 2
Lowder, J.E.: TF1-ThM2, 1

— M —

Moseley, M.W.: TF1-ThM2, 1

— N —

Nedfors, N.: TF1-ThM11, 2

— O —

Oliva, A.I.: TF1-ThM1, 1
Oyler, N.A.: TF1-ThM10, 2

— P —

Paquette, M.M.: TF1-ThM10, 2
Polop, C.: TF1-ThM1, 1

— R —

Reed, R.A.: TF1-ThM9, 2

Rodríguez Cañas, E.: TF1-ThM1, 1
Rogers, B.R.: TF1-ThM9, 2

— S —

Sacedón, J.L.: TF1-ThM1, 1
Siew, Y.K.: TF1-ThM12, 3
Snyders, R.: TF1-ThM6, 2
Steigerwald, A.D.: TF1-ThM5, 1

— T —

Tengstrand, O.: TF1-ThM11, 2
Tókei, Zs.: TF1-ThM12, 3
Tolk, N.H.: TF1-ThM5, 1

— V —

Van Besien, E.: TF1-ThM12, 3
Van Elshocht, S.: TF1-ThM12, 3
Varga, K.: TF1-ThM5, 1
Vasco, E.: TF1-ThM1, 1

— W —

Weiss, S.M.: TF1-ThM9, 2
Weller, R.A.: TF1-ThM9, 2

— Z —

Zhang, E.X.: TF1-ThM9, 2
Zhao, L.: TF1-ThM12, 3
Zvanut, M.E.: TF1-ThM2, 1