Selective Deposition as an Enabler of Self-Alignment Focus Topic
Room: 210F - Session SD+AS+EM-ThM

Fundamentals of Selective Deposition
Moderator: Scott Clendenning, Intel Corporation, Suvi Haukka, ASM Microchemistry Ltd., Finland

8:00am **SD+AS+EM-ThM1 Fundamental Examinations of Surface Chemistry-Driven Approaches to Selective Area Atomic Layer Deposition**, *W. Zhang, J.-R. Chen,* ***James Engstrom***, Cornell University

Most approaches taken to date concerning selective area growth have involved the use of masking layers consisting of photoresists or self-assembled monolayers (SAMs). While some success has been achieved with this approach there are a number of disadvantages intrinsic to these methods. First, SAMs are very difficult to form defect free, and second, and perhaps more important, these masking layers themselves must be patterned or deposited selectively. A second approach to selective area ALD relies on intrinsic reactivity differences between exposed surfaces, which, unfortunately, may be limited to a few special cases. Here we seek to develop a more general approach to achieving selective area growth. We initially focus on the first half-cycle of ALD, where demonstrating selectivity for this part of the ALD process is a necessary, but not sufficient condition for selective area growth. We are examining two specific approaches to the surface chemistry: (*i*) the use of adsorption reversal agents; and (*ii*) the use of molecular blocking agents. Here for a thin film precursor we examine transition metal complexes with the generic structure, $M(XR_m)_n$, where M is the transition metal and XR_m is the coordinating ligand. In pursuing strategy (*i*) we examine the introduction of a second species in the first half-cycle that can act as a coordinating ligand, e.g., HXR'_m, or $HXR'_{m-1}R''$, etc. In pursuing strategy (*ii*) species (Y) are selected that can effectively compete for adsorption sites, dependent on the composition of the substrate. Concerning strategy (*i*) we are currently investigating reactions between transition metal amido compounds and a series of amines ($X = N$). We have found a somewhat unexpected result for this chemistry: the partial pressure of H_2NR' produces similar effects on both a metal (Cu) and a dielectric (SiO_2) surface, where a low partial pressure attenuates the irreversible adsorption of the thin film precursor, while a high partial pressure results in no adsorption of the precursor. An investigation of the reactions between the thin film precursor and a molecular blocking agent with the structure HSR'', gave much more encouraging results. Here we found complete blockage of chemisorption of the thin film precursor on a Cu surface, whereas on SiO_2 the molecular blocking agent had no effect on the adsorption of the metal for the first half-cycle. We will conclude this presentation with a discussion of the mechanisms that are likely operative in both cases, making use of *in situ* measurements involving X-ray photoelectron spectroscopy, and also initial results concerning the effectiveness of this approach for multiple (5-20) cycles of ALD.

8:20am **SD+AS+EM-ThM2 Mechanistic Understanding of Surface-Selective Chemical Vapor Deposition of Copper Films Using a Molecular Inhibitor**, ***Elham Mohimi***, *S. Babar, B. Trinh, G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana Champaign

Surface-selective chemical vapor deposition of thin films can enable the fabrication of nanoscale devices by eliminating difficult patterning and etching steps. However, stray nucleation of film on the non-growth surface due to defect or impurity sites remains a challenging problem. We previously demonstrated the use of molecular growth inhibitors in copper CVD to control morphology, ranging from a smooth and continuous thin film to particles in a narrow size distribution. Here, we show that an inhibitor can also be used to afford essentially perfect selective growth. Addition of vinyltrimethylsilane (VTMS) molecules during copper CVD from the Cu(hfac)VTMS precursor reduces the growth rate of copper on copper by a factor of four, but reduces the Cu deposition on thermal SiO_2 or porous carbon doped SiO_2 to below one monolayer (area averaged). In-situ FTIR and mass spectroscopy show that the VTMS undergoes associative desorption with adsorbed Cu(hfac) intermediate on the non-growth surface, and is responsible for the surface selective deposition of copper only on the intended (metallic) substrate areas. The processing window for this method is wide in terms of VTMS pressures (> 1 mTorr), growth times (1-90 min), and substrate temperature (100-180°C).

8:40am **SD+AS+EM-ThM3 Selective Deposition of Copper-Manganese Alloy for Interconnects**, ***Roy Gordon***, Harvard University **INVITED**

As copper interconnections are made smaller, they fail more easily by electromigration. The dominant pathway for motion of Cu atoms is along the interfaces between Cu and the surrounding insulator surfaces. In current technology, a tantalum nitride diffusion barrier and a Ta or Co adhesion layer are placed between Cu and the insulators. Because these layers are more resistive than Cu, the composite interconnect line has a higher resistance than one that would consist entirely of pure Cu. Here we describe how selective placement of manganese within the insulator surface can provide the necessary stabilization, adhesion and barrier properties for Cu lines without the resistance penalty of TaN/(Ta or Co) layers. After trenches and vias are etched into the insulator, CVD is first used to deposit a thin layer of manganese nitride conformally on all exposed surfaces of the insulator as well as on the Cu exposed at the bottoms of the vias. Then less than a monolayer of iodine is chemisorbed onto the MnN_x from ethyl iodide vapor. Next, this iodine catalyzes selective, bottom-up CVD of Cu-Mn alloy so that it fills even the narrowest trenches and vias without any voids or seams at the centerlines. The iodine "floats" on the growing surface of the Cu, and is finally removed by chemical-mechanical polishing along with the Cu-Mn overburden and the MnN_x on top of the insulator. During subsequent anneals, Mn rapidly diffuses out from the MnN_x and from the Cu-Mn alloy into the near-surface regions of the insulator to form an insulating layer of $MnSi_xO_yN_z$ surrounding the Cu. The necessary Cu adhesion and barrier properties are provided by this insulating layer of $MnSi_xO_yN_z$ selectively placed just inside the surfaces of the insulators. During anneals, Mn and nitrogen originally located on the Cu surfaces at the bottoms of vias disappear as the Mn and N are re-distributed by diffusion to nearby insulator surfaces. The result is direct, low-resistance connection between Cu in vias with Cu in the metallization level below. This selective migration of Mn leaves pure, low-resistance Cu completely filling the entire volume of trenches and vias, providing the lowest possible line resistance. Thus Mn is placed selectively only where it is required to increase adhesion and lifetime before failure by electromigration, to prevent diffusion of Cu into the insulator and to avoid corrosion of Cu by water or oxygen. The same sequence of process steps can apply Cu to the walls of through-silicon-vias to conduct signals from one chip to another. This process can also form Cu seed layers for electrodeposition of Cu-filled vias for distributing power through silicon chips.

9:20am **SD+AS+EM-ThM5 Selective Growth of First Row Transition Metal Films by Atomic Layer Deposition**, ***Charles Winter***, Wayne State University **INVITED**

Our laboratory seeks to develop the growth of metallic first row transition metal thin films using atomic layer deposition (ALD). The microelectronics industry is calling for the growth of metallic first row transition metal films by the ALD method for a variety of applications, including copper metallization, seed layers for copper metallization, copper/manganese alloys for self-forming copper diffusion barriers, and magnetic alloys. The ALD growth of noble metal thin films has been explored extensively in the past ten years, due to the positive electrochemical potentials of these metal ions and relative ease of reduction to the metallic state. The low temperature ALD of high purity, low resistivity Cu films has been described, but ALD routes to the other metallic first row transition metal films remain poorly developed, largely because of the negative electrochemical potentials of most of the ions and a corresponding lack of powerful reducing co-reagents that can convert precursors in positive oxidation states to the metals. We will describe the synthesis, structure, and properties of a large series of new first row transition metal ALD precursors containing alkoxide ligands that combine high volatilities, high thermal stabilities, and high reactivities toward reducing agents. We will also report borane reducing agents that can react with the metal precursors to afford metallic films. Additionally, we will overview the thermal growth of metallic copper, nickel, cobalt, iron, manganese, and chromium thin films from these new precursors. Importantly, the growth of these metals is highly selective for noble metal substrates, such as ruthenium, palladium, and platinum. The noble metal substrates appear to activate the borane reducing agents, thus enabling selective metal growth. Chemical insights into the selective growth will be presented.

11:00am **SD+AS+EM-ThM10 Etching and Chemical Functionalization of Silicon Nitride Surfaces for Selective Deposition**, *L.-H. Liu, T. Peixoto, W. Cabrera, D. Dick, J.-F. Veyan,* University of Texas at Dallas*, D.J. Michalak, R. Hourani,* Intel Corporation*, M.D. Halls,* Schrodinger, Inc.*, S.P. Pujar, H. Zuilhof,* Wageningen University, Netherlands*, **Yves J. Chabal***, University of Texas at Dallas

The ability to process silicon nitride and oxide films and chemically functionalize their surfaces by wet chemical methods is critical for selective deposition. The nature of HF-etched silicon nitride surface is complex and somewhat controversial. We have therefore performed an extensive study of HF etching of both Si_3N_4 and SiO_2 surfaces, combining spectroscopic techniques (Infrared absorption, X-ray photoemission, Low energy ion scattering), imaging (atomic force microscopy) and contact angle measurements with first principles calculations, as a function of HF concentration. We have also performed post-treatment in cold and hot water, and chemical functionalization with a range of organic molecules to help determine the chemical nature of the HF-etched surfaces.

The nature of silicon nitride surfaces is complex. We find that immediate rinsing in deionized water after HF wet-chemical etching yields smooth silicon nitride surfaces with clear evidence for Si-F surface termination. Low energy ion scattering experiments and XPS measurement as a function of gentle sputtering with Gas cluster ion beams (GCIB) confirm that the F is all located at the surface (i.e. not distributed into the bulk), and in the form of Si-F with high temperature stability (up to 600 ºC in ultra-high vacuum). Hydrolysis in water is very slow at room temperature, but can be achieved at high temperature (~90 % removal at 70 ºC for 30 min). However, water is found to etch silicon nitride, as evidence by a loss of Si_3N_4 phonon absorption, suggesting that the removal of the surface fluorine may not only be due to surface reaction through a direct exchange mechanism via pentavalent Si intermediate, but also to the hydrolyzation of Si_3N_4 itself through back-bond chemical attack by water. In addition to F, we find that there is also surface -NH_2 species, as evidenced by IR active -NH_2 bending modes at 1550 cm^{-1}, which we estimate to be only ~20 % monolayer from analysis of reaction with aldehyde molecules. However, this coverage appears sufficient to protect the Si_3N_4 surface. Finally, LEIS and XPS indicate that there is oxygen at the surface, which could either be in the form of -OH or Si-O-Si. Functionalization with alkylsiloxanes reveals that ~50 % of the surface contains Si-OH. In summary, the sum of the concentrations (50 %, 20 %, 50 % in ML), i.e. exceeding 1 ML, suggests that the etched surface may be atomically rough. Overall, these findings provide a method for selective deposition by using first aldehyde reaction for Si_3N_4 functionalization, followed by silane reaction for SiO_2 functionalization.

11:20am **SD+AS+EM-ThM11 Area Selective Deposition of Ultrathin Magnetic Cobalt Films via Atomic Layer Deposition***, **John Ekerdt**, H. Nallan, T. Ngo, S. Chopra, Z. Zhang*, University of Texas at Austin

Ferromagnetic thin films find applications in a variety of fields, such as electronics, spintronics, RF technology, energy, etc. With ever-decreasing device feature sizes, film conformity and crystalline structure become very important to determining magnetic properties. As such, atomic layer deposition (ALD) is a very attractive technique for magnetic film deposition as it ensures atomic level conformity. Since ALD film growth necessarily involves a film nucleation step, it is possible to engineer the surface energy of the substrate to cause preferential wetting and nucleation in only desired areas, resulting in area selective ALD (AS-ALD). Unlike conventional photolithography-based fabrication, a bottom-up patterning approach could eliminate the need for etch steps, reducing the cost of fabrication and overcoming scaling limitations in manufacturing devices. This work investigates the selective deposition of cobalt oxide via ALD that is subsequently reduced to carbon-free cobalt metal for use as the free magnetic layer within the magnetic tunnel junction of spin-transfer torque random access memory.

Alkylchlorosilanes and poly(trimethylsilylstyrene) are utilized to block water and cobalt bis(N-tert butyl, N'-ethylpropionamidinate) from an oxide substrate, such as silicon dioxide, hafnium dioxide and magnesium oxide, ensuring selective deposition of CoO films. Poly(trimethylsilylstyrene) is the half of a lamellar forming diblock copolymer that remains after self-assembly and feature development. The alkylchlorosilanes can be blanket deposited through the vapor phase or stamped onto the oxide surface using a poly(dimethylsiloxane) stamp. Cobalt oxide ALD proceeds on the exposed oxide surface. Strontium and Al are deposited atop the CoO films to scavenge oxygen during thermal annealing to yield cobalt metal films. Alternatively, reducing gases such as CO and H_2 can be employed as an oxygen sink during thermal reduction of CoO to Co metal. Finally, we demonstrate control over the tunability of the coercivity of the resultant films by controlling the reduction conditions.

11:40am **SD+AS+EM-ThM12 Area-Selective Al_2O_3 Pattern Grown by Atomic Layer Deposition***, **Seunggi Seo**, H. Jung, I.K. Oh, H. Kim,* Yonsei University, Republic of Korea*, J. Yoon, C. Yoo, H.-J. Kim, Y.-B. Lee*, LG Display Co., Ltd., Republic of Korea

Over many past years, area-selective atomic layer deposition (AS-ALD) has been developed for fabricating 3D nanostructures. ALD is a method to deposit thin films by self-limiting surface reactions between supplied gaseous precursors. Since ALD is a surface sensitive deposition technique, surface modification of substrate renders the deposition of films to be area-selective. Most previous studies on AS-ALD have utilized self-assembled monolayer (SAM), which inhibits the chemical reaction between substrate and precursors, so that the film cannot grow on SAM-coated area. AS-ALD has been studied on various materials, such as TiO_2, ZnO, and HfO_2. Although Al_2O_3 has been widely used for ALD, there is no experimental report on AS-ALD Al_2O_3 by using SAM. Rather, a previous report on the calculation of surface reactions between TMA and SAM by density functional theory (DFT) has been presented[1]. That paper describes that CH -terminated SAM shows no thermodynamic driving force for the reaction between them, leading to AS-ALD Al_2O_3 by using TMA.

In this work, we systematically investigated AS-ALD of Al_2O_3 on SAM in various conditions, such as SAM coating methods, the kinds of SAM and substrate, and ALD process parameters. Addressing previous calculation report, Al_2O_3 was deposited on CH_3-terminated SAM, octadecyltrichlorosilane (ODTS) and octadecylphosphonic acid (ODPA).

However, we observed Al_2O_3 layers were formed on SAM coated SiO_2 and Ti substrate, which is inconsistent with previous report. To clarify, we investigated ALD Al_2O_3 on SAM coated substrate by using various analytic techniques such as contact angle measurement, Fourier transform infrared spectroscopy, ellipsometry, X-ray photoelectron spectroscopy (XPS), X-ray-reflectometry (XRR), and α-scanning. We observed TMA was physisorbed on CH_3-terminated SAM, leading to Al_2O_3 deposition. Alternatively, we moved to our research toward the change of SAM coating methods, dipping and stamping, to lift both Al_2O_3 and underneath SAM coating off. Since stamping method is a faster process than dipping one, so that SAM by stamping might remain randomly distributed as forming weak bonding between SAMs and substrate. Moreover, we chose ODPA as a SAM due to its poor adsorption on SiO_2. We observed that both Al_2O_3 and its underneath ODPA stamped on SiO_2 were lifted-off from the substrate, resulting in area-selective Al_2O_3 pattern. This result opens a new way to patterning techniques for many areas of technology.

[1] Xu et al./ Chem. Mater. 2004, 16, 646-653

Selective Deposition as an Enabler of Self-Alignment Focus Topic
Room: 210F - Session SD+AS+EM+PS-ThA

Process Development for Selective Deposition and Self-aligned Patterning
Moderator: John Ekerdt, The University of Texas at Austin, Chuck Winter, Wayne State University

2:20pm **SD+AS+EM+PS-ThA1 Surface Chemistry Related to Selective Deposition**, ***Suvi Haukka***, ASM Microchemistry Ltd., Finland, *J.W. Maes*, ASM Belgium **INVITED**

The shrinking device dimensions in semiconductor manufacturing call for new innovative processing approaches. One of these considered is selective deposition which has gained increasing interest among semiconductor manufacturers today. Selective deposition would be highly beneficial in various ways, for instance, it would allow a decrease in lithography and etch steps reducing the cost of processing and enable enhanced scaling in narrow structures making bottom up fill possible. Chemical vapor deposition (CVD) and especially atomic layer deposition (ALD) as very surface sensitive techniques are considered enabling techniques.

Selective deposition typically deals with a selective deposition method where, for instance, a metal layer is selectively deposited on metal surface over dielectric surface, or a dielectric layer is selectively deposited on hydrophilic polymer over a more hydrophobic polymer. In most of the selective deposition schemes of today the passivation is used for the surface on which no deposition is desired. The most known method is to use SAM´s (self-assembled monolayers) which are silicon compounds with long carbon chains. Besides the SAM passivation of surfaces also the clever selection of precursors with built-in selectivity in certain process conditions could be applied.

In this paper, the chemistry challenges in the various selective deposition approaches and passivation means are reviewed. In addition, results from the selective deposition of metal on metal over dielectric surface in a Cu capping application and from selective strengthening of DSA (direct self-assembly) layers are presented.

3:00pm **SD+AS+EM+PS-ThA3 Selective Deposition - The New Patterning Paradigm?**, ***Florian Gstrein***, Intel Corporation **INVITED**

Top-down patterning techniques based on optical lithography have made consumer electronics ever more powerful, ubiquitous and affordable. This is largely due to the ability of lithographic techniques to transfer trillions of mask features to wafers at defect densities approaching virtually zero in high-volume manufacturing. While the resolution of optical lithography tools is typically considered to be the main challenge for continued device scaling, it is actually accurate pattern placement, which has emerged as the biggest concern. Novel bottom-up patterning approaches such as selective deposition are needed to overcome shortcomings in pattern placement accuracy.

The talk will first outline the challenges patterning processes based on 193i pitch division and EUV lithography face in terms of alignment accuracy and how complementary patterning techniques such as selective deposition can reduce pattern placement errors. One of the great challenges of selective deposition is defect mitigation, especially as the sensitivity to killer defects increases as device dimensions scale. Defect mitigation requires a fundamental understanding of the chemical selectivity of surfaces. While molecules can recognize chemical functionality on a surface, selective deposition processes based on atomic layer deposition (ALD) or chemical vapor deposition (CVD) are exceedingly rare and largely limited to specific precursors and substrates. For metal deposition, inherent selectivity was achieved through judicious precursor ligand design. Experimental results will be presented in the context of a theoretical investigations aimed at calculating the kinetic barriers that govern the selectivity of metal deposition. The use of self-assembled monolayers (SAMs) as passivants and/or blocking layers for subsequent deposition is an attractive way of overcoming the non-selectivity of many CVD or ALD processes. Here, the critical parameters for selective blocking are choice of the terminal group, surface termination, carbon chain length, and proper precursor choice. Using SAMs, selective deposition of dielectrics with respect to a variety of surfaces was achieved. The talk will conclude with our vision of how defects can be mitigated: It comprises a fundamental understanding of the chemical nature of the surface, precursors with high kinetic barriers for defect formation, passivation of defect nucleation sites, and the removal of defects post deposition. Selective deposition, if properly resourced and developed, can provide powerful means to future scaling and is one way of ensuring that patterning will continue to support Moore's Law in the foreseeable future.

4:00pm **SD+AS+EM+PS-ThA6 Area-Selective Molecular Layer Deposition: Enhanced Selectivity via Selective Etching**, ***Richard Closser***, *D.S. Bergsman, F.H. Minaye Hashemi, S.F. Bent*, Stanford University

Recent developments in electronic devices are pushing toward smaller and smaller features of both metal and dielectric patterns, along with a desire to produce selectively deposited organic thin films on such patterns. Techniques that allow for a high degree of control over the thickness and conformality of organic thin films, such as molecular layer deposition (MLD), are ideal candidates to meet these selective deposition requirements. Using MLD, several types of thin film polymers can be deposited with angstrom-level control due to the sequential, self-limiting surface reactions resulting in monomer-by-monomer growth. Selectivity in the MLD polymer growth is then achieved by utilizing the chemical functionally between the solid substrate surface and the gas phase monomer precursors.

Previously, we have shown the ability to selectively deposit thin film polymers by MLD onto pre-patterned metal and dielectric substrates by utilizing a blocking layer of octadecylphosphonic acid (ODPA) self-assembled monolayers (SAMs) that deposits onto metals more readily than onto dielectric films. Although this process can prevent MLD for up to 6 nm of deposition, selectivity of polymer growth is lost for thicker films, and therefore we are exploring new methods for increasing the MLD selectivity. For the current studies, ODPA SAM is deposited onto a patterned metal/dielectric (Cu on SiO_2) substrate to act as the MLD blocking layer. Once the SAM is fully deposited, polyurea films are grown onto the substrate by MLD to a desired thickness which can be controlled by the number of monomer dose cycles used. An acid etchant is then used to remove the surface oxide of the metal along with the SAM layer while leaving intact the polymer film deposited onto the dielectric. X-ray photoelectron spectroscopy, Auger electron spectroscopy, and ellipsometry measurements show that this process removes undesired MLD film that was deposited on the metal. Studies on patterned substrates confirm selective polymer film growth onto the dielectric over the metal. The etchant removal technique thus increases the selectivity of MLD growth by more than an order of magnitude when compared to the SAM blocking layer alone. Due to the increased selectivity with the etching based process, selective deposition of MLD films as thick as 12 nm have been demonstrated. Atomic force microscopy results show slight surface roughening due to etching while the bulk of the metal/dielectric pattern remains intact. This increase in MLD selectivity should allow for novel applications of selective polymer film deposition.

4:20pm **SD+AS+EM+PS-ThA7 Nucleation and Steady State ALD of Metallic Tin Using $SnCl_4$ and a Silyl Pyrazine Reducing Agent**, ***Eric Stevens***, *M.B. Mousa, G.N. Parsons*, North Carolina State University

Metal atomic layer deposition (ALD) processes are typically limited to noble, high work-function metals where uniform nucleation and conformal growth can be problematic. Recent work suggests that 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (DHP) could be an effective reducing agent for deposition of metals with highly negative electrochemical potentials. This work investigates DHP as a potential reducing agent for tin metal ALD using tin (IV) chloride ($SnCl_4$).

Experiments were carried out in a custom-built, hot-wall reactor using N_2 carrier gas, an operating pressure of 1.3 Torr, and temperatures between 130 and 170°C. The DHP source was heated to 70°C to maintain a vapor pressure ~1.2 Torr. Initial films were deposited at 130°C on silicon using a $SnCl_4/N_2/DHP/N_2$ exposure sequence of 4/50/10/50 seconds, then analyzed ex-situ by X-ray photoelectron spectroscopy (XPS) with Ar depth profiling. In sputtering deeper into the film, XPS exhibited both Sn-Sn and Sn-O peaks at 485 and 486.7 eV, respectively, where a decrease in Sn-O and an increase in Sn-Sn peak intensities suggests native oxidation of the film upon exposure to air. Furthermore, 7% Cl and 19% N were found in the films after sputtering, presumably from an incomplete reaction and/or incorporation of reaction byproducts.

To better understand surface reactions and growth mechanisms, we characterized the ALD process at 130, 150, and 170°C using *in situ* quadrupole mass spectrometry (QMS) and quartz crystal microbalance (QCM). QCM analysis at 130 and 150°C showed continued growth with extended exposures, consistent with non-ALD growth. Deposition at 170 °C was more repeatable and more closely approached surface saturation. At 170°C, QCM showed a clear mass increase during the $SnCl_4$ dose and a corresponding mass decrease during the DHP dose, consistent with DHP

removing Cl and reducing the Sn-Cl surface. Moreover, the QMS results showed peaks exclusively during DHP doses at m/z values of 80 (pyrazine) and 65, 93, 95 (trimethylsilyl chloride), which are the most probable byproducts of DHP reacting with a chlorinated surface.

Using gold-coated QCM crystals at 170°C, Sn growth proceeds slowly for the first ~150 ALD cycles, whereas growth on QCM crystals previously coated with Sn show a more rapid transition to steady-state growth (<20 cycles). We are currently investigating the nucleation on different substrates and how process conditions can be tuned to achieve selective deposition. Understanding the surface reaction and growth mechanisms of tin metal deposition using DHP could provide a foundation for deposition of metal thin-films that were previously unattainable.

4:40pm **SD+AS+EM+PS-ThA8 Determination of the Minimum Saturating Dose during Atomic Layer Deposition of Alumina and Titania on Si(100) and Si(100)-H**, *D. Dick,* University of Texas at Dallas*,* ***Joshua Ballard****, J. Randall,* Zyvex Labs*, Y.J. Chabal*, University of Texas at Dallas

Atomic layer deposition (ALD) has become an important process step in semiconductor manufacturing, where the self-limiting nature of each step of the process permits atomic scale control over the ultimate layer thickness in addition to relatively fast processing with high pressure reactors. However, it has been shown that ALD can be used to selectively deposit material onto patterned surfaces, requiring not only saturation of each deposition cycle in desired areas but also suppression of deposition in those areas where it is undesirable. One mechanism for improving practical selectivity would be to find the minimum exposure that is saturates the growth where desired in order to avoid excess overall reaction probability in areas where inhibited growth is preferred.

To investigate this, we have examined the deposition in vacuum (“UHV ALD”) of Al_2O_3 and TiO_2 with TMA and $TiCl_4$, respectively, on both hydrophobic, H-terminated Si(100) surfaces and hydrophilic OH-terminated Si(100) surfaces prepared by H_2O exposure of clean Si(100)-(2x1) surfaces. Surface reactions and relative coverages are determined by in-situ IR spectroscopy, and ex-situ XPS. We find that good selectivity can be achieved at 150ºC. Preliminary data and calculations also suggest that an initial wetting layer of TMA on clean Si(100) promotes subsequent growth of TiO_2 or other high-k dielectrics. Finally, we will discuss how these findings have made it possible to develop a full multi-cycle process for a custom low-pressure ALD system equipped with scanning tunneling microscopy and atomic force microscopy.

5:00pm **SD+AS+EM+PS-ThA9 Selective Growth of GeSbTe Phase-Changing Materials Utilizing Self-Aligned Confined Structure**, ***ByungJoon Choi****,* Seoul National University of Science and Technology, Republic of Korea*, T. Eom, C.S. Hwang*, Seoul National University, Republic of Korea

GST Phase changing material, typically GeTe–Sb_2Te_3 pseudo-binary solid solution, has been extensively studied for rewritable digital versatile optical disks or phase change random access memory (PcRAM), on account of the drastic change of its optical reflectivity or electrical resistivity between amorphous and crystalline phases. As the device size of PcRAM is scaled down, GST materials should be confined into the contact-plug for reducing its programming current, which cannot be achieved by any physical deposition method.

Among the various metal-organic (MO) precursors, the combination of $Ge(iBu)_4$, $Sb(iPr)_3$ and $Te(iPr)_2$ has been extensively studied for plasma enhanced chemical vapor depostion or its variant methods with plasma-activated H_2 gas as a reducing agent of the MO-precursors. Plasma-enhanced pulsed CVD was attempted using the precursor pulse sequence consisting of Sb–Te–Ge–Te cycles (each elemental cycle is composed of precursor injection and Ar + H_2 plasma reduction steps). The chemical composition of the films was appropriately controlled by the cycle ratio and sequence of each precursor pulse. The linear growth with the number of cycles was shown, and the GPC (growth-per-cycle, i. e. growth rate) was determined to be 0.73 nm/super-cycle from the slope at a wafer temperature of 200˚C.

Strong substrate dependency can be utilized in the selective growth of GST material on a TiN contact-plug formed in the SiO_2 inter-layer dielectric (ILD). Higher selectivity (difference of GPC) between TiN contact-plug and SiO_2 ILD layer was achieved by pulsed CVD with increasing the amount of $Te(iPr)_2$ injection. The reason for the selective growth was believed to have originated from the adverse interference of the residual gas (unreacted $Te(iPr)_2$ or its derivatives) to the chemical adsorption of Sb nuclei on the SiO_2 surface, which functions as a nucleation site for further GST growth. It was reported that amide-based Ge precursors also showed strong selectivity at a particular temperature, enabling Sb and Te precursors to be chemisorbed on the Ge seed layer, which could be utilized for selective growth of GST.

The most feasible explanation for the substrate-dependent growth behavior of the GST film is the electron donation from the substrate, which would enhance the precursor decomposition and removal of ligands from the adsorbed precursor molecules. The nucleation and growth behaviors of the GST films were studied on Si substrates with various nucleation or buffer layers. It turned out that the types of substrates have a crucial impact on the nucleation behaviors and the chemical composition of the film.

5:20pm **SD+AS+EM+PS-ThA10 Toward an All- Vapor Process for Area Selective Atomic Layer Deposition***,* ***FatemehSadat Hashemi****, S.F. Bent*, Stanford University

Modern electronic devices containing planar and 3-D structures utilize a number of metal/dielectric patterns in both the front and back end. The scaling of next generation electronic devices makes achieving these patterns increasingly difficult and motivates the development of novel processing methods. One such method−area selective deposition−has the opportunity to play an important role in significantly reducing process complexities associated with current top-down fabrication of patterned structures by eliminating some of the deposition and etching steps that are time-consuming and expensive.

Atomic layer deposition (ALD) is a good choice for area selective deposition because its chemical specificity provides a means to achieve selectivity on a spatially patterned substrate. Area selective ALD, reported previously by several groups, requires improvements for the process to be compatible with current device fabrication goals. Most previous studies of area selective ALD have achieved deposited thicknesses on the order of only a few nanometers and the selectivity was generally obtained by passivation of the surface using self-assembled monolayers (SAMs) in the regions where ALD was not desired. Existing methods are usually performed by dipping the substrates into a solution containing the SAM-forming molecules for several hours. A more desirable all-vapor process would require vapor delivery of the SAMs. This method would provide better SAM coverage on porous or three-dimensional structures, potentially decreasing the required deposition time for the passivation layer, and allowing the SAM passivation step to be integrated with the rest of the ALD process.

In this work, we investigate area selective dielectric-on-dielectric deposition by selectively depositing organic alkanethiol SAM as the blocking layer on metal parts of a metal/dielectric (Cu/SiO_2) pattern. We compare area-selective ALD achieved by introduction of the thiolate SAM in both the solution and vapor phase. We show that while in both cases the SAM can prevent subsequent deposition of metal oxide dielectric films via ALD, vapor deposition provides stronger passivation in a shorter exposure process on the metal. We also report results on regenerating the thiol SAM protecting layer from the vapor phase between ALD cycles and show that this approach is effective in improving the blocking properties of the SAM on Cu. This strategy provides the ability to significantly improve selective deposition of dielectrics. Moreover, it is a significant step toward an all-vapor process for area selective deposition, opening up the possibility for new applications in next generation electronic devices.

5:40pm **SD+AS+EM+PS-ThA11 Selective Deposition of ALD Metal oxides and Metal Thin Films by Fab-Friendly Surface Treatments***,* ***Kandabara Tapily****, K.-H. Yu, S. Consiglio, R. Clark, D. O'Meara, C. Wajda, G. Leusink*, TEL Technology Center, America, LLC

For the last 5 decades, the semiconductor industry has relied on the continued scaling down of the device feature size in order to improve performance and increase bit density according to Moore’s law. However, with the delay in implementation of extreme ultraviolet lithography (EUV) in high volume manufacturing,[1] patterning beyond the 14 nm technology node is getting extremely difficult to manage due to the overlay control and the increase in manufacturing cost due to multi-layer alignments. In order to keep reducing the device feature size, new patterning solutions are needed such as selective deposition and selective etching of materials. Atomic layer deposition (ALD) has emerged as one of the leading film deposition techniques as a result of the semiconductor device scaling.[2] ALD provides excellent film control, uniformity and high conformality. ALD is highly surface reaction driven and it is possible to modify the substrate surface to activate or deactivate growth on selected area hence selective-area ALD (SA-ALD). Selective-area ALD can simplify and reduce the high manufacturing cost associated with highly aggressive patterning schemes by eliminating certain lithography steps. Thin films can now be selectively deposited or removed from a desired area. Most selective-area ALD studies in the literature are conducted with the use of self-assembled monolayers (SAMs) in order to deactivate or activate growth on certain areas.[3-5] SAMs are thin organic films that form spontaneously in tightly packed oriented molecules on solid surfaces. A key enabler of SAMs is the ability to turn these organic layers into patterned layers. However, thermal stability and the slow formation process into well packed layer are some of the major drawbacks of SAMs.[5]

In this study, a non SAMs based approach was used to inhibit ALD growth of metals and metal oxides. Using different surface treatments, it was observed the growth of the ALD thin films can be modulated, see Fig.1 and Fig.2 respectively. ALD Al_2O_3 growth was suppressed by a combination of the vapor HF and cyclical low temperature plasma hydrogen treatment and deposition. Additionally, ALD TaN growth was also inhibited by the use of a combination trimethylsilane (TMS) and dimethylamine (DMA) treatment of the surface prior to ALD deposition.

Reference

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Authors Index

Bold page numbers indicate the presenter

— A —

Abelson, J.R.: SD+AS+EM-ThM2, 1

— B —

Babar, S.: SD+AS+EM-ThM2, 1
Ballard, J.: SD+AS+EM+PS-ThA8, **4**
Bent, S.F.: SD+AS+EM+PS-ThA10, 4; SD+AS+EM+PS-ThA6, 3
Bergsman, D.S.: SD+AS+EM+PS-ThA6, 3

— C —

Cabrera, W.: SD+AS+EM-ThM10, 2
Chabal, Y.J.: SD+AS+EM+PS-ThA8, 4; SD+AS+EM-ThM10, **2**
Chen, J.-R.: SD+AS+EM-ThM1, 1
Choi, B.J.: SD+AS+EM+PS-ThA9, **4**
Chopra, S.: SD+AS+EM-ThM11, 2
Clark, R.: SD+AS+EM+PS-ThA11, 4
Closser, R.G.: SD+AS+EM+PS-ThA6, **3**
Consiglio, S.: SD+AS+EM+PS-ThA11, 4

— D —

Dick, D.: SD+AS+EM+PS-ThA8, 4; SD+AS+EM-ThM10, 2

— E —

Ekerdt, J.: SD+AS+EM-ThM11, **2**
Engstrom, J.R.: SD+AS+EM-ThM1, **1**
Eom, T.: SD+AS+EM+PS-ThA9, 4

— G —

Girolami, G.S.: SD+AS+EM-ThM2, 1
Gordon, R.: SD+AS+EM-ThM3, **1**
Gstrein, F.: SD+AS+EM+PS-ThA3, **3**

— H —

Halls, M.D.: SD+AS+EM-ThM10, 2
Hashemi, F.H.: SD+AS+EM+PS-ThA10, **4**
Haukka, S.: SD+AS+EM+PS-ThA1, **3**
Hourani, R.: SD+AS+EM-ThM10, 2
Hwang, C.S.: SD+AS+EM+PS-ThA9, 4

— J —

Jung, H.: SD+AS+EM-ThM12, 2

— K —

Kim, H.: SD+AS+EM-ThM12, 2
Kim, H.-J.: SD+AS+EM-ThM12, 2

— L —

Lee, Y.-B.: SD+AS+EM-ThM12, 2
Leusink, G.: SD+AS+EM+PS-ThA11, 4
Liu, L.-H.: SD+AS+EM-ThM10, 2

— M —

Maes, J.W.: SD+AS+EM+PS-ThA1, 3
Michalak, D.J.: SD+AS+EM-ThM10, 2
Minaye Hashemi, F.H.: SD+AS+EM+PS-ThA6, 3
Mohimi, E.: SD+AS+EM-ThM2, **1**
Mousa, M.B.: SD+AS+EM+PS-ThA7, 3

— N —

Nallan, H.: SD+AS+EM-ThM11, 2
Ngo, T.: SD+AS+EM-ThM11, 2

— O —

Oh, I.K.: SD+AS+EM-ThM12, 2
O'Meara, D.: SD+AS+EM+PS-ThA11, 4

— P —

Parsons, G.N.: SD+AS+EM+PS-ThA7, 3
Peixoto, T.: SD+AS+EM-ThM10, 2
Pujar, S.P.: SD+AS+EM-ThM10, 2

— R —

Randall, J.: SD+AS+EM+PS-ThA8, 4

— S —

Seo, S.: SD+AS+EM-ThM12, **2**
Stevens, E.: SD+AS+EM+PS-ThA7, **3**

— T —

Tapily, K.: SD+AS+EM+PS-ThA11, **4**
Trinh, B.: SD+AS+EM-ThM2, 1

— V —

Veyan, J.-F.: SD+AS+EM-ThM10, 2

— W —

Wajda, C.: SD+AS+EM+PS-ThA11, 4
Winter, C.H.: SD+AS+EM-ThM5, **1**

— Y —

Yoo, C.: SD+AS+EM-ThM12, 2
Yoon, J.: SD+AS+EM-ThM12, 2
Yu, K.-H.: SD+AS+EM+PS-ThA11, 4

— Z —

Zhang, W.: SD+AS+EM-ThM1, 1
Zhang, Z.: SD+AS+EM-ThM11, 2
Zuilhof, H.: SD+AS+EM-ThM10, 2