Tuesday Morning, May 24, 2022

Topical Symposia Room Town & Country A - Session TS6-2-TuM

A Session to Acknowledge the Contributions of Joe Greene to the ASED, ICMCTF, AVS, and IUVSTA II Moderator: Scott Barnett, Northwestern University, USA

8:00am TS6-2-TuM-1 Metal-Ion-Controlled Thin Film Growth: What Have We Learnt During the Last Decade?, *Grzegorz (Greg) Greczynski* (grzegorz.greczynski@liu.se), Linköping Univ., IFM, Thin Film Physics Div., Sweden; *I. Petrov, J. Greene*, University of Illinois at Urbana Champaign, USA; *L. Hultman*, Linköping University, IFM, Thin Film Physics Division, Sweden INVITED

Ion irradiation is a key tool for controlling the nanostructure, phase content, and physical properties of refractory ceramic thin films grown by magnetron sputtering. Up until recently, gas ion irradiation was used to enhance adatom mobility in the surface region. Development of high power pulsed magnetron sputtering (HiPIMS), which provides metal-ion plasmas with tunable degree of ionization, enabled systematic studies of the effects of metal-ion irradiation on properties of refractory ceramic thin films. The original motivation for the use of metal-ions stems from the fact that they are film constituents, hence they can provide the benefits of ionmixing (film densification at low film-growth temperatures) without causing the high compressive stresses associated with trapping of gas ions in interstitial sites. Since 2012 we have explored several pseudobinary TM nitride model systems including TiAlN, TiSiN, VAIN, TiTaN, TiAlTaN, and TiAlWN.[1] Experiments were carried out in a hybrid HiPIMS/DCMS configuration.[2]A substrate bias V_s was synchronized with the metal-ionrich portion of the HiPIMS pulses to allow for a control of metal-ion energy, based on the input from time-resolved mass spectrometry analyses. This enabled us to suppress the role of gas ion irradiation and allowed us to study the influence of intense $M_{1^{+}}$ and $M_{2^{+}}$ metal-ion fluxes on film growth kinetics, microstructure, and physical properties over a wide range of M_1M_2N alloy compositions. We established that the effects of metal-ion irradiation depend on the mass of incident ion with respect to that of film constituents.Irradiation with lower-mass metal-ions (e.g. Al⁺ or Si⁺) results in the near-surface trapping with the depth controlled by the V_s amplitude. This enabled unprecedented control over the phase content of metastable ternary nitrides and the growth of NaCl-structure M1M2N solid solutions far above the M1N concentration range achieved with DCMS.[3] At the other extreme, bombardment of the growing film surface with pulsed high-mass metal ion fluxes (e.g., W⁺ or Ta⁺) during HiPIMS/DCMS deposition of Ti₁₋ _xTa_xN, Ti_{1-x-y}Al_xTa_yN, and Ti_{1-x-y}Al_xW_yN alloys provides fully-dense, low stress, films without intentional substrate heating. The high metal-ion mass irradiation leads to effective low-energy recoil generation that provide sufficient adatom mobility, necessary to obtain high-quality fully-dense films, in the absence of conventionally used resistive heating. Thus, the process energy consumption is greatly reduced, while the new possibilities open up for coating temperature-sensitive substrates.

8:40am TS6-2-TuM-3 Predictive Kinetics-based Epitaxial Film Growth Modeling for the SiGe, Si:B and SiGe:B Systems, Glenn Glass (glenn.glass@intel.com), Intel Corporation, USA INVITED CVD growth of Si-based epitaxial thin films continues to hold relevance in industrial applications as well as a model system for scientific discovery. Observation of thin film growth rate trends from hydride precursors combined with quantitative temperature-dependent surface measurements of dangling bond reaction-site densities are combined as input parameters. We demonstrate a model with no fitting parameters that predicts film growth rates across a wide range of temperature, gas flow and flow ratios. The combination of surface bond density measurements (activation energy and frequency factor in the Polanyi–Wigner formalism) and growth rates provides insight into surface segregation behavior that can drive significant second-order effects including roughening and relaxation.

9:20am TS6-2-TuM-5 Growth Kinetics of Spontaneous Superlattices, and Single Wall Carbon Nanotubes Using Gas Phase Precursors, Yonglim Foo (Yonglim.Foo@SingaporeTech.edu.sg), Singapore Institute of Technology, Singapore INVITED

The segregation of C during Si_{1-y}C_y/Si(001) growth during gas-source molecular beam epitaxy, using Si₂H₆ and CH₃SiH₃ has a strong influence on the growth kinetics. During growth of the initial Si-rich layer, strain-driven C segregation to the subsurface results in charge transfer from surface Si *Tuesday Morning, May 24, 2022*

atom dangling bonds to C backbonds. This decreases the Si₂H₆ sticking probability, and, hence, the instantaneous deposition rate, thereby enhancing C segregation. This results in an interesting observation, where alloy superlattice structures consisting of alternating Si-rich and C-rich layers form spontaneously during constant Si₂H₆ and CH₃SiH₃ precursor fluxes at Ts = 725–750 C. The Si-rich layer continues until a critical C coverage is reached allowing nucleation of a C-rich layer which grows until the excess subsurface C is depleted. The process then repeats with periods tunable through the choice of Ts and y_{avg}.

The second section of the talk will be on the early career research work by author, which is heavily influenced by Professor Joe Greene's attention to growth kinetics. The growth dynamics of a single-walled carbon nanotube (SWNT) was observed in real-time using an in situ ultrahigh vacuum transmission electron microscope at 650 °C. SWNTs preferentially grow on smaller sized catalyst particles (diameter \leq 6 nm) with three distinct growth regimes (incubation, growth, and passivation). All of the observed SWNTs grow via a base-growth mechanism with C diffusion on active Ni catalyst sites. Under the same experimental conditions, formation of carbon nanocages was observed on larger Ni catalyst particles. The evolution of SWNTs or nanocages is dependent on catalyst size, and this can be rationalized from both energetics and kinetics considerations.

10:00am TS6-2-TuM-7 Engineering of Soft Materials for Stretchable Electronics, *Nae-Eung Lee (nelee@skku.edu)*, Sungkyunkwan University, Korea (Republic of) INVITED

Stretchable electronics is promising for wearable sensor applications. In particular, wearable sensor devices with a form factor of skin-attachable patch which can sense skin strains, monitor vital signs and detect biomarkers from collected body fluids for disease diagnostics, and can be also used to detect the hazardous environmental factors around human have been extensively investigated. For successful implementation of various components into such stretchable skin-attachable sensor patches, engineering of soft substrates and functional materials is of great importance for skin-conformality, durability, stability, and minimal straininduced signal interference. In this presentation, structural engineering of conventional elastomeric substrates and synthesis of intrinsically stretchable materials for application to stretchable electronics will be discussed. Firstly, structurally engineered substrates of mogul-patterned, trench-patterned, or skin-mimicking elastomers which can mitigate the stress level on the functional layers on them have been designed and developed. The applications of the structurally engineered elastomeric substrates to stretchable physical sensors (strain, pressure, and temperature), chemical sensors (gases) and biosensors (protein, enzyme) by employing low-dimensional nanoscale materials (0D, 1D and 2D), nanocomposites and their hierarchical nanohybrids onto them will be highlighted. Secondly, I will present the synthesis of intrinsically stretchable, transparent, and tough copolymer substrate with excellent temperature and chemical resistance applied to stretchable substrate and microfluidics. In addition, other forms of intrinsically stretchable functional materials such as stretchable solid or hollow microfibers with biodegradability or conductivity will be also demonstrated for electrode materials or microfluidic channel materials for stretchable bioelectronics.

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