

## Area Selective ALD

### Room Baekeland - Session AS2-WeA

#### Area Selective Deposition II

**Moderators:** Stacey Bent, Stanford University, Rachel Nye, North Carolina State University

**4:00pm AS2-WeA-11 Intrinsic Area-Selective Atomic Layer Deposition of Aluminium Nitride, Bernhard van der Wel, T. Aarnink, A. Kovalgin, University of Twente, the Netherlands**

Group III-V nitrides (in short III-N such as AlN, GaN, InN and their alloys) are thermally and chemically stable semiconductors suitable for use in optical and high-power electronics as their bandgaps cover a spectral range from deep ultraviolet to near infrared [1]. Fabrication of mono-crystalline III-N substrates is expensive, as well as their realization on silicon wafers, typically involving high-temperatures and thick buffer layers. Fabrication of poly-crystalline variants are a viable route to reduce fabrication costs and deposit with a low thermal budget ( $\leq 400$  °C).

Atomic layer deposition (ALD) is well-known to offer high conformality, large area uniformity and film thickness control at sub-nm scale. Self-limiting surface reactions in ALD, requiring presence of certain chemical groups on the surface for enabling such reactions, can be beneficially utilized to achieve area-selective deposition. The latter is required to overcome critical alignment requirements during film patterning and reduce the amount of lithography steps [2].

In this work, we demonstrate inherent area-selective atomic layer deposition (ASALD) of Aluminium Nitride (AlN) films in purely thermal mode (350 °C) and at a low reactor pressure (1.5e-3 mbar), from trimethylaluminum (TMA) and ammonia (NH<sub>3</sub>). AlN is selectively grown on patterned substrates, consisting of areas of sputtered AlN and thermal SiO<sub>2</sub> ranging from 2x2  $\mu\text{m}^2$  to 10x10 mm<sup>2</sup>. Proper pre-treatment facilitates growth on the sputtered AlN. Film growth is monitored in-situ by spectroscopic ellipsometry (SE) and verified by ex-situ SE and atomic-force microscopy. After 350 cycles the film thickness on sputtered AlN is approximately 12.5 nm, whereas on the SiO<sub>2</sub> area the thickness is less than 1 nm. The interfaces, confirming selective deposition, are examined by transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS, sputter profiling) confirmed the selectivity and showed a stoichiometric Al to N ratio with oxygen and carbon contaminations as low as 8% and 3%, respectively.

[1] D. A. Neumayer and J. G. Ekerdt, "Growth of Group III Nitrides. A Review of Precursors and Techniques," *Chem. Mater.*, vol. 8, no. 1, pp. 9–25, Jan. 1996.

[2] A. J. M. Mackus, M. J. M. Merckx, and W. M. M. Kessels, "From the Bottom-Up: Toward Area-Selective Atomic Layer Deposition with High Selectivity," *Chem. Mater.*, vol. 31, no. 1, pp. 2–12, 2019.

**4:15pm AS2-WeA-12 Surface-Diffusion Control Enables Tailored-Aspect-Ratio Nanostructures in Area-Selective Atomic Layer Deposition, Philip Klement, D. Anders, L. Gumbel, M. Bastianello, F. Michel, J. Schörmann, M. Elm, Institute of Experimental Physics I & Center for Materials Research (ZfM), Justus Liebig University Giessen, Giessen, Germany; C. Heiliger, Institute of Theoretical Physics & Center for Materials Research (ZfM), Justus Liebig University Giessen, Giessen, Germany; S. Chatterjee, Institute of Experimental Physics I & Center for Materials Research (ZfM), Justus Liebig University Giessen, Giessen, Germany**

Area-selective atomic layer deposition is a key technology for modern microelectronics as it eliminates alignment errors inherent to conventional approaches by enabling material deposition only in specific areas. Typically, the selectivity originates from surface modifications of the substrate that allow or block precursor adsorption. The control of the deposition process currently remains a major challenge as the selectivity of the no-growth areas is lost quickly.

Here, we show that surface modifications of the substrate strongly manipulate the surface diffusion. The selective deposition of TiO<sub>2</sub> on poly (methyl methacrylate) and SiO<sub>2</sub> yields localized nanostructures with

tailored aspect ratios. Controlling the surface diffusion allows to tune such nanostructures as it boosts the growth rate at the interface of the growth and no-growth areas. Kinetic Monte-Carlo calculations reveal that species move from high to low diffusion areas. Further, we identify the catalytic activity of TiCl<sub>4</sub> during the formation of carboxylic acid on poly (methyl methacrylate) as the reaction mechanism responsible for the loss of selectivity, and show that process optimization leads to higher selectivity. Our work enables the precise control of area-selective atomic layer deposition on the nanoscale, and offers new strategies in area-selective deposition processes by exploiting surface diffusion effects.

**4:30pm AS2-WeA-13 Study on Area-Selective Atomic Layer Deposition of Al<sub>2</sub>O<sub>3</sub> with a Series of Al Precursors, Il-Kwon Oh, Ajou University, Korea (Republic of)**

**INVITED**

Area-selective atomic layer deposition (AS-ALD) offers the advantage of exploiting surface chemistry to deposit a material in a targeted area. Therefore, it may allow a reduction in the number of lithography and etch steps, resulting in lowering of errors in the patterning process as well as a decrease in manufacturing costs. For example, a self-aligned hard mask fabricated by AS-ALD can guide etching of via holes and deposition of metal wires in the metallization process to avoid shorts between metal layers.

Several metal oxide systems, such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZnO, and HfO<sub>2</sub>, have been explored for AS-ALD processes. For a hard mask, Al<sub>2</sub>O<sub>3</sub> possesses advantages over other metal oxides due to its high hardness as well as chemical inertness for etching selectivity. However, despite extensive studies on ALD Al<sub>2</sub>O<sub>3</sub>, there are few studies on AS-ALD of Al<sub>2</sub>O<sub>3</sub>. Furthermore, literature suggests that Al<sub>2</sub>O<sub>3</sub> may be comparatively difficult to block; for example, the blocking selectivity of Al<sub>2</sub>O<sub>3</sub> is limited to only ~6 nm whereas ZnO can be blocked for over ~30 nm. The difference in blocking highlights the importance of precursor chemistry for AS-ALD, which motivates the current study to elucidate the mechanism of Al<sub>2</sub>O<sub>3</sub> AS-ALD based on a comparative study of Al precursors.

In this work, the recent development of AS-ALD is introduced. Furthermore, as an example, fundamental study on AS-ALD Al<sub>2</sub>O<sub>3</sub> is presented. Four Al precursors; trichloroaluminum (AlCl<sub>3</sub>), dimethylaluminum chloride (Al(CH<sub>3</sub>)<sub>2</sub>Cl), trimethylaluminum (Al(CH<sub>3</sub>)<sub>3</sub>), and triethylaluminum (Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>) are used for comparison, offering a comparative study of precursor ligand properties (reactivity, polarity, and geometric factors) by changing both the number of methyl (Me) and chloride (Cl) group in AlMe<sub>x</sub>Cl<sub>3-x</sub> (x=0, 1, and 3) and the chain length of alkyl ligands in AlC<sub>n</sub>H<sub>2n+1</sub> (n=1 and 2). Results of quantum chemical calculations of the reaction pathways show product energetics that are strongly correlated with experimental observations. The blocking properties of the four Al precursors will be compared and the results discussed based on the growth mechanism. Finally, Al<sub>2</sub>O<sub>3</sub> selective pattern is successfully fabricated, which would be useful for back-end-of-line (BEOL) semiconductor process. By pursuing first principles design of selective ALD processes, this work may enable new methods for additive nanoscale.

**5:00pm AS2-WeA-15 Selective Hydration of TiO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>: A Strategy for Site-Selective Atomic Layer Deposition at Surface Defects, A. Martinson, E. Kamphaus, J. Jones, N. Shan, Argonne National Laboratory, USA; C. Luo, A. Hock, Illinois Institute of Technology; L. Cheng, Argonne National Laboratory, USA; Ashley R. Bielinski, Argonne National Laboratory**

While ALD is most commonly employed in uniform conformal growth, more selective precursors and processes may allow for more precise synthetic strategies including targeted reaction at subtly unique surface sites including those that lead to electronic defects. We outline a selective hydration strategy to target reaction at the step edges of rutile TiO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>. We computationally and experimentally investigate the feasibility of facet- and site-selective ALD through accurate asymmetric slab models from which the free energy of adsorption at unique surface sites is leveraged to predict step selectivity. Computational evaluation of ALD precursor adsorption free energies on multiple dehydrated facets further refine the feasibility of a temperature-dependent selective hydration strategy. Initial experiments of Ga<sub>2</sub>O<sub>3</sub> ALD nucleation on TiO<sub>2</sub> single crystals and MgO ALD on In<sub>2</sub>O<sub>3</sub> broadly support the computational predictions and strategy. The strategies outlined here provide one possible route to selectively target growth at structural defects of oxide surfaces.

# Wednesday Afternoon, June 29, 2022

5:15pm AS2-WeA-16 Self-Assembled Monolayer and “Click” Chemistry Deposition Treatments for Area-Specific Processing, *Chad Brick, R. Liberatore, Gelest, Inc; B. Arkles, Department of Chemistry, Temple University; J. Goff, Gelest, Inc*

Self-assembled monolayers (SAMs) formed or modified by rapid “click” chemical reactions are receiving significant attention due to their demonstrated ability to promote or facilitate area-specific or area-selective deposition utilizing processes that occur on time scales compatible with high-throughput manufacture and cyclic deposition schemes. By precision tailoring of the chemical structure of the SAM layer, the selectivity and speed of the reactions with both the underlying substrate and subsequent deposition cycles can be enhanced in order to provide rapid, selective processes with few or no chemical byproducts. In this work we demonstrate that cyclic azasilanes and cyclic thiasilanes can rapidly bond to the surface of hydroxyl-covered substrates in the vapor phase, with saturated coverage being reached in several seconds in a manufacturing-worthy atomic layer deposition tool. The effects of processing parameters, including pulse time, temperature, substrate type, and pre-treatment on the deposition profile, as well as the subsequent reactivity of cyclic azasilanes to further modify the chemical nature of the surface are discussed, with an emphasis on rapid “click” chemical processes compatible with high throughput. It was observed that on hydroxyl (OH)-terminated surfaces such as silicon native or thermal oxide the cyclic silanes reach a saturation point in approximately five seconds under typical ALD conditions over the temperature range of 30 °C to 300 °C, as determined by water contact angle and ellipsometry. The reactivity and selectivity of cyclic azasilanes to other oxide surfaces as well as non-oxides such as copper, silicon nitride, and HF-etched silicon will be discussed, as will process to remove azasilane monolayers after deposition.

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