Thin Films Division
Room 615 - Session TF-ThA

Ex-situ Characterization

Moderator: J.J. Nainaparampil, Air Force Research Laboratory

2:00pm **TF-ThA1 Working Smarter with Microanalytical Tools**, ***M.J. Edgell***, Charles Evans & Associates **INVITED**

New materials development and high yield production lines are key to future generations of integrated circuits (ICs). Material and contamination characterization is therefore an integral part of the semiconductor industry. The capabilities of analytical tools are continuously improving to meet the needs of the National Technology Roadmap for Semiconductors (NTRS). The analytical improvements include electron and ion beam resolution, detector technology, and surface sensitivity. This paper reviews several ex-situ analytical tools, such as AES, RBS, SIMS, SEM, SIMS, TXRF, TOF-SIMS, XPS, used in today's high technology industries. The strengths and weaknesses of the techniques and their applications will be discussed.

2:40pm **TF-ThA3 Near Surface Chemical Dependence of Electronic States at Al-Doped TiO@sub 2@(110)Ultrathin Films**, ***S.H. Goss***, *L. Brillson,* Ohio State University*; S.A. Chambers,* Pacific Northwest National Laboratory

Impurity doping of TiO2 has important catalytic and photocatalytic applications.@footnote 1@ Al doping is known to enhance TiO2's chemical properties and is used extensively in surface coatings. We have used electron excited nanoscale luminescence spectroscopy (EENLS) to observe the dependence of electronic states with chemical composition of Al-doped TiO2 ultrathin films. Using incident electron beams of varying energy to probe depths from 150 nm below the free surface, we observe: mid-gap state emission at 1.4 eV due to Al doping, O vacancy emission at 2.5 eV, and near band edge (NBE) transitions at 3.0 eV. The 1.4 eV emission appears specifically within a 20 nm, 6% Al - doped TiO2 layer stacked on 4% and 2% doped layers, all grown epitaxially on TiO2 substrates. No 1.4 eV emission is evident for these deeper layers. Recombination involving this 1.4 eV level increases dramatically with annealing at 600 C under 5-x 10e7 L O2 treatment, while the 2.5 eV peak decreases. As mid-gap recombination increases, NBE emissions decrease strongly, indicating a pronounced decrease in free carrier concentration near the free surface. Auger electron spectroscopy (AES) shows Ti and O in correct proportion and only C contamination at the free surface. Mid-gap emission intensities show no correlation with surface C concentration which range from

3:00pm **TF-ThA4 Microstructure and EL Properties of the ZnS:Mn Luminescence Materials with Co-dopants**, ***Q. Zhai***, *K.E. Waldrip, J. Li, J.S. Lewis, K. Jones, P.H. Holloway,* University of Florida*; M. Puga-Lambers, M. Davidson,* MICROFABRITECH

ZnS:Mn thin films were deposited onto glass substrate with pre-deposited indium tin oxide (ITO) and aluminum titanium oxide (ATO) layers, using magnetron sputter source. Transmission electron microcopy (TEM) indicated that the microstructure of the as-deposited films was heavily faulted with fine columnar grains formed through most of the film and a 100nm layer of equiaxed fine grains at the ATO/ZnS:Mn interface. The electroluminescence (EL) properties of the as-deposited films were poor. Post deposition rapid thermal annealing (RTA) with and without co-dopants was studied. KCl co-doped samples showed remarkable improvement in EL brightness after an RTA of 5 min. at 700@super o@C. The threshold voltage was slightly increased. Grain growth from 80nm as-deposited to 200nm after RTA was observed, and the fine-equiaxed-grain crystal layer was removed. Energy dispersive X-ray (EDX) spectra analysis of plan-view transmission electron microscoy (PTEM) samples detected no segregation of any element. Ga@sub 2@S@sub 3@ co-doped samples had no improvement in EL brightness after 5 min. RTA at 800@super o@C, but the threshold voltage was reduced. Grain growth was less than the samples without Ga@sub 2@S@sub 3@, and the fine-equiaxed-grain layer was still visible. EDX results showed Ga segregation at grain boundaries and triple points. When both KCl and Ga@sub 2@S@sub 3@ were introduced into the films through double thermal evaporation/annealing, the sample co-doped with Ga@sub 2@S@sub 3@ at 800@super o@C followed by KCl at 700@super o@C gave the best EL results, but the properties were still inferior to the samples with only a KCl treatment. EDX on PTEM samples detected both K and Ga segregated to grain boundaries and triple points of these samples. The diffusion of co-dopants was analyzed by dynamic secondary ion mass spectrometry (SIMS). Detailed electrical properties of these samples are being studied. A correlation between EL properties and the microstructure will be presented.

3:20pm **TF-ThA5 Structural Determination of Wear Debris Generated from Sliding Wear Tests on Ceramic Coatings Using Raman Microscopy**, ***C.P. Constable***, *J. Yarwood, P. Hovsepian, L.A. Donohue, W.-D. Münz,* Sheffield Hallam University, UK

During sliding, the high pressure at the point of contact can contribute to high flash temperatures, which are not accurately measurable. The magnitude of these flash temperatures has been quoted as being up to several hundred degrees Celsius for some systems but remains a topic for debate. Tribologists interested in ceramic coatings are realising that the wear debris can bear the signature of the wear process and the composition of the debris can enable an estimate of these contact temperatures. Raman microscopy is utilised here for the identification of compounds, especially oxides, generated during the wear process to endeavour to gain a better understanding of tribochemical reactions. A series of PVD ceramic hard coatings; CrN/NbN, CrN, NbN, TiAlN/VN, TiAlCrYN and TiCN have been deposited on steel substrates using the cathodic arc/unbalanced magnetron deposition technique. Ball-on-Disk sliding wear tests against corundum were performed for all the above coatings. The debris generated were characterised using vibrational spectroscopy; namely Raman microscopy. The high spatial resolution (2µm), in-situ capability, sensitivity to structural changes and non-destructive nature make this technique ideal for the study of such small amounts of wear debris. Previous work has centred on TiN coatings. This paper attempts to broaden the discussion to include other more complex monolithic and multilayered superlattice coatings. Under dry sliding conditions of 5N normal load, 10cms@sup -1@ in ambient air (humidity ~33%) titanium based alloy coatings were found to provide TiO@sub 2@ (rutile) debris. However the addition of fine layers of VN to the TiAlN system provided lower friction coefficient, wear rate and less debris through the possible formation of a lubricious surface oxide. CrN and NbN based coatings were also found to produce debris with Raman bands corresponding to various oxides.

3:40pm **TF-ThA6 Effect of Rapid Thermal Annealing Temperature on the Formation of CoSi Studied by X-ray Photoelectron Spectroscopy and Micro Raman Spectroscopy**, ***J. Zhao***, *L. Ballast, T. Hossain, R. Trostel, B. Bridgman,* Advanced Micro Devices

Silicides are widely used on poly-Si as low resistance gate electrodes and local interconnects. Among all silicides, CoSi@sub 2@ attracts a special interest, not only because of its low resistance and its technical advantages in processing, but also its excellent match with Si. CoSi is the intermediate phase in the conversion sequence of pure Co, CoSi and CoSi@sub 2@. In this paper, we investigated the effect of rapid thermal annealing (RTA) temperature on the formation of CoSi using X-ray photoelectron spectroscopy (XPS) and micro Raman spectroscopy. With pure Co deposited on single crystalline Si wafer and capped by Ti thin film, the wafers were rapid thermal annealed at 450, 460, 470, 480 and 490@super o@C, respectively. These wafers were then stripped with SPM (H@sub 2@SO@sub 4@/H@sub 2@O@sub 2@). XPS was used to determine the chemical composition of the CoSi thin films and Auger parameter was continuously monitored along with ion sputtering to provide chemical state depth profile. XPS depth profile shows that uniform CoSi film was developed with RTA at 470@super o@C. The wafer with RTA at 450@super o@C has a pure Co layer in between the CoSi film and Ti cap. After strip, the thinnest CoSi film was observed with this wafer among the five. On the other hand, the wafer with RTA at 490@super o@C shows significant amount of Ti diffusion into the CoSi film. After strip, XPS depth profile indicates that this wafer has residue Ti on the top of CoSi surface. Micro Raman spectroscopy was used as a non-destructive method to characterize the film thickness and uniformity of the CoSi films on Si wafer. The product, @theta@d (@theta@ - absorption coefficient, d - film thickness) was calculated from both the Si excitation wavelength of 521cm@super -@ and CoSi excitation wavelengths of 206cm@super -@ and 224cm@super -@. The correlation of the measured Raman peak intensity ratio, the calculated product @theta@d and the sheet resistance of CoSi thin film were also elucidated.

4:00pm **TF-ThA7 Optical Metrology for Process Development and Control of Universal Anti-Reflective Layers**, ***J.M. Holden***, Nanometrics, Inc.*; Y. Wang, Z. Karim, K. MacWilliams,* Novellus Systems

A two-layer, inorganic anti-reflective layer (ARL) consisting of a high extinction coefficient SiO@sub x@N@sub y@ bottom layer and a low extinction coefficient SiO@sub x@N@sub y@ top layer is used as a

"Universal" ARL or UARL. The UARL is useful in damascene lithography or anywhere substrate reflectance is unknown or uncontrollable. The optical dispersions of individual films of the structure are characterized by Variable Angle Spectroscopic Ellipsometry (VASE@footnote 1@). Minimal parameter models are used to describe refractive index, n(@lambda@), and extinction coefficient, k(@lambda@), dispersions for top and bottom films. The dispersion models are implemented on a metrology tool that uses combined reflectance and spectroscopic ellipsometry (R+SE). Quantities relevant to DUV lithography, n(248 nm), k(248 nm), and thickness, t, are measured identically by VASE and R+SE methods. The metrology tool was used for process development and is applicable to process monitoring in a fab environment. Individual films are deposited as either a single film deposited on a single deposition station (static) or deposited in a multi-station, sequential deposition. The effect of interface layers in the sequentially deposited films can be detected weakly from ellipsometric data but not from reflectance. Normal incidence reflectance measurements and lithography simulations for typical DUV exposure tools indicate no significant differences between static and sequentially deposited films. @FootnoteText@ @footnote 1@VASE is a trademark of the J. A Woollum Company.

4:20pm **TF-ThA8 Temperature Dependence of Structure and Electrical Properties of Germanium-Antimony-Tellurium Thin Films**, *J. González-Hernández,* ***E. Prokhorov,*** *Y.V. Vorobiev,* Centro de Investigacion y de Estudios Avanzados del IPN, Mexico

The interest in the study of Ge:Sb:Te thin films is due to their use as optical and electrical devices materials. Both of these applications are based on structure change from amorphous to crystalline. Thus, understanding of the mechanism of crystallization in this material is important from the basic technological point of veiw. In this work we have studied the kinetics of the crystallization of Ge:Sb:Te films prepared by thermal evaporation. For that, in situ resistance and capacitance measurements during heating were used. The transformation kinetics from amorphous to crystalline phase was analyzed on the basis of the annealing behavior. The results were interpreted using Kissinger model, from which, the activation energy of the crystallization process is obtained. Using X-ray diffraction, Raman spectroscopy and optical microscope measurements, we have observed that during heating at different heating rates, crystallization of film is accompanied by Te phase segregation. The number and size of Te inclusions depend on the heating rate and film thickness. From our measurements we found that the capacitance measurements is the new highly sensitive method to control the crystallization process in the thin films. It provides additional information not obtained using other methods.

Author Index

Bold page numbers indicate presenter

— B —
Ballast, L.: TF-ThA6, 1
Bridgman, B.: TF-ThA6, 1
Brillson, L.: TF-ThA3, 1
— C —
Chambers, S.A.: TF-ThA3, 1
Constable, C.P.: TF-ThA5, **1**
— D —
Davidson, M.: TF-ThA4, 1
Donohue, L.A.: TF-ThA5, 1
— E —
Edgell, M.J.: TF-ThA1, **1**
— G —
González-Hernández, J.: TF-ThA8, 2
Goss, S.H.: TF-ThA3, **1**
— H —
Holden, J.M.: TF-ThA7, **1**
Holloway, P.H.: TF-ThA4, 1
Hossain, T.: TF-ThA6, 1
Hovsepian, P.: TF-ThA5, 1
— J —
Jones, K.: TF-ThA4, 1
— K —
Karim, Z.: TF-ThA7, 1
— L —
Lewis, J.S.: TF-ThA4, 1
Li, J.: TF-ThA4, 1
— M —
MacWilliams, K.: TF-ThA7, 1
Münz, W.-D.: TF-ThA5, 1
— P —
Prokhorov, E.: TF-ThA8, **2**
Puga-Lambers, M.: TF-ThA4, 1
— T —
Trostel, R.: TF-ThA6, 1
— V —
Vorobiev, Y.V.: TF-ThA8, 2
— W —
Waldrip, K.E.: TF-ThA4, 1
Wang, Y.: TF-ThA7, 1
— Y —
Yarwood, J.: TF-ThA5, 1
— Z —
Zhai, Q.: TF-ThA4, **1**
Zhao, J.: TF-ThA6, **1**