Friday Morning, May 24, 2024

Plasma and Vapor Deposition Processes
Room Town & Country B - Session PP5-FrM

Plasma Surface Interactions and Diagnostics

Moderator: Arutiun P. Ehiasarian, Sheffield Hallam University, UK

8:00am **PP5-FrM-1 The Role of Plasma in Plasma Enhanced Atomic Layer Deposition***, **Scott Walton (scott.walton@nrl.navy.mil)**, D. Boris, M. Johnson, V. Wheeler,* US Naval Research Laboratory, USA*; M. Sales, P. Litwin,* NRC, USA*; J. Woodward,* US Naval Research Laboratory, USA*; S. Rosenberg,* Lockheed Martin Space Advanced Technology Center, USA*; J. Hite, D. Pennachio, M. Mastro,* US Naval Research Laboratory, USA **INVITED**

Plasma-enhanced atomic layer deposition (PE-ALD) is a low temperature, conformal, layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas-phase chemistry to produce amorphous, crystalline, and epitaxial films of varying types and characteristics. The plasma-based advantages come at the cost of a complex array of process variables that can drastically impact the growth modes and resulting film properties. Accordingly, understanding the process-structure-property relationship is both critical and challenging. We approach this problem by combining plasma diagnostics and material characterization techniques. Plasma diagnostics are used to inform the choice of process conditions for PE-ALD systems including VUV-NIR spectroscopy, charged particle collectors near the substrate, and spatially resolved Langmuir probe measurements to characterize the plasma used in commercial and research PE-ALD tools. In particular, we assess the spatial variation of plasma parameters, flux and energy of ions reaching the substrate surface, and the relative fractions of atomic and molecular species generated in the plasma under a variety of operating powers, gas pressures, and gas input flow fractions typically used to grow nitride, oxide, and fluoride films. Changes in plasma parameters are then linked with changes in growth modes and film properties using both ex situ and in situ characterization techniques. Select example systems including AlF_3, InN, TiO_2 and Ga_2O_3, will be discussed. This work supported by the Naval Research Laboratory base program.

8:40am **PP5-FrM-3 Navigating the Complexity of Microwave Plasma-Assisted ALD During AlN and TiN Fabrication***, **Caroline Hain (caroline.hain@empa.ch)**, K. Maćkosz,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; C. Guerra,* Swiss Cluster AG, Switzerland*; T. Nelis,* BFH, Bern University of Applied Sciences, Switzerland*; J. Michler, I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Plasma-based atomic layer deposition (ALD) techniques are becoming increasingly relevant, offering extended control over process parameters such as temperature range, precursor/co-reactant chemistries and surface reactions. This freedom allows for a wider choice of substrates and thin film materials, as well as the ability to precisely tailor material properties critical to specific applications. Nevertheless, the complexity introduced by plasma necessitates a more detailed understanding of the deposition environment. This study aims to characterise *in situ* the surface reactions occurring during electron cyclotron resonance (ECR) microwave plasma-assisted ALD and their influence on the deposited films, in this case using the examples of aluminium nitride (AlN) and titanium nitride (TiN). Trimethylaluminium (TMA) and tetrakis(dimethylamido)titanium (TDMATi) were used as precursors for AlN and TiN, respectively, with plasma-activated nitrogen serving as co-reactant. Two types of time-of-flight mass spectrometers (ToFMS) were used to identify neutral and ionic species produced during the sequential ALD cycles. Optical emission spectroscopy (OES) was utilized to identify the nitrogen species produced during the nitrogen plasma step, while Langmuir probe measurements determined the plasma spatial potential, density, and electron temperature as a function of microwave power and distance from the source. Finally, the chemical composition, thickness, density, and structure, as well as surface uniformity of deposited AlN and TiN thin films were investigated via a combination of scanning and transmission electron microscopy (SEM/TEM), X-ray reflectometry (XRR) and ellipsometry. This work offers insights on the complexity of plasma-assisted ALD processes and paves the way for informed optimisation and application-based customisation of deposited thin films.

9:00am **PP5-FrM-4 Advanced Ion Energy Measurement Tools to Understand the Effect of Ion Energy on Film Properties***, **Thomas Gilmore (thomas.gilmore@Impedans.com)**,* Impedans, Ireland

In any plasma assisted deposition process, ion surface interactions can influence the film properties significantly. Ion energies determine if deposition, sputtering or implantation occurs, while ion flux determines the rate of this processing. The ion/neutral ratio impacts the thin film properties. Measuring these values for various chamber conditions can not only aid in process development, but also facilitate process transfer, as these ion parameters are the direct process drivers.

We, at Impedans Ltd, offer solutions to the requirements of ion energy and flux measurements. Our collection of sensors includes the Semion, Quantum and Vertex RFEAs for wafer level measurements. In this talk we will demonstrate the role of energetic ions in plasmas and how they affect the properties of materials etched or deposited in plasma processing. We will show how to use measured ion flux, ion energies and ion-neutral fractions to optimize industrial plasma-assisted processes. The *Semion RFEA* measures the ion energies hitting a surface, the ion flux, negative ions, and bias voltage at any position inside a plasma chamber using an array of integrated sensors [1-3] over a region of 300 mm large size wafer with down to 44 ns time resolution. On the other hand, the *Quantum system* is an energy resolving gridded quartz crystal microbalance (QCM), used to measure the ion-neutral fraction hitting a surface inside a plasma reactor. This instrument also measures the etching/deposition rate, ion energy, ion flux and bias voltage [4, 5]. The Vertex RFEA design has a variable aspect ratio (AR), controlled using a potential difference between its grids. A variable AR controls the ion angular spread passing through the sensor for detection. The Vertex product produces a plot of ion energy distribution versus AR [6].

We will highlight the successful measurements done by our RFEA product range in selected applications (like pulsed source and /or bias, tailored waveform biasing, etc) enabling better control of film properties of different materials and various plasma chemistries.

References

[1] Impedans Ltd, Dublin, Ireland [www.impedans.com]

[2] S. Sharma et al., Ph.D. Thesis, Dublin City University (2016)

[3] H. B. Profijt et al., J. Vac. Sci. Technol. A 31, 1 (2013)

[4] M. H Heyne et al., 2D Mater. 6, 035030 (2019)

[5] S. Karwal et al., Plasma Chemistry and Plasma Processing 40, 697–712 (2020)

[6] S. Sharma et al., Rev. Sci. Instrum. 86, 113501 (2015)

9:20am **PP5-FrM-5 Plasma Polymerization Processes***, **Dirk Hegemann (dirk.hegemann@empa.ch)**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

Plasma polymer films are deposited via reactive intermediate species as formed in a low temperature plasma. Over the last decades, the understanding of the mechanisms behind plasma polymerization processes has steadily been improved, which will be discussed. Basically, the highly non-equilibrium conditions provide an average energy per molecule in the plasma, known as specific energy input (SEI), yielding plasma chemical reactions by inelastic collisions (excitation, dissociation, and ionization). Due to the related energy distribution, the probability for the activation mechanism to produce film-forming species can be described by a simple Arrhenius-like equation, where temperature is replaced by SEI. The potential of this approach to optimize plasma polymerization processes for surface functionalization is demonstrated on the basis of siloxanes, hydrocarbons, and further gaseous mixtures.

Hexamethyldisiloxane (HMDSO) has been well studied in the past revealing insights into the plasma chemical reaction pathway, which can thus be used as a model monomer following Arrhenius-like behaviour. Nano-scaled controlled film deposition is obtained considering the flux of film-forming radicals, etchants, and energetic species. Thus, dense to porous, hydrophilic to hydrophobic films can be generated. Such films are investigated for the chemical modification of catalytic substrates, as durable barrier layers and bioactive surfaces.

Furthermore hydrocarbon molecules are mixed with reactive gases such as CO_2 or NH_3 to investigate the penetration of radicals into complex 3D structures, which is studied using cavity techniques. Various applications in technical and biomedical fields will be presented.

Finally, an outlook is given about the applicability of the presented approach for plasma gas conversion based on comparable plasma chemical processes.

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