Atomic Scale Processing Focus Topic
Room B130 - Session AP+EL+MS+PS+SS+TF-TuA

Advancing Metrology and Characterization to enable Atomic Layer Processing

Moderators: Eric A. Joseph, IBM T.J. Watson Research Center, Jessica Kachian, Intel Corporation

2:20pm **AP+EL+MS+PS+SS+TF-TuA1 In Situ Ellipsometry Characterization Of Atomic Layer Processes: A Review*, James Hilfiker*,** *G.K. Pribil, J. VanDerslice,* J.A. Woollam Co., Inc. **INVITED**

Atomic layer processes such as atomic layer deposition (ALD) and atomic layer etch (ALE) provide monolayer-level thin film deposition or etch. Spectroscopic ellipsometry (SE) is ideally suited for the characterization requirements of such very thin layers. In situ SE provides real-time feedback, which is invaluable for establishing new atomic layer processes. In situ SE characterization has been adopted by many researchers due to its versatility. SE measurements are sensitive to deposition or etch at the (sub)monolayer level. The real-time evolution of film thickness provides details on nucleation periods or delays, the growth or etch rates per cycle, and verifies the self-limiting nature of a process. Multiple experiments can be performed within a single run by modifying the process conditions, allowing quick qualification of deposition temperatures, chemical exposure times, plasma influences, and purge times. In this paper, we will review the areas where in situ SE has been applied to both atomic layer deposition and etch.

We will also discuss the applications of in situ SE that benefit from a broad wavelength range. SE is best known for determining film thickness and optical constants. This characterization can be accomplished for many types of materials – dielectrics, semiconductors, organics, and even metals – provided the layer remains semi-transparent. Other material properties affect the optical constants and can be determined via this relationship. In situ SE has been used to estimate the crystal structure, composition, and even conductivity of thin films. We will discuss the advantages and limitations of in situ SE, which in many ways has proven to be an ideal partner for atomic layer processes.

3:00pm **AP+EL+MS+PS+SS+TF-TuA3 Elucidating the Mechanisms for Atomic Layer Growth through In Situ Studies*, Jeffrey Elam,*** Argonne National Laboratory **INVITED**

Atomic Layer Deposition (ALD) provides exquisite control over film thickness and composition and yields excellent conformality over large areas and within nanostructures. These desirable attributes derive from self-limiting surface chemistry, and can disappear if the self-limitation is removed. Understanding the surface chemical reactions, i.e. the ALD mechanism, can provide insight into the limits of self-limitation allowing better control, successful scale up, and the invention of new processes. In situ measurements are very effective for elucidating ALD growth mechanisms. In this presentation, I will describe our recent investigations into the growth mechanisms of ALD nanocomposite films comprised of conducting (e.g. W, Mo and Re) and insulating (e.g. Al_2O_3, ZrO_2 and TiO_2) components using in situ measurements. These ALD nanocomposites have applications in particle detection, energy storage, and solar power. We have performed extensive in situ studies using quartz crystal microbalance (QCM), quadrupole mass spectrometry (QMS), Fourier transform infrared (FTIR) absorption spectroscopy, and current-voltage measurements. These measurements reveal unusual ALD chemistry occurring upon transitioning between the ALD processes for the two components. This results in unique reaction products that affect the properties of the films in beneficial ways. The knowledge gained from our in situ studies of the ALD nanocomposite films has helped us to solve problems encountered when we scaled up the ALD processes to large area substrates.

4:20pm **AP+EL+MS+PS+SS+TF-TuA7 Surface, Interface, or Film: A Discussion of the Metrology of ALD Materials in Semiconductor Applications*, G. Andrew Antonelli,*** *N. Keller,* Nanometrics **INVITED**

Atomic layer deposition, etching, and interface engineering are enabling technologies for semiconductor manufacturing. These processes have led to an explosion in the use of laboratory techniques such as transmission electron microscopy and the need to bring such instruments closer to or into the fab itself. However, there remains a need for in-line, non-destructive, non-contact metrology capable of quickly characterizing and monitoring these extremely thin films on test structures, on product, or in device as these data are the only meaningful method for monitoring of ultimate device performance. Indeed, in cases such as the use of selective deposition or etching, no test vehicle other than the ultimate product may be relevant. A variety of measurement techniques with a focus on x-ray and optical probes as applied to this class of problems will be reviewed. Examples will be provided on relevant logic such as the Gat-All-Around FET and memory devices such as 3D NAND.

5:00pm **AP+EL+MS+PS+SS+TF-TuA9 In Line and Ex Situ Metrology and Characterization to Enable Area Selective Deposition*, Christophe Vallee*,** *M. Bonvalot, B. Pelissier, J-H. Tortai, S. David, S. belahcen, V. Pesce, M. Jaffal, A. Bsiesy,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; R. Gassilloud, N. Posseme,* CEA-LETI, France*; T. Grehl, P. Bruner,* IONTOF GmbH, Germany*; A. Uedono,* University of Tsukuba, Japan

Innovation in materials, architectures (3D), gap filling technologies, lithography and etch processes are mandatory at every node of CMOS or memory devices. These challenging integration issues can be facilitated by the use of an integration scheme currently being intensively investigated known as area selective deposition (ASD). Criteria for an adequate area selective deposition process are: growth only on specific regions, high throughput compatible with industrial demands, no so-called mushroom profiles into adjacent features as well as no nuclei defectivity on undesired sites. Several routes can be developed to achieve an ASD process with ALD. The one discussed here concerns the deposition/etch approach which takes benefit from an *in situ* etching step inserted in a standard ALD cycle [1]. By incorporation of anisotropic or isotropic etching steps in the ALD process, "surface" selective deposition, as well as topographically selective deposition (TSD) have been obtained [2, 3]. The major current shortcoming of this approach lies in the deep insight which is required regarding elementary atomic-scale reaction mechanisms. Indeed, in the case of an ALD/ALE Area Selective Deposition process, a highly precise control of etching and its selectivity at the atomic scale is needed. Controlling the nature and density of defects induced by etching or passivation steps and understanding their impact on the physical and electrical properties of selectively deposited films are of course also required. Moreover, in order to optimize these processes, an accurate understanding of the underlying reasons why passivation after a low number of ALD cycles, is no more effective. Thus, *in situ* as well as *ex situ* monitoring and metrology are mandatory.

In this presentation, we will discuss how to optimize and understand atomic-scale reaction mechanisms in an ALD/ALE ASD process using combined *in situ* or *ex situ* measurements, such as ellipsometry, XPS, XRR, LEIS, FIB-STEM, and positron annihilation. We will show that when crosslinked, these technics are very effective to perform atomic scale metrology and characterization. As an example, we will discuss F atom localization and density in selectively deposited oxides thanks to a F-based ALE chemistry incorporated in the ALD process. In the case of a topographically selective deposition (TSD) process attempts will be presented to understand ion/surface interactions when low energetic ions are extracted from the plasma of the PEALD reactor both during deposition and plasma-ALE steps.

[1] R. Vallat et al, JVSTA **35** (2017) 01B104

[2] R. Vallat et al, JVSTA **37** (2019) 020918

[3] A. Chacker et al, APL **114** (2019)

5:20pm **AP+EL+MS+PS+SS+TF-TuA10 Recent Progress in Thin Film Conformality Analysis with Microscopic Lateral High-aspect-ratio Test Structures*, Riikka Puurunen,*** Aalto University, Finland **INVITED**

Conformal thin films which cover complex 3D shapes with a film of uniform properties (thickness, composition, etc.) are increasingly demanded applications such as semiconductor devices, microelectromechanical systems, energy conversion/storage and catalysis. Atomic layer deposition (ALD) and its counterpart atomic layer etching (ALE) [together known as atomic layer processing (ALP)], are increasing in usage largely thanks to their known conformal character.

A question that needs to be asked in the R&D of 3D applications using conformal ALD/ALE processes is: how conformal is conformal; is the conformality sufficient to meet the specs? In semicon industry, vertical vias and cross-sectional transmission electron microscopy (TEM) are standardly used for conformality analysis. Recently, microscopic lateral high-aspect-ratio (LHAR) test structures have been developed to improve the conformality analytics capabilities. LHAR structures e.g. enable detailed conformality analysis at arbitrarily high aspect ratios (e.g., >5000:1), where no film can coat the 3D structure fully, thereby exposing the saturation

profile characteristic for the process. This, in turn enables the kinetic analysis of the process and e.g. extraction of the sticking coefficients related to the growth reactions.

This invited talk will address recent progress related to the fabrication and the use of microscopic LHAR conformality test structures. After the breakthrough with the first prototypes (PillarHall LHAR1; Gao et al. 2015, Mattinen et al. 2016; reviewed in Cremers et al., 2019), third and fourth generation prototypes have been developed (PillarHall LHAR3 and LHAR4). This work will review the conformality analysis progress enabled by the microscopic LHAR structures and discuss the benefits and challenges of this approach. Recent published progress includes the conformality modelling by Ylilammi et al. (2018) and experimental extraction of sticking coefficient by Arts et al. (2019). In addition, several other ongoing conformality analysis cases will be presented.

References

Arts, Vandalon, Puurunen, Utriainen, Gao, Kessels, Knoops, J. Vac. Sci. Technol. A 37, 030908 (2019); https://doi.org/10.1116/1.5093620

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Ylilammi, Ylivaara, Puurunen, J. Appl. Phys. 123, 205301 (2018); https://doi.org/10.1063/1.5028178

6:00pm **AP+EL+MS+PS+SS+TF-TuA12** ***In operando*XPS Study on Atomic Layer Etching of Fe and Co Using $Cl_2$and Acetylacetone or Hexafluoroacetylacetone***, **_Zijian Wang_**, *O. Melton, D. Angel, B. Yuan, R.L. Opila,* University of Delaware

Etching of transition metals is one of the major challenges in magnetoresistive random-access memory (MRAM) device fabrication. In this work, atomic layer etching of iron and cobalt surfaces with halogen and an organic molecule was studied. We successfully performed etching of Fe and Co thin films via forming volatile metal complexes at low temperature with cyclic sequential reactions of Cl_2 and acetylacetone (acac) or hexafluoroacetylacetone (hfac) . The etching reaction mechanism of acac and hfac reacting with Clorine-modified Fe and Co surfaces was investigated: the surface was first activated with Cl_2 gas, and subsequently, the top layer of chlorinated metal was removed by reaction with a diketone (acac/hfac). The extent of Cl_2 reaction determines the etching rate of the metal. At substrate temperatures lower than 135°C, acac could remove the chlorinated Fe metal layer from Fe surfaces, but not chlorinated Co from Co surfaces. *In-operando* x-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) simulation shows that the reaction of acac or hfac with Chlorinated Fe or Co surfaces is likely following a complex reaction pathway instead of simple diketone substitution for the metal chloride. Diketone decomposition may play an important role in the etching process.

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