## Area Selective ALD
## Room Premier Ballroom - Session AS-TuP
## Area Selective ALD Poster Session

**AS-TuP-1 Use of Low Energy Ion Scattering for the Analysis of Area Selective ALD Processes**, ***Thomas Grehl***, *P Brüner,* ION-TOF GmbH, Germany*; C Vallee,* LTM-UGA, France*; R Gassilloud,* U Grenoble Alpes, CNRS, LTM*; V Pesce, A Bsiesy, B Pelissier,* Univ. Grenoble Alpes, LTM, France

Low energy ion scattering (LEIS) is a surface analytical technique that enables the characterization of the outermost atomic layer of a sample. The sample is bombarded with noble gas ions with kinetic energies of a few keV, and the energy spectrum of the backscattered ions is recorded. Ions scattered by different atom species in the first atomic layer give rise to distinct elemental peaks in the energy spectrum. As the result of the scattering process is independent of the chemical environment of the target atom, the peak intensities are directly proportional to the surface coverage of the respective element. The elemental composition of the surface can thus be determined in a quantitative way.

In addition to surface scattering events, noble gas ions scattered in deeper atomic layers undergo material-dependent energy losses proportional to their penetration depth. These processes lead to additional sub-surface features in the energy spectra, which can be evaluated to obtain layer thickness values and the depth distribution of elements in the first few nm of a sample.

The extreme surface sensitivity of just a single monolayer is a unique property of LEIS that is not available with other surface analytical techniques like XPS or SIMS, which always integrate over several monolayers. This makes LEIS an ideal tool to study layer growth in ALD processes. The monolayer sensitivity is especially useful to analyze the early stages of film growth, with questions about topics like surface coverage, layer closure, nucleation delay, growth mode, growth rate, or the presence of impurities.

Additional complexities arise in the field of area selective deposition (ASD). A higher number of process steps are involved, and often additional reactants lead to more complex chemical interactions. Growth areas and non-growth areas are present simultaneously, and surface analytical tools become increasingly important to develop, understand, and improve deposition processes.

One example of an ASD process, developed at LTM, includes an atomic layer etching (ALE) step once nucleation sets in on the non-growth area. The area is then passivated to restore its non-growth properties, and deposition is resumed. This cycle is repeated until the desired film thickness is obtained on the growth area. In this study, we apply LEIS to a series of model samples of thin ALD $TiO_2$ layers, created to improve understanding of this ASD process. The passivation step and the precise point where nucleation re-starts on the passivated area are of special interest. Moreover, the influence of the fluorine-based plasma etching on the deposited $TiO_2$ layers is investigated.

**AS-TuP-2 Area-Selective Atomic Layer Deposition of Zinc Sulfide Based on Inherent Selectivity*,*** ***Chao Zhang****, Z Han, M Vehkamaki, M Leskelä, M Ritala,* University of Helsinki, Finland

The need for simplifying and improving complex electronic device fabrication has motivated the research on area-selective atomic layer deposition (ALD). Area-selective ALD is a bottom-up approach enabling deposition of thin films only on the desired surface areas, thereby accomplishing film patterning more easily as compared with conventional lithography .[1]

It is well known that ALD process involves chemical reactions between precursors and reactive sites existing on substrate surfaces. So, in principle area-selective ALD can be achieved by surface modification including surface passivation and activation. Surface passivation means that reactive sites on the substrate surface are blocked by passivation layers, thus losing their reactivity with ALD precursors. Area-selective ALD by surface passivation has already been studied for years, focusing on using self-assembled monolayers (SAMs) or polymers as resist layers to prevent the film growth.[2]On the contrary, surface activation provides an opposite way to attain selective film growth by patterning of seed layers that can promote ALD film growth catalytically. For example, Färm et al. proved an easy way that used micro contact printed $RuO_x$ films as a seed layer for catalyzing ruthenium ALD process .[3]

Here, a new approach based on inherent selectivity of an ALD process is presented for area-selective ALD. It is found that ALD of ZnS, using elemental zinc and sulfur as precursors at a deposition temperature of 500ºC, takes place on Au surfaces but not on Si surfaces with about 2 nm native $SiO_2$ on top. As a reason for this selectivity, it is suggested that sulfur adsorbs much stronger on Au than on $SiO_2$. The continuous ZnS growth even after the Au surface is completely covered with ZnS can be similarly explained in terms of strong adsorption of sulfur on ZnS. Alternatively, the selectivity could also arise from Zn alloying with Au, this alloy then reacting with the subsequent sulfur pulse. Patterned Au structures used in our experiment consist of three different size dots (500, 250, 50 µm), prepared by electron beam evaporation (EBE) with a shadow mask. After the deposition of ZnS on this patterned surfaces, ZnS films were detected only on Au dots as confirmed by EDX measurements.

**References**

[1] S. E. Atanasov, B. Kalanyan, and G. N. Parsons, Journal of Vacuum Science & Technology A **34,** 01A148 (2016).

[2] A. Mackus, A. Bol, and W. Kessels, Nanoscale **6,** 10941 (2014).

[3] E. Färm, S. Lindroos, M. Ritala, and M. Leskelä, Chemistry of Materials **24,** 275 (2012).

**AS-TuP-3 Selective Etching of Native Silicon Oxide in Preference to Silicon and Silicon Oxide***, C Ahles,* ***Jong Youn Choi****, A Kummel,* University of California San Diego

The selective removal of native $SiO_x$ in the presence of $SiO_2$ would be of great importance to the semiconductor industry given the ubiquity of these two materials in electronic devices. Methods of native $SiO_x$ removal have been well studied and typically rely upon HF chemistry. Aqueous HF treatment suffers from an inevitable air exposure of the Si sample and is not selective for native $SiO_x$ versus bulk $SiO_2$. The Siconi™ process utilizes a $NF_3/NH_3$ plasma to remove native $SiO_x$ leaving behind a $(NH_4)_2SiF_6$ salt as the etch product. This salt is then removed in a subsequent anneal. While this process is known to work well for removing native $SiO_x$ on Si, the selectivity of this process versus thermal $SiO_2$ has not been studied. In this study, the etch rates of Si and $SiO_2$ subjected to a $NF_3/NH_3/Ar$ plasma were examined. Under the optimized conditions of $NF_3$:$NH_3$:Ar = 1:10:1.5 at 45°C, 190 mTorr and 100 W no etching of Si is observed with negligible or no etching of $SiO_2$.

The etch rates of Si and $SiO_2$ subjected to a $NF_3/NH_3/Ar$ plasma were measured in-situ using a pair of quartz crystal microbalances (QCMs). It was found that the etch rate of Si shows a strong dependence on the temperature, with the Si etching at a rate of 25 nm/min at 50°C while no etching of Si is observed at 40°C. At 45°C, it was found that the native $SiO_x$ on Si is rapidly etched under these conditions, after which there is only deposition (presumably of $NH_4F$ and $NH_4FHF$ salts). X-Ray Photoelectron Spectroscopy (XPS) measurements show that after the dry clean the Si surface has a N:F ratio of 1:3, consistent with $(NH_4)_2SiF_6$ formation. A subsequent anneal at 120°C removes the salt and leaves a very clean Si surface (1% O, 6% C, 1% F and 92% $Si^0$). Atomic Force Microscopy (AFM) shows that the Si surface has a root mean square (RMS) roughness of 1.1 Å. For comparison, the RMS roughness of a degreased Si sample (containing native $SiO_x$) which was not subjected to the dry clean was found to be 2.2 Å. This is consistent with no etching of the underlying Si, as etching would be expected to roughen the surface. XPS analysis of $SiO_2$ after the dry clean showed that on $SiO_2$ the N:F ratio was closer to 1:2, suggesting the presence of $NH_4FHF$ instead of $(NH_4)_2SiF_6$ (the expected etch product of $SiO_2$). Annealing at 120°C removed most of the $NH_4FHF$ salt, leaving behind only 4% F and 2% N. AFM measurements show that the degreased $SiO_2$ has an RMS roughness of 4.3 Å while after the dry clean the RMS roughness is very similar (3.8 Å), consistent with no etching of $SiO_2$. The reason for this selectivity may be due to the presence of more strained Si-O bonds or undercoordinated Si atoms in native $SiO_x$ than in $SiO_2$.

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