Wednesday Morning, November 8, 2023

Thin Film Division
Room A105 - Session TF1+PS-WeM
Emerging and Advanced Materials and Processes

Moderators: Subhadra Gupta, University of Alabama, **April Jewell**, Jet Propulsion Laboratory

8:00am **TF1+PS-WeM-1 Modified Reactive Sputter Deposition of Titanium Nitride Thin Films via HIPIMS with Kick-Pulse***, A. Miceli, D. Santavicca,* ***Stephen Stagon****,* University of North Florida **INVITED**

Direct current (DC) and radio frequency (RF) sputtering methods have been commonplace in industry for several decades and widely studied in the literature. Hard films of nitrides, such as titanium nitride (TiN), have been deposited using reactive DC sputtering onto cutting tools and medical devices extensively as well. For these applications, the films require excellent adhesion, high density, and high hardness. High-Power Impulse Magnetron Sputtering (HIPIMS) has emerged over the last several years as a method to produce films with increased density and mechanical properties. Process-structure-property relationships for reactive HIPIMS are not well developed. Additionally, conventional HIPIMS suffers from relatively low deposition rates, which become a challenge or barrier to adoption for applied TiN coatings that are typically greater than several microns in thickness. This work aims to look at increasing this deposition rate while maintaining the beneficial effects of HIPIMS by utilizing the short duration "kick-pulse" in the voltage/current cycle, leading to higher instantaneous deposition rates and increased adatom energy level. TiN films are deposited onto silicon (Si) wafers under varied reactive sputtering conditions, including DC, HIPIMS, and HIPIMS with kick-pulse. Structural characterizations are performed using scanning electron microscopy (SEM) and X-ray diffraction (XRD). Optical and electrical properties of the resulting films are also characterized using reflection UV-Vis spectroscopy and 4-point probe techniques. The deposition rate, morphology, and chemical composition of the films are highly affected by the processing conditions, with the kick-pulse producing significant increase in deposition rate and observed grain size. Further investigation will aim to develop a modified structural zone model to include HIPIMS with and without kick-pulse.

8:40am **TF1+PS-WeM-3 Time-Resolved ALD Reaction Heat***,* ***Ashley Bielinski****, E. Kamphaus, L. Cheng, A. Martinson,* Argonne National Laboratory **INVITED**

Atomic layer deposition (ALD) is a surface synthesis technique that consists of sequential self-limiting surface reactions between molecular precursors and a substrate.Differences in the substrate surface as well as the precursor ligands can have a significant influence on the properties of the deposited film and the formation of interfaces, even within a given material system. ALD processes are often empirically optimized with only a simplified chemical understanding of the surface reactions.While this is sufficient for some applications, emerging technologies such as area-selective ALD and site-selective ALD seek to leverage the chemical selectivity between precursor molecules, inhibitors, and the substrate surface.To better understand and direct ALD surface reactions, we must improve our fundamental understanding of the surface reaction mechanisms and energetics.

Pyroelectric calorimetry enables in situ, time-resolved measurements of the heat generated by ALD surface reactions. We present a pyroelectric calorimeter optimized to operate under standard ALD conditions with resolution down to 0.1 µJ/cm^2 and 50 ns.This process of ALD calorimetry was used to measure the heat generation rates from trimethylaluminum (TMA), tetrakis(dimethylamino)zirconium (TDMAZr) and water to form Al_2O_3 and ZrO_2.The aerial heat generation rates were combined with in situ spectroscopic ellipsometry and ex situ Rutherford backscattering measurements to calculate the reaction thermodynamics on a per atom basis.These results were then compared with computational first principles models as well as calculations of the standard reaction enthalpies.The total measured heat was in good agreement with the standard enthalpies, but the computational models showed greater deviation.Pyroelectric calorimetry provides a unique opportunity to validate and provide benchmarks for computational models, helping to evaluate the accuracy of proposed models and mechanisms.

The heat generation rates were also analyzed to compare reaction kinetics.For example, the water reaction occurred at significantly different speeds on the TMA and TDMAZr saturated surfaces. Due to the high time-resolution, we were able to resolve, for the first time, a multi-step reaction for TDMAZr reacting with hydroxylated ZrO_2. Heat generation rates provide new insight into ALD processes, helping us to untangle the thermodynamics, kinetics, and mechanisms of these heterogenous surface reactions.

9:20am **TF1+PS-WeM-5 Reducing Hysteresis in Atomic Layer Deposited VO_2 Thin Films***, V. Wheeler,* ***Peter Litwin****, S. Bennett, M. Currie,* US Naval Research Laboratory

VO_2 is a phase change material that undergoes a first order crystalline phase transition at a critical temperature (T_c = 68°C), resulting in significant changes in intrinsic electrical and optical properties, especially in the infrared. Optical and electrical variations associated with this phase transition are of particular interest as passive and active components of electronic and optoelectronic devices, including RF limiters, thermal regulation, and modulated signaling. Realizing this type of device often requires the integration of thin, conformal VO_2 films with complex, non-planar structures (like metamaterials). Thus, atomic layer deposition (ALD) is an ideal deposition method in these cases.

While ALD is useful for integrating highly uniform and stoichiometric films with dissimilar materials, the low deposition temperature results in amorphous films that do not exhibit the required phase change for device applications. Thin VO_2 films deposited by many methods, including ALD, typically require a post-deposition anneal to induce the crystallization necessary for large, abrupt, usable changes in properties during the phase transition. This anneal can be accomplished in many ways such as a slow traditional anneal in specific partial oxygen environments or using environmentally independent laser processes to rapidly crystallize the film. However, the microstructure and resulting phase change properties are highly dependent on the method of crystallization and can lead to deleterious effects like large hysteresis windows (> 10°C) during heating and cooling through the phase transition of these films. For optimum performance in device applications, the hysteresis needs to be reduced or even eliminated.

In this work, we will discuss developing novel processes towards achieving crystalline ALD VO_2 films and the impact they have on reducing hysteresis, including the introduction of nucleation layers and tailoring of plasma properties during plasma enhanced ALD. As an example, we have found that hysteresis can be reduced to a few degrees using ALD TiO_2 films, independent of crystallinity, phase, or thickness of the TiO_2 film itself, but ALD Al_2O_3 or HfO_2 buffer layers do not impact the hysteresis at all. When possible, we will discuss the possible causes and mechanisms behind hysteretic performance improvements.

9:40am **TF1+PS-WeM-6 Magnetron Sputtering Deposition and Stabilization of the Bismuth Sesquioxide (Bi_2O_3) High-Temperature Equilibrium Phase***,* ***Sandra E. Rodil****, A. Martinez, O. Depablos-Rivera,* Universidad Nacional Autónoma de Mexico

Bismuth sesquioxide (Bi_2O_3) exhibits a dynamic polymorphism characterized by two thermodynamically stable phases. The first is the monoclinic (α) phase, which remains stable from room temperature (RT) up to 730 °C, while the second is the defect-fluorite cubic (δ) phase, stable above 730 °C and up to the material's melting point (830 °C). Additionally, during the cooling/heating process, two metastable phases (β-tetragonal and γ-bcc) are formed, and their transformation temperature depends on factors such as the cooling rate, ambient conditions (vacuum or air), and oxygen concentration.

The production of the δ-Bi_2O_3 phase as a thin film date back to 1999, when it was first demonstrated using electrodeposition, followed by magnetron sputtering. The crystallographic structure of the films has been analyzed through X-ray diffraction patterns and visible Raman spectra. However, caution must be exercised when interpreting Raman spectra, as the broadband at 600 cm^{-1} associated with the defect-fluorite cubic (δ) phase can also be observed in other phases. To address this issue, we critically analyzed the assignments provided in the literature for this broad Raman mode and proposed an alternative explanation consistent with its observation in all films. Our proposal attributes the 600 cm^{-1} band to the presence of residual-weakly bonded [BiO_n] units located at the grain boundaries of the nanocrystalline films. This band is not exclusive to the defective fluorite cubic structure of Bi_2O_3. Interestingly, we found a similar signal in the Raman spectra of the Bi_4O_7 phase, which had not been reported before, suggesting possible incorrect assignments to the δ-phase. We employed a density functional approximation of the Bi_4O_7 molecular structure to gain further insights to calculate the Raman active bands. The theoretical estimations showed excellent agreement with experimental data, reinforcing the validity of our proposed explanation.

Finally, our investigations revealed that doping with heterovalent ions allows for stabilizing films exhibiting the δ-Bi_2O_3 phase within a temperature range from room temperature to 600 °C. This exciting discovery opens new possibilities for using these films as ionic conductors, potentially finding applications in various technological fields.

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