Thin Films Division
Room A124-125 - Session TF+PS-TuA
Epitaxial Thin Films

Moderator: Robert Grubbs, Sandia National Laboratories

2:20pm **TF+PS-TuA-1 In-situ Epitaxy of Ultrathin Ni Ferrite Films Studied by Surface Sensitive Time-resolved High Energy X-ray Diffraction*, Joachim Wollschläger*, *M Hoppe, T Pohlmann,* University Osnabrück, Germany*; F Bertram,* DESY, Hamburg, Germany**

Ultrathin films of transition metal ferrites show a large variety of electronic and magnetic properties due to their inverse spinel structure. Therefore, they are of large interest in different fields as catalysis, spintronic and spincaloritronic. The performance of ultrathin ferrite films for devices, however, is strongly coupled to their structure and to their interface properties which are determined by the details during film growth. Therefore, we developed an experimental setup to study the structure of ultrathin films during deposition using surface sensitive time-resolved high energy x-ray diffraction (tr-HEXRD). Here, a large area detector is used to record large parts of reciprocal space while the sample is rotated during growth. The setup offers good time resolution within the range of seconds. Thus, it is possible to record both evolving Bragg peaks of the film and crystal truncation rods (CTRs) while the film is formed and to analyse the diffraction data with respect to evolving film structure.

Here, we present studies performed during growth of Ni ferrite films on $SrTiO_3$(001) at various temperatures. This epitactical system is characterized by a lattice mismatch of 7.5% taking into account the doubled lattice constant of the perovskite $SrTiO_3$. Recording simultaneously several CTRs and evolving Bragg peaks, we could follow the temporal evolution of the film structure in detail. Having past the initial stages of growth, the temporal evolution of the lattice constants depends on the growth temperature. Following the standard model of relaxation of epitactical films, we expected that the strained films show lateral compressive and vertical tensile strain. Our experiments, however, show the opposite relaxation behaviour. This unusual relaxation is attributed to the interface between spinel film and perovskite substrate.

2:40pm **TF+PS-TuA-2 Van der Waals Layer Promoted Heteroepitaxy in Sputter-deposited Transition-metal Carbide and Sulfide Thin Films*, Koichi Tanaka*[1]**, *P Arias, M Liao, Y Wang, H Zaid, A Aleman,* University of California, Los Angeles*; K Hojo,* Nagoya University, Japan*; A Deshpande, M Goorsky, S Kodambaka,* University of California, Los Angeles

Over the past decade, two-dimensional (2D) layered materials such as graphene, MoS_2, etc., have attracted considerable attention for a variety of applications, primarily in nanoelectronics and optoelectronics. An exciting and relatively little explored application of these van der Waals (vdW) layered materials is their use as templates for crystal growth. In the recent years, vdW layers present at the substrate-film interface have been shown to promote 'remote epitaxy', by relaying the epitaxial registry between the film and the substrate.

Here, we demonstrate that the crystallinity of sputter-deposited thin films can be significantly improved using vdW layered materials as buffer layers on growth substrates. Using 2θ hexagonal boron nitride (hBN, $a = 0.250$ nm and $c = 0.667$ nm) as the buffer layer, we grow hexagonal-MoS_2 ($a = 0.315$ nm and $c = 1.23$ nm), trigonal-structured Ta_2C ($a = 0.310$ nm and $c = 0.494$ nm), and NaCl-structured TaC (a = 0.446 nm) of desired thickness on Al_2O_3(0001) substrates via ultra-high vacuum direct current magnetron sputtering of Mo and TaC targets respectively, in Ar/C_2H_4 and Ar/H_2S gas mixtures. hBN layers are deposited in the same system via pyrolytic cracking of borazine (~600 L) onto the substrates at prior to the growth of the thin films. The as-deposited films are characterized using a combination of *in situ* using Auger electron spectroscopy and low-energy electron diffraction and *ex situ* X-ray diffraction (XRD), X-ray photoelectron and Raman spectroscopies, and transmission electron microscopy (TEM) based techniques.

We find notable differences in the layers deposited on hBN-covered Al_2O_3(0001) compared to those grown on bare substrates: significantly stronger 0002 (or 111 in case of TaC) reflection intensities and observation of Laue oscillations in ω-2θ XRD scans and higher intensity of MoS_2 characteristic peaks in Raman spectrum. Furthermore, we show that inserting hBN layers at regular intervals results in highly-0002-oriented growth and suppression of polycrystallinity in thicker Ta_2C films. Our results indicate that hBN layers enhance the crystallinity, irrespective of the crystal structure, of sputter-deposited thin films.

3:00pm **TF+PS-TuA-3 Molecular Beam Epitaxy Applied to Tensile-Strained Quantum Dots for Quantum Optics and Band-Structure Engineering*, Paul Simmonds,*** Boise State University **INVITED**

Since the early 1990s, solid-state self-assembled quantum dots (QDs) have been the subject of intensive research for devices and technologies ranging from high-stability lasers, to intermediate band solar cells. Driven by compressive strain, semiconductor QDs form spontaneously on the (001) surfaces of both III-V and group IV materials during growth by molecular beam epitaxy (MBE). But several years ago, I became interested in the question of why QD self-assembly seemed to be limited to materials with this specific combination of compressive strain, and a (001) surface orientation. For example, why could we not grow QDs under *tensile* rather than compressive strain or on non-(001) surfaces, especially since QDs with these characteristics are predicted to be highly desirable for certain applications. The low fine-structure splitting of (111) QDs should make them ideal entangled photon sources; tensile-strained QDs would have dramatically reduced semiconductor band gaps, with implications for infrared optoelectronics and nanoscale band structure engineering.

The first step towards answering this question was to understand how the competition between plastic and elastic strain relief mechanisms made it enormously challenging to synthesize non-(001) or tensile-strained QDs without the formation of crystallographic defects. The outcome of this analysis was the discovery of a robust new approach to QD self-assembly based on MBE that overcomes these difficulties, and enables the reliable, controllable growth of defect-free, tensile-strained QDs on (111) and (110) surfaces.

I will describe the model upon which tensile-strained QD self-assembly is founded, and then discuss the application of this novel growth mode to several different material systems. I will present data confirming that the (111)-oriented QDs we can now grow do indeed show promise as entangled photon sources. I will highlight the possibilities for band structure engineering that are now available with tensile-strained QDs, using the example of transforming germanium into a direct band gap semiconductor.

In summary, I hope to demonstrate that tensile-strained self-assembly represents a powerful new tool for heterogeneous materials integration, and nanomaterial development.

5:00pm **TF+PS-TuA-9 Low-temperature Homoepitaxial Growth of N-type Superlattices for Ultrastable, Ultrafast X-Ray and Charged Particle Detectors*, April Jewell,*** Jet Propulsion Laboratory, California Institute of Technology*; M Hoenk,* Jet Propulsion Laboratory*; Q Looker, M Sanchez, B Tierney,* Sandia National Laboratories*; A Carver,* Jet Propulsion Laboratory*; S Nikzad,* Jet Propulsion Laboratory, California Institute of Technology

We present a low-temperature process for the homoepitaxial growth of antimony superlattices in silicon. The all low temperature superlattice doping process is compatible as a post-fabrication step for device passivation. We have used low-temperature molecular beam epitaxy (MBE) to embed atomically thin (2D), highly concentrated layers of dopant atoms within nanometers of the surface. This process allows for dopant densities on the order of 10^{13}-10^{14} cm^{-2} (10^{20}-10^{21} cm^{-3}); higher than can be achieved with three-dimensional (3D) doping techniques. This effort builds on our prior work with n-type delta doping; we have optimized our growth processes to achieve delta layers with sharp dopant profiles. By transitioning from a standard effusion cell to a valved cracker cell for antimony evaporation, we have achieved carrier densities approaching 10^{21} cm^{-3} with peak distribution at ~10 Å FWHM for single delta layers. We will discuss details related to growth optimization, and show results from in situ monitoring by electron diffraction. We will also report on elemental and electrical characterization of our films.

The performance of our low-temperature 2D-doping processes has been validated by applying both p-type and n-type superlattice-doping to fully depleted photodiodes. The superlattice-doped devices show significantly higher responsivity than the equivalent ion-implanted devices. Additionally, when exposed to pulsed X-rays the superlattice-doped devices exhibit fast response and recovery times required for use in pulsed power experiments.

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[1] **National Student Award Finalist**

5:20pm **TF+PS-TuA-10 Epitaxial Growth of Ultrathin Molybedenum Nitrides on Ru(0001) and Ag(100)**, ***Asim Khaniya**, M Sajid, A Kara, W Kaden,* University of Central Florida

Molybdenum-nitrides are known to possess interesting mechanical, electronic, and catalytic properties. For example, (i) hexagonal δ-MoN exhibits mechanical elasticity and hardness values comparable to cubic BN and diamond, (ii) both hexaganol and cubic phases of molybdeumn nitrides are known to be superconducting, and (iii) mixed-phase structures have been shown to outperform commercial hydrotreatment catalysts for selective nitrogen removal from heterocyclic organic feedstocks. To better understand these properties, many groups have worked to create improved recipes to grow different phase-pure crystallographic phases of the material. To-date, the most successful procedures have leveraged epitaxy to improve long-range bulk order, but have lacked the well-defined, planar terminations suitable for controlled surface-science investigations. To establish such samples, our group has opted to use low energy nitrogen ions in tandem with molybdenum physical vapor deposition to grow and characterize molybdenum-nitride films on Ru(0001) and Ag(100) supports, which have been chosen to template the growth of hexaganol and cubic phases of the nitride. At the time of this abstract submission, we have succeeded in the growth of a δ-MoN-like film that appears to grow layer-by-layer and in registry with the Ru(0001) support, and are now in the early stages of repeating the process to create γ-Mo_2N on Ag via an analogous process. This talk will focus on the interesting aspects of these materials (particularly those relevant to catalysis), our approach to film preparation, and a thorough analysis of the physical properties of the resultant films and growth modes via: XPS, LEED, He^+ Ion Scattering Spectroscopy, STM, and DFT.

5:40pm **TF+PS-TuA-11 Using Time and Temperature of the Purge Step to Control Crystallinity, Phase Assemblage, and Epitaxy in Atomic Layer Deposited (ALD) Thin Films**, ***Mark Losego**, B Piercy, R Petrie,* Georgia Institute of Technology

The purge step between precursor and co-reactant doses in an atomic layer deposition (ALD) process is often viewed as a process liability. The goal for most manufacturing processes is to make this purge step as short as possible without disrupting the quintessential self-limited growth of ALD. In our lab, we have instead viewed this purge step as a potential opportunity to influence the crystallinity and phase assemblage of our materials. In actuality, each of these purge steps are an opportunity to allow surface diffusion to rapidly reform the film's microstructure before the next layer is deposited. Throughout the literature are interesting, but often conflicting reports of how ALD films crystallize with temperature and thickness. In our recent work, we have asked some simple questions, like how does the onset of such crystallinity change with purge time? We have found, for example, that the onset of anatase formation in the $TiCl_4$-H_2O ALD system can be reduced by more than 40 °C by simply extending the purge time between each cycle. While potentially time intensive, these results have implications for depositing crystalline materials on temperature-sensitive substrates, like polymers. We also find that often an initial seeding of the crystallinity can lead to accelerated growth of crystalline phases with subsequent cycles. In a second paradigm to be discussed, we have introduced a high-temperature pulsed heating source to an ALD system to intentionally crystallize materials and drive epitaxial growth. As proof-of-concept, we have studied epitaxial growth of ZnO on c-plane sapphire using a diethylzinc (DEZ) / water chemistry. DEZ is known to decompose above about 180˚C, and the DEZ-H_2O system cannot be grown epitaxially on c-sapphire with traditional thermal ALD approaches. Here, we show that heating pulses up to 900˚C can be used to drive epitaxy. Interestingly, we find that a template layer of only 20 pulsed heating ALD cycles is sufficient to template ZnO epitaxy with subsequent low temperature ALD growth (180 °C) to film thicknesses of up to 100 nm.

6:00pm **TF+PS-TuA-12 The Role of Template Layers in Heteroepitaxial ALD Growth of Crystalline La_2O_3 on GaN(0001)**, ***Pei-Yu Chen**, T Hadamek,* University of Texas at Austin*; S Kwon,* University of Texas at Dallas*; F Al-Quaiti, A Posadas,* University of Texas at Austin*; M Kim,* University of Texas at Dallas*; A Demkov, J Ekerdt,* University of Texas at Austin

The high switching frequency, operating temperatures and voltages make GaN the material of choice for higher power applications and instrumental to reducing power consumption. In many of these applications, there is a need for a high quality gate dielectric. Lanthanum sesquioxide, La_2O_3, is one of the promising gate insulator candidates. In this work, we compare La_2O_3 thin films grown by atomic layer deposition (ALD) and molecular beam epitaxy (MBE), and explore the formation of ALD-La_2O_3 films on GaN(0001). An island growth mode (Volmer-Weber growth) was observed when La_2O_3 films were deposited directly on GaN(0001) at 250 °C by ALD using tris(N,N'-diisopropylformamidinato)-lanthanum as the precursor and H_2O as the co-reactant. Only with use of a thin template layer, 2 nm-thick hexagonal La_2O_3 grown by MBE or 3 nm-thick cubic Er_2O_3 grown by ALD, can a 2-dimensional ALD-La_2O_3 thin film be formed. The 2-dimensional ALD-La_2O_3 growth on templated-GaN(0001) was confirmed by RHEED and AFM. The macrostructure and microstructure of ALD-La_2O_3 films were verified with XRD, STEM, and atomic structure modeling. The ALD-La_2O_3 film retains a cubic structure on ALD-Er_2O_3 templated-GaN(0001) while it transforms from the cubic phase to mixture of cubic and hexagonal phases on MBE-La_2O_3 templated-GaN(0001) when the film is thicker than 15 nm. Hexagonal La_2O_3 is more thermodynamically stable than cubic bixbyite La_2O_3; the stabilization of cubic ALD-La_2O_3 on ALD-Er_2O_3 templated-GaN(0001) can be attributed to the use of the cubic ALD-Er_2O_3 template and relatively low growth temperature. Analogies are presented for the In_2O_3 system, which has similar cubic bixbyite and hexagonal structures as La_2O_3, except the phases are reversed in In_2O_3. We calculate the surface energy of hexagonal In_2O_3 and compare the result with reported cubic In_2O_3 values to explore the relative contribution of bulk and surface energies in stabilizing the structure of thin crystalline films. Stabilization of thin cubic ALD-La_2O_3 on hexagonal MBE-La_2O_3 templated-GaN(0001) is attributed to likely surface energy differences between cubic and hexagonal La_2O_3.

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