Thin Films
Room Naupaka Salons 4 - Session TF-WeM

Nanostructural and Surface Morphological Evolution: Experiment and Theory

Moderator: Andres De Luna Bugallo, CINVESTAV-Unidad Queretaro, Mexico

8:00am **TF-WeM-1 Nanostructure and Morphological Evolution During Thin Film Growth of Metals and Silicides Using Real-time Diagnostics**, ***Gregory Abadias**, C Furgeaud,* Institut Pprime, CNRS-Université de Poitiers, France*; B Krause,* KIT, Germany*; A Jamnig,* Institut Pprime, CNRS-Université de Poitiers and IFM Linköping University, Sweden*; K Sarakinos,* Linköping University, Sweden*; J Colin, L Simonot, A Michel, C Mastail,* Institut Pprime, CNRS-Université de Poitiers, France **INVITED**

Thin metallic films deposited on Si are still largely used in many technological areas, such as microelectronics, catalysis, architectural glazing or plasmonics. In the case of high-mobility metals on weakly interacting substrates (e.g. Ag on SiO_2), the growth proceeds in a 3D fashion, known as Volmer-Weber. The control of islands size and shape at the beginning of growth is vital for many applications as the characteristic length scales and physical attributes of ultrathin films are mostly set-in during the coalescence stage.

By employing a panel of *in situ* and real-time diagnostics, we could obtain valuable insights on the thin film growth dynamics, as well as stress evolution, in a variety of sputter-deposited metallic systems (Ag, Cu, Au, Pd and Mo). More particularly, the characteristic thickness of film percolation and film continuity can be determined from a combination of real-time electrical resistivity and wafer curvature measurements. This will be highlighted for the case of Ag and Cu deposited on amorphous carbon as a function of deposition rate F and deposition temperature T_s.

We will also provide examples on how chemical alloying or interface reactivity can affect the growth morphology and stress evolution of Ag and Cu films. Growth monitoring was performed *in situ* by employing either surface differential reflectance spectroscopy or spectroscopic ellipsometry. We will show that strategies based on interfacial or alloying design can be efficiently employed to manipulate growth and obtain ultra-thin, ultra-smooth, continuous layers.

Finally, we will discuss the case of silicide formation during growth of metal layers with lower adatom mobility (e.g. Mo) on silicon. By coupling simultaneously X-ray diffraction, X-ray reflectivity and wafer curvature during sputter-deposition of metal layers on amorphous Si, information about thickness-dependent crystalline phases, texture, grain growth and microstrain can be gained. This will be demonstrated for Mo/Si and Pd/Si systems. A complex nanostructure formation is uncovered from these synchrotron studies, pointing out to different silicide formation mechanisms and subsequent structural development.

8:40am **TF-WeM-3 Seeding and Growth of Metallic Ultra-thin Film Deposited on Amorphous Polymeric Substrates**, ***Jitesh Hora**, D Evans, E Charrault, P Murphy,* Future Industries Institute, University of South Australia, Australia

Abstract: In order to add a new functionality to materials**,** applying thin film coatings is among one of a feasible route. Ultra-thin films deposited by physical vapor deposition techniques on plastic substrates have found significant roles in a variety of industrial applications like in electronics, automotive, etc. [1] This is due to their attractive properties such as high electrical conductivity and transparency, light weight, mechanical flexibility and so forth.[1] There are challenges involved for deposition of a film on polymers, like limitation related to the deposition temperature, due to the low thermal stability of the polymers and to control the formation of cracks on coating due to mechanical stress and environmental effects like the effect of humidity and moisture uptake [2]. In order to overcome the challenges, also to minimise the material use and to get the same functionality as that from thick film, there is a fundamental need to understand the seeding and growth of films deposited by physical vapour deposition technique on different polymeric substrates (stiff and flexible) by exploring the effect of compliance of substrates. This research work aims to understand the structure-property relationships of an ultra-thin film (UTF) on different amorphous polymeric materials. Investigating the structure-property relationships of these advanced materials will lead to an understanding of the link between the growth and seeding with the effect of substrates nature and its effect on composite material properties. In this work, we present the effect of amorphous polymeric substrate mechanical properties on seeding and growth of ultra-thin metallic film deposited using magnetron sputtering, (DC) technique. When same material is deposited under similar conditions on different compliant polymeric substrates we observed different coating growth morphology.

Acknowledgments

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This work was performed in part at the South Australian node of the Australian National Fabrication Facility under the National Collaborative Research Infrastructure Strategy.

References

[1]. J. Hora, C. Hall, D. Evans, and E. Charrault, (2017), Inorganic Thin Film Deposition and Application on Organic Polymer Substrates. Advanced Engineering Materials, 2017.1700868.

[2]. N. Bradley, J. Hora, C. Hall, D. Evans, P. Murphy, and E. Charrault, Influence of post-deposition moisture uptake in polycarbonate on thin film's residual stress short-term evolution. Surface and Coatings Technology, 2016. 294: p. 210-214.

9:00am **TF-WeM-4 *In situ* Studies of Surface Morphological Evolution During Indium Nitride Growth by Atomic Layer Epitaxy**, ***Charles Eddy, Jr.**, N Nepal, S Rosenberg,* U.S. Naval Research Laboratory*; V Anderson,* Sotera Defense Solutions*; J Woodward,* U.S. Naval Research Laboratory*; C Wagenbach,* Boston University*; A Kozen,* U.S. Naval Research Laboratory*; Z Robinson,* College at Brockport - SUNY*; L Nyakiti,* Texas A&M University*; S Qadri,* U.S. Naval Research Laboratory*; M Mehl,* U.S. Naval Academy*; K Ludwig,* Boston University*; J Hite,* US Naval Research Laboratory

Nitride semiconductors have had significant commercial success, but full bandgap engineering of these materials is prohibited by the high temperatures used in conventional growth methods. Recently, we have developed a growth method –low temperature atomic layer epitaxy (ALEp) – that has empirically produced crystalline semiconductor films with properties comparable to those from conventional growth processes, but at roughly half the growth temperature [1,2]. This has eliminated miscibility gaps in ternary III-N semiconductor films and enabled the realization of full bandgap engineering from 0.7 eV to 6.1 eV.

Despite these empirical successes, the fundamental mechanisms involved in ALEp are unknown and the full promise of the method unrealized. To obtain such enabling knowledge we have employed synchrotron-based grazing incidence small angle x-ray scattering (GISAXS) to study the low temperature atomic level processing (ALP) of GaN substrate surfaces for epitaxy and ALEp nucleation and growth of InN on said surfaces. GISAXS allows real-time, in situ monitoring of the surface morphology during these processes.

In this presentation, we will introduce the GISAXS method and the apparatus we have developed to conduct in situ GISAXS measurements of the aforementioned ALP and ALEp processes. We monitor the evolution of GaN substrate surface morphology during a series of low-temperature ALPs including: gallium flash off (GFO), hydrogen plasma clean, and nitrogen plasma nitridation. We learn that the optimum surface results from a GFO conducted at 500° C for only 10 cycles followed by a hydrogen plasma clean. Further, we learn that conventional plasma nitridations are detrimental to smooth surface evolution. When employed to study ALEp InN nucleation and growth, GISAXS data, coupled with Porod[3] and 2D Fourier Transform analysis, affords a clear picture that the growth proceeds by island nucleation and growth and not by the conventionally accepted layer-by-layer growth associated with atomic layer deposition. We have monitored the evolution of island nucleation density, island spacing, island shape and island size as a function of key ALEp growth parameters. We observe that the islands are generally tens of nm or less in size and evolve from a spherical mound shape to a cylindrical shape. Finally, we will present the variations between 2D and 3D growth modes with growth parameter variations that provide insights on process modifications to promote higher quality electronic materials growth.

1. Nepal et al., Cryst. Growth and Des., 13, 1485 (2013)

2. Nepal et al., Thin Solid Films 589, 47 (2015).

G. Porod, Kolloid Z., 124, 83 (1951).

9:20am **TF-WeM-5 Nanostructured Material Surface and Thin Film Interface Characterization by X-ray Photoelectron Spectroscopy**, ***Jisheng Pan,*** Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), Singapore

It is well known that X-ray photoelectron spectroscopy (XPS) is a very powerful tool for understanding the nature of solid surfaces. Although many newly developing tools with high spatial resolution play important role in the analysis of individual nanostructured features of materials XPS is still considered as an essential tool for understanding several important aspects of nanostructured materials that cannot easily be observed using other techniques. However, the question of how the nanostructured material features impact XPS data have been heavily debated in the scientific community, which limits its application in characterization of nanostructured materials. For example, there is consistent observation of cluster-size-dependent binding energy (BE) shifts. But there is substantial disagreement over the assignment of these shifts to initial or final state effects. As a result, the measured PES data can't directly match to the electronic property of clusters because among the initial and final state effects, only the initial state effect involves information of changes in the electronic structure before photoemission, and hence is directly related to nanostructured material properties and is relevant for understanding other chemical process and reactions. In the first part of the presentation, I will talk to you the issues raised specifically for XPS analysis of nanostructured materials and followed by the method to overcome limitations through some examples of application of XPS to study nanostructured materials. In the second part, band energy alignment of different material interfaces such as semiconductor/semiconductor, metal/semiconductor, metal/insulator, semiconductor/insulator, 2D material interfaces determination by XPS will be presented. The performance of any type of hetero-junction device is determined by band energy alignment (band offsets) of material interfaces which form the hetero-junction. Therefore, accurately determining heterojunction band offsets and tuning them to a desired application would have an obvious impact on the optimization of the devices. The effects of chemical shift, differential charging, band bending and photoemission final state on the XPS measurement accuracy and reliability will be discussed.

9:40am **TF-WeM-6 Sputter Epitaxy via Inverse Stranski-Krastanov Growth Mode: A Method of Single Crystal Growth *beyond* Lattice Matching Condition**, ***Naho Itagaki,*** *D Yamashita, K Kamataki, K Koga, M Shiratani,* Kyushu University, Japan

Success in semiconductor devices has been limited thus far because of lattice-mismatch problems between growth layers and substrate. Here, we report on a new method of single crystal growth beyond lattice matching condition, sputter epitaxy via "inverse Stranski-Krastanov (SK) growth mode". Regarding heteroepitaxy on large lattice mismatched substrates, there are two primary modes by which thin films grow: 1) Volmer–Weber (VW: island formation) mode and 2) Stranski–Krastanov (SK: layer-plus-island) mode. In both modes, crystal growth ends up in formation of three-dimensional (3D) island (Fig. S1), making fabrication of single crystalline films challenging. On the other hand, in "inverse" SK mode, 3D islands are initially formed, and subsequent growth of 2D layers occurs on the 3D islands (Fig. S1 (c)). This 3D-2D transition, which is just opposite to the 2D-3D transition in SK mode, is caused by introducing impurity atoms into the growth atmosphere during the initial stage of crystal growth. In this study, we demonstrate the inverse SK growth of ZnO films on 18%-lattice mismatched sapphire substrates, where nitrogen is employed as impurity.

First, 3D island layers of 10 nm thickness were deposited by N_2/Ar sputtering. Next, 2D layers of 1 µm thickness were deposited on the 3D island layers by O_2/Ar sputtering.

We have successfully grown ZnO single crystals on sapphire substrates via inverse SK mode. XRD and AFM analyses revealed that the 3D island layers consist of nm-sized islands with high crystal quality (Fig. S2 (a)). Since the strain induced by the lattice mismatch is relaxed through the island formation, smaller islands have lower density of misfit dislocation, resulting in high crystal quality. In a conventional method, however, such small islands hardly grow because of the cost of additional surface energy due to the increased surface area. Therefore, we consider that the role of nitrogen is to reduce the surface energy through the adsorption on the island surface, taking the advantages of its active but ZnO-insoluble natures. In fact, our calculation indicates that nitrogen addition leads to 4-nm-sized island growth owing to the lowered surface energy (Fig. S3). Furthermore, we found that after cessation of N_2 supply, crystal grains that grow originating from the 3D islands rapidly coalesce to form 2D layer, and eventually grow in a layer-by-layer (2D growth) fashion (Fig. S2 (b)).

We believe that our findings on this growth mode will offer new opportunities for designing materials with unprecedented properties.

This work was supported in part by JSPS KAKENHI 18H01206 and NTT collaborative research.

10:20am **TF-WeM-8 Self-organized Nanostructure Formation in Functional Nitride Alloy Thin Films – Playing Games with Physical Metallurgy**, ***Lars Hultman,*** Linkoping University, Sweden **INVITED**

This presentation reviews a multitude of tricks that can be used to promote self-organized nanostructuring in materials. These are used to enhance mechanical and electronic properties for transition metal and group-III nitride alloy thin films prepared by physical vapor deposition. The structural design is obtained by surface- and bulk-driven phase transformation in metastable TiAlN, ZrAlN, HfAlN, TiSiN, MoVN, VWN, and InAlN model systems, and analyzed by XRD, HREM, FIB, APT, and phase field modeling. *Ab initio* calculations are employed to assess phase stability and decomposition behavior from lattice mismatch and electronic band structure effects. The concept of age hardening in transition metal nitride alloys is reviewed for isostructural model systems. Spinodal decomposition is thus established for TiAlN by the formation of cubic-phase nm-size domains in a checker-board-pattern of TiN and AlN at temperatures corresponding to cutting tool operation. 2-D-nanolabyrinthine structuring in ZrAlN is obtained from with intergrowth of non-isostructural phases *c*-ZrN/*w*-AlN: {110}‖{11-20} interfaces. Superhardening in TiN/Si_3N_4 nanocomposites takes place due to Si segregation forming a few-monolayer-thick SiN_x tissue phase, which is a vacancy-stabilized cubic-SiN_x layer. A hardness maximum at 34 GPa – short of ultrahard - is observed in TiN/SiN_x(001) superlattices at the epitaxial-to-amorphous thickness-limit for the SiN_x layers. Thermodynamically-driven Si segregation in c-$Ti_{1-x}Si_xN$ is proven in atom probe tomography on the sub-nm scale using ^{15}N isotopic substitution to resolve mass spectral overlap between Si and N. For $In_xAl_{1-x}N$, we report curved-lattice epitaxial growth of nanospirals with controllable chirality as well as core-shell nanorod formation. Finally, the possibility to intercalate atomic layers of Au in non-Van-der Waals nanolaminated Ti_3SiC_2 (MAX phase) is demonstrated.

11:00am **TF-WeM-10 Effect of Atomic Layer Deposition Grown VO2 Film Morphology and Crystallinity on Opto-Electronic Phase Transition.**, ***Jason Avila,*** ASEE postdoc fellow*; M Currie, B Downey, V Wheeler,* Naval Research Laboratory

VO_2 is a promising material for a variety of opto-electronic applications due to its metal-to-insulator phase transition occurring near room temperature. Atomic layer deposition (ALD) is an advantageous technique to deposit VO_2 due to its excellent conformality and ability to deposit thin films at low temperatures allowing for growth on a variety of substrates and device architectures. Such conformality is especially useful for complex optical devices with non-planar structures such as waveguides or diffraction gratings. There is, however, no current ALD method for direct growth of crystalline VO_2, therefore post deposition annealing is required to achieve crystallinity. In this study, we examine the impact of annealing conditions on the resulting phase, crystallinity, composition, morphology, and metal-to-insulator transition of as-grown amorphous ALD VO_2 films on sapphire. By controlling annealing conditions such as temperature, time, and O_2 pressure, this study demonstrates a control over film morphologies and phase transition properties of the VO_2 film. One such example is decreasing the VO_2 film roughness by an order of magnitude by changing the annealing temperature by 100 °C, which simultaneously improves the hysteresis of the metal-to-insulator film transition. Through these efforts, the structure-property relationship of VO_2 will be revealed, which can then provide a guide for tailoring of optimal film properties for specific electronic and optical applications.

11:20am **TF-WeM-11 Relationship between Relaxation ratio and growth temperature of GaInN by RF-MBE**, ***Yusuke Nakajima,*** *T Honda, T Yamaguchi, T Onuma,* Kogakuin University, Japan

Full-color micro-LED displays [1] requires a monolithic integration of blue, green and red LEDs. In this case, realization of GaInN-based red LEDs with high efficiencies is one of the technical issues. One of the difficulties of these fabrications is due to lattice mismatch between GaN and GaInN layers as the indium composition is increased [2]. At present, the GaInN substrate is still in the research stage. Thus, fabrication of GaInN underlying layers is one of the technique to overcome the lattice-mismatch problems. The lattice-relaxed underlying layers are required for the red LEDs. On the other hand, the lattice relaxation requires the generations of threading dislocations (TDs). These points show the GaInN underlying layers require

the lattice relaxation and reduction of TDs. We consider that growth temperature is an important parameter in GaInN growth.

In this paper, lattice relaxation in GaInN layer growth by RF-MBE with different growth temperature is reported. Their photoluminescence (PL) spectra are also discussed. The growth temperatures were fixed at 520, 540, 560, 580 and 600 ° C. The indium compositions were of grown layers 25±5%. The lattice relaxations of these layers were estimated using the patterns of reciprocal space mapping in X-ray diffraction (RSM).

GaInN layers on GaN templates were grown by RF-MBE. GaN templates were grown by MOVPE. The growth time was 60 minutes. The thickness of all grown layer was approximately 0.4μm. The RSMs show that the high relaxation was observed from the low-temperature grown layer nevertheless indium compositions were constant of 25%. On the other hand, PL peaks were shifted towards higher energy side as a function of growth temperature. These mean that the high indium segregation will be occurred in the layers grown at low temperature. Detailed relaxation ratio depended on growth temperature will be discussed.

Acknowledgment

The authors would like to thank Spring-8, Dr. Sasaki and Takahasi of QST and Profs. Nanishi and Araki of Ritsumeikan University for their help with the experiments.

[1] Jacob Day *et al*., Appl. Phys. Lett. **99**, 031116 (2011).

[2] S.Shinji et al., Appl. Phys. Lett **6** 111004(2013).

11:40am **TF-WeM-12 The Effect of Interface Structure on MgO/Al/MgO Multilayer Photocathodes***, **Jeff Terry**, Z Lee, L Spentzouris,* Illinois Institute of Technology

Early research and development of photocathode material was based on characterizing compounds with low work function and high quantum efficiency. Recent theoretical and experimental work has shown that the metal-insulator junctions can give rise to changes in the band structure at the interface, which in turn leads to a change in work function and quantum efficiency.

In addition to concerns about work function and quantum efficiency, many modern photoinjector designs also require low beam emittance. Beam emittance is an intrinsic property of the photocathode, therefore it is important to be able control the growth and quantify the factors that lead to such growth. Nemeth [Phys. Rev. Lett. 104, 046801 (2010)] used DFT to model metal- insulator multilayer junction. The model indicate that it is possible to reduce the emittance of the photoemitted beam. Velazquez et al [Appl. Surf. Sci. 360, 762 (2016)] has demonstrated that the work function of lab grown thin film multilayers had trends that match the theory. However the model predicted an exponential decrease of work function, but experimental measurements suggests a linear decrease.

It has been suggested that the surface roughness of the lab grown thin film multilayers might be the main cause of the discrepency. Our multilayer then films are synthesized using Pulsed Laser Deposition. We have developed growth methodology to systematically control the surface roughness. We characterize these interfaces with photoelectron spectroscopy, Kelvin-probe measurements, and quantum efficiency measurements. We track these measured changes with the interface roughness to better understand the role of chemistry at the interfaces.

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