Area Selective ALD
Room 113-115 - Session AS-TuA
Area Selective Deposition II

Moderators: Adrie Mackus, Eindhoven University, Netherlands, Bonggeun Shong, Hongik University

1:30pm **AS-TuA-1 Integrated Isothermal Atomic Layer Deposition and Thermal Atomic Layer Etching: "Atomic-Level Processing" for Area-Selective Patterning of TiO_2***,* ***Seung Keun Song,*** North Carolina State University*; P Lemaire,* Lam Research Corp.*; G Parsons,* North Carolina State University

Area-Selective Atomic Layer Deposition (AS-ALD) is attracting more attention from the semiconductor industry as a possible solution to alignment issues typically faced when scaling down transistor feature sizes. To address this challenge we show a new approach to AS-ALD, where self-limiting thermally-driven atomic layer etching (ALE) is chemically coupled with self-limiting thermal atomic layer deposition (ALD) to yield several nanometers of TiO_2 thin film formation on receptive SiO_2 surfaces at 170°C, with no measurable grown on adjacent areas of hydrogen-terminated silicon (100). When TiO_2 ALD using $TiCl_4$ and H_2O is done 170°C on non-oxidized hydrogen-terminated silicon, we find an incubation time of ~30 cycles is required before substantial TiO_2 nuclei appear. On SiO_2 surfaces, however, TiO_2 nucleation proceeds rapidly, allowing 10-20 Å of deposition before nucleation on Si-H. Using this inherent nucleation delay combined with a novel self-limiting thermal ALE procedure employing sequential doses of WF_6 and BCl_3, we create a new isothermal "Atomic-Level Process", where the atomic-scale chemical control of ALD is intimately coupled with that of thermal ALE to build up on a prepared surface, precise nanoscale constructs with pre-selected location and dimension. Using the integrated ALD/ALE sequence, we achieve in excess of 200 TiO_2 ALD cycles, yielding ~ 4 nm of TiO_2 on SiO_2, before visible nuclei form on Si-H, as determined by SEM, ellipsometry and TEM analysis. Process and materials analysis using in-situ QCM and ex-situ AFM and XPS further confirm our findings. To date, extending the ALD/ALE sequence to more than 500 ALD cycles leads to incomplete TiO_2 etch removal from Si-H, ascribed to changes in Si-H during prolonged exposure to deposition and etch species. This demonstrated Atomic Level Process for improved control in selective deposition offers substantial opportunities for integrated area-selective ALD, and provides a viable pathway to explore other Atomic Level Processes for parallel and wafer-scale synthesis of nanoscale and sub-nanoscale constructs.

1:45pm **AS-TuA-2 Inherent Substrate Selectivity and Nucleation Enhancement during Ru ALD using the RuO_4-Precursor and H_2-gas.***,* ***Matthias Minjauw,*** Ghent university, Belgium*; H Rijckaert, I Van Driessche, C Detavernier, J Dendooven,* Ghent University, Belgium

Ruthenium is a candidate to replace copper in future sub-10 nm interconnects. At these dimensions the resistivity of Ru lines is expected to be lower compared to Cu due to the lower sensitivity to size effects.[1] In addition, it is likely that Ru interconnects won't require a diffusion barrier, and will show a better electromigration performance.[2] At feature sizes below 10 nm it will be difficult to align subsequent lithography steps, and the conformality of the deposition method is increasingly important, such that area selective atomic layer deposition (ALD) of ruthenium is of high interest.[3]

We first report inherent area selective ALD of Ru on H-terminated Si (Si-H) versus SiO_2, using the thermal RuO_4 (ToRuS^{TM})/ H_2-gas ALD process.[4] In situ spectroscopic ellipsometry (SE) on blanket substrates shows that Ru growth initiation occurs from the first cycle on Si-H, while on SiO_2 the growth is delayed, resulting in a substrate selectivity window of ~ 70 cycles (Figure 1, a). Area selective Ru ALD was evaluated using a patterned substrate of 1-10 µm wide Si-H lines separated by 10 µm wide SiO_2 regions, and exposing it to 20 cycles of the RuO_4 / H_2-gas ALD process. Ex situ scanning electron microscopy (SEM) and cross section high resolution transmission electron microscopy (HRTEM) measurements show that a 4.5 nm Ru film could be deposited on the Si-H, with no Ru detected on the SiO_2 (Fig. 2). In vacuo X-ray photoelectron spectroscopy (XPS) experiments showed that exposure of Si-H to a single RuO_4 pulse leads to the oxidation of the Si surface, together with the deposition of RuO_2. On SiO_2 however, the surface is already oxidized, and in vacuo XPS shows that for the same exposure to RuO_4 no Ru is deposited on the surface (Fig. 3). Therefore, we propose that the mechanism behind the inherent substrate selectivity is the oxidation of the Si-H surface by RuO_4. Secondly, we report for a methodology to enhance the nucleation of the RuO_4 / H_2-gas process on oxide substrates. In vacuo XPS and in situ SE experiments show that a single exposure of SiO_2 to trimethylaluminum (TMA) makes the surface reactive towards RuO_4, which allows for Ru growth initiation from the first cycle (Fig. 1, b; Fig. 3). We propose that this is due to the combustion of surface CH_3-groups by RuO_4. As TMA is known to be reactive towards many oxide substrates, this methodology presents a way to achieve Ru metallization of virtually any surface.

[1] S. Dutta et al. *IEEE Elec. Dev. Lett.* **2017**, 38, 949.

[2] O. V. Pedreira *et al. 2017 IEEE IRPS, Monterey, CA*, 6B-2.1.

[3] P. C. Lemaire et al. *J. Chem. Phys.* **2017**, 146, 052811.

[4] M. M. Minjauw et al. *J. Mater. Chem. C*. **2015**, 3, 132.

2:00pm **AS-TuA-3 Surface Preparation and High Nucleation for Selective Deposition using Anhydrous Hydrogen Peroxide***, D Alvarez,* ***Jeffrey Spiegelman,*** *K Andachi,* RASIRC

Creative surface protecting agents are being used in efforts to explore novel methods for Area Selective Deposition (ASD). These agents include self-assembled monolayers, patterned photoresists, plasma deposited films and others. At the same time, fast nucleation and growth of metal oxide films require creation of fully covered reactive surfaces. Surface treatment ideally will:

1. Generate high density or complete surface functionalization
2. Eliminate or minimize sub-surface oxidation
3. Increase speed and uniformity of nucleation compared to H_2O
4. Not react with organic functionality or photoresist on adjacent surfaces

Anhydrous hydrogen peroxide has been largely ignored as a potential novel reactive chemistry. There are several reasons for this. First, there is no precedent in the literature. Second, when delivered H_2O_2 is typically mixed with H_2O, which dominates the reaction. Third, this material has only recently become available in a packaged form that could integrate into selective deposition process equipment.

Hydrogen Peroxide is an attractive chemistry for area selective deposition because of both its oxidation properties and proton transfer properties. The chemistry compares favorably to Ozone (oxidation potential = 2.1V versus 1.8V for H_2O_2). It also has slightly stronger proton transfer than water (water pKa = 7.0 versus 6.5 for H_2O_2). Most critically, H_2O_2 has a very weak O-O bond, with Bond Energy = 36 kcal/mole, suggesting more energetically favorable reactivity at reduced temperatures.

Results from our work show good correlation with selective deposition requirements:

1. Nucleation surface density of hydroxyl groups (-OH) is 3-5 times greater using anhydrous hydrogen peroxide versus water on metal surfaces
2. No sub-surface oxidation on Si surfaces using anhydrous H_2O_2 for monolayer hydroxyl (-OH) surface functionalization
3. Faster nucleation and growth of Al_2O_3 on Si-H surfaces when using anhydrous H_2O_2 versus water
4. Little to no photoresist removal at temperatures up to 300°C with anhydrous H_2O_2

Other testing shows that metal oxide film quality grown using anhydrous H_2O_2 are nearly identical to those grown with ozone methods. Metal oxide films include aluminum oxide, hafnium oxide, and zirconium oxide.

The presentation will discuss details of newly discovered reactivity of anhydrous H_2O_2 on several surfaces and will outline potential ASD pathways.

2:15pm **AS-TuA-4 An Inherently Selective Atomic Layer Deposition of $MoSi_x$ -on Si (001) in Preference to Silicon Nitride and Silicon Oxide***,* ***Jong Youn Choi,*** *C Ahles,* University of California San Diego*; R Hung, N Kim,* Applied Materials*; A Kummel,* University of California San Diego

As metal-oxide-semiconductor field effect transistors (MOSFETs) shrink into the <10 nm regime, it becomes a significant challenge to minimize electrical loss with a decreasing pitch especially at the contact regions. To reduce resistance in a compact geometry, selective atomic layer deposition (ALD) of transition metal disilicides is of great interest. In previous studies, selective ALD of tungsten (W) via a fluorosilane elimination process was demonstrated using WF_6 and SiH_4 or Si_2H_6.[1,2] Selectivity was achieved by an inherently favorable reactivity of the precursors on hydrogen-terminated Si versus OH-terminated SiO_2. In this study, sub-stoichiometric $MoSi_x$ (x= 0.7–1.4) was selectively deposited by ALD on H-terminated Si (001) in preference to SiO_2 and SiN using MoF_6 and Si_2H_6 at 120°C. In-situ, X-ray Photoelectron Spectroscopy (XPS) was used to investigate the chemical composition of $MoSi_x$ ateach experimental step. To confirm selective deposition on the nanoscale, $MoSi_x$ was deposited on a Si sample patterned with SiO_2 and Si_3N_{4-} and cross-sectional Tunneling Electron Microscopy (TEM) was performed. It was observed that the Si-H surface termination allowed nucleation of $MoSi_x$ on Si in contrast to the inherently chemically passive (non-reactive) SiO_x and SiN surfaces. This substrate-dependent selectivity was retained for $MoSi_x$ growth of up to 10 nm with a proper N_2 purge gas to prevent any CVD components on SiO_2 and SiN. Performing additional Si_2H_6 doses after the ALD cycles allowed the incorporation of more Si into the film and increased the stoichiometry to be closer to $MoSi_2$. The $MoSi_x$ catalyzes this self-limiting CVD of Si while retaining selectivity over SiO_2 and SiN. In-situ Scanning Tunneling Microscopy (STM) showed that $MoSi_x$ ALD on Si produced an atomically flat surface with a root mean square (RMS) roughness of 2.8 Å. Post-annealing in ultra-high vacuum at 500°C for 3 minutes further decreased the RMS roughness to 1.7 Å. A depth profiling XPS study revealed that the bulk of the $MoSi_x$ film is close to stoichiometric $MoSi_2$ with <10% oxygen and fluorine. The TEM imaging shows that the selectivity is retained on the nanoscale and that $MoSi_x$ can be selectively deposited on Si without substrate consumption. This is enabled by just taking advantage of the selective ALD of substiochiometric $MoSi_x$ combined with the ability of the substiochiometric $MoSi_x$ films to selectivity induce self-limiting Si deposition from Si_2H_6.

1. Ph. Gouy-Pailler *et al.*, Thin Solid Films, **241**, 374 (1994)

2. B. Kalanyan *et al.*, Chem. Mater., **28**, 117-126 (2016).

2:30pm **AS-TuA-5 Investigating the Difference in Nucleation during Si-based ALD on Different Surfaces (Si, SiC, SiO_2 and SiN_x) for Future Area-Selective Deposition (AS-ALD)**, ***Ekaterina A. Filatova,*** Tyndall National Institute, University College Cork, Ireland*; A Mameli, A Mackus,* Eindhoven University of Technology, Netherlands*; F Roozeboom,* Eindhoven University of Technology and TNO, Netherlands*; W Kessels,* Eindhoven University of Technology, Netherlands*; D Hausmann,* Lam Research Corp.*; S Elliott,* Schrödinger, Inc., Ireland

Area-selective atomic layer deposition (AS-ALD) allows nanostructures of arbitrary composition and lateral shape to be built with atomic precision on pre-selected substrate locations. Most current approaches for AS-ALD are based on local inhibition (e.g. with self-assembled monolayers) or activation. However, for some applications of AS-ALD (e.g. in self-aligned fabrication) it is relevant to be able to exploit differences in chemical behavior of a pre-patterned substrate. For this reason, investigating inherent differences in nucleation on diverse substrates is of crucial importance for developing future AS-ALD processes. In this paper we are focussing on substrates of silicon and silicon-based dielectric materials (SiC, SiO_2 and SiN_x) used in electronics.

In order to investigate the possibility of area-selective deposition of Si-based materials using aminosilane precursors, nucleation on four different Si-based surfaces (Si:H, SiC:H, SiO_2:OH and Si_3N_4:NH_2/NH) was analyzed. First, we investigated the difference in precursor adsorption on these surfaces during the exposure of di(isopropylamino)silane (DIPAS), di(sec-butylamino)silane (DSBAS) and bis(t-butylamino)silane (BTBAS) precursors by calculating their adsorption energies using ab-initio modelling. From density functional theory (DFT) calculations, we found that DSBAS is thermodynamically favorable to react with Si_3N_4 and SiO_2, but not with SiC and Si at 0K. To experimentally corroborate these results, SiN_x was deposited using Plasma-Enhanced ALD from DSBAS precursor and N_2 plasma on three different surfaces (H_2 plasma-exposed SiC, HF-last c-Si and c-Si with native SiO_2). In-situ spectroscopic ellipsometry (SE) measurements were performed after every half-cycle to analyze the DSBAS adsorption reaction on these surfaces. During the first DSBAS dosing cycle on the SiO_2 surface a change in the SE signal was observed, suggesting initial DSBAS adsorption, while no changes were observed on the Si and SiC surfaces. The selective adsorption of DSBAS on SiO_2 is in agreement with the DFT predictions. The subsequent N_2 plasma half-cycle modifies the non-growth surface into SiN_x, after which the selectivity is lost. These results illustrate that it is generally difficult to achieve area-selective ALD for nitrides, because of the nitridation of all the exposed substrate surfaces during the plasma step.

We conclude, that during ALD on Si-based substrate materials DSBAS reacts selectively with SiO_2 and SiN_x surfaces but not with Si and SiC surfaces. Our results highlight the role of DFT calculations in predicting possible routes towards AS-ALD process development.

2:45pm **AS-TuA-6 Strategies for Area Selective Atomic Layer Deposition and Applications in Catalysis*, Rong Chen,*** *K Cao, X Liu, J Cai, B Shan, J Zhang,* Huazhong University of Science and Technology, China **INVITED**

Atomic layer deposition (ALD) is a mainstay technology for the semiconductor industry since it allows deposition of nanometer-thin layers of desired materials onto a substrate in a very controlled and uniform manner. Recently, ALD has been adapted to design and synthesize composite catalysts that allow them to promote multiple chemical reactions. In fabrication of composite catalysts, the selective approaches of ALD are of great importance to exert spatial control of deposition to fabricate three dimensional nanostructures.

In this talk, strategies for selective ALD and enabled nanostructures for catalytic applications will be discussed. Selective ALD allows directional and precise tailoring of the structural size, composition, interfaces, and active sites, that is of great importance for catalysis applications. Two major types of selective ALD approaches are introduced, template selective method via surface modification of self-assembled monolayers (SAMs) and reverse SAMs passivation, as well as inherently selective deposition. With these methods, core shell nanoparticles, oxide overcoating structures ranging from porous coating to ordered structures, and oxide surrounding structures could be fabricated controllably. Theoretical simulations, spectroscopic and microscopic analysis, and catalytic performance are carried out to verify the results. These strategies of selective ALD demonstrate unique advantages to design and fabricate highly stable and active catalysts on the atomic scale, providing unique opportunities to understand the structure–property relationship of catalysis.

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