ASD17

2ND AREA SELECTIVE DEPOSITION WORKSHOP

AREA SELECTIVE DEPOSITION WORKSHOP 2017

20-21 April, 2017
Eindhoven, The Netherlands

TU/e Technische Universiteit
Eindhoven
University of Technology

COST action MP1402
HERALD
Hooking together European Research in Atomic Layer Deposition

Program - 2nd Area Selective Deposition workshop - ASD2017 – April 21

8.00 - 9.00	Registration & coffee			
9.00 - 9.10	Welcome		Adrie Mackus	Eindhoven University of Technology
9.10 – 9.50	Session chair: Erwin Kessels	New strategies for area selective deposition	Stacey F. Bent	Stanford University
9.50 - 10.30		Perfectly selective thin film CVD using inhibitor molecules	John R. Abelson	University of Illinois at Urbana-Champaign
10.30 - 11.00	Break & posters			
11.00 - 11.40	Session chair: Simon Elliott	Insight in nucleation mechanisms of semiconducting 2D metal sulfides and application to area selective deposition	Annelies Delabie	IMEC, KU Leuven
11.40 - 12.20		Design and synthesis of catalytic nanoparticles via area selective atomic layer deposition	Rong Chen	Huazhong University of Science and Technology
12.20 - 13.00		Understanding selectivity in thermal atomic layer etching using sequential, self-limiting fluorination and ligand-exchange reactions	Younghee Lee	University of Colorado at Boulder
13.00 - 14.15	Lunch & poster session			
14.15 - 14.35	Session chair: Stacey Bent	Advanced process technologies for sub-10 nm patterning	Gert Leusink	TEL Technology Center
14.35 - 14.50		Effects of hydroxyl density and metal oxide composition on inherent substrate selective ALD of tungsten	Paul C. Lemaire	North Carolina State University
14.50 - 15.05		Area-selective ALD of silicon oxide using acetylacetone as inhibitor in a three-step cycle	Alfredo Mameli	Eindhoven University of Technology
15.05 - 15.20		Investigating the difference in nucleation of silicon-based materials Si, Si_3N_4, SiO_2 and C-doped SiO_2 during PECVD/PEALD for future selective area deposition (S-ALD)	Ekaterina A. Filatova	Tyndall National Institute
15.20 - 15.45	Break			
15.45 - 16.05	Session chair: Dennis Hausmann	Selective CVD metal deposition for nano device fabrication	Son Van Nguyen	IBM Semiconductor Research
16.05 - 16.20		Area selective Ru ALD for sub 7 nm bottom-up metal interconnects	Ivan Zyulkov	KU Leuven, IMEC
16.20 - 16.35		Area selective deposition of metal films	John G. Ekerdt	Universtiy of Texas at Austin
16.35 - 16.55		Selective deposition: a materials supplier’s perspective	Jean-Marc Girard	Air Liquide Advanced Materials
16.55 - 17.20	Break			
17.20 - 17.40	Session chair: Soley Ozer	Strategies for area selective atomic layer deposition	Jan Willem Maes	ASM Belgium
17.40 - 17.55		Selective deposition using the inherent substrate-dependent growth initiation based on nucleation delay and on the joint use of plasma etching mode	Remy Gassillouda	CEA, LETI
17.55 - 18.15		Applications of area selective deposition	David Thompson	Applied Materials
18.15 - 19.00	Moderators: Gregory Parsons, Adrie Mackus	Discussion session		
19.00 - 21.00	Drinks & snacks			

Invited academia	Invited industry	Contributed

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2ND AREA SELECTIVE DEPOSITION WORKSHOP

ORAL PRESENTATIONS

TU/e Technische Universiteit Eindhoven University of Technology

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Hooking together European Research in Atomic Layer Deposition

New strategies for area selective deposition

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With the growing need for fabrication of nanostructures, selective deposition is likely to become an important process to achieve pattern features at the ~10 nm length scale. Both two-dimensional planar geometries and three-dimensional structures will benefit from selective deposition processes, with bottom-up growth strategies providing advantages in reduced process complexity and improved pattern fidelity. In this presentation, we will describe area selective deposition based on atomic layer deposition (ALD). ALD is a good choice for selective deposition because its chemical specificity provides a means to achieve selectivity on a spatially patterned substrate. Typically, in area selective ALD, self-assembled monolayers (SAMs) are used to passivate the surface, using SAMs in the regions where deposition is not desired. We will show that the process provides good selectivity for thin deposited films. However, a major challenge is that area selective ALD processes typically break down after more than a few nanometers of material is deposited, degrading the selectivity between active and passive regions of the substrate. We will describe new strategies to overcome the growth on the SAM and achieve significantly higher selectivity in area selective ALD. In one approach, to improve the blocking properties of the SAM on copper surfaces, the SAM is repaired between ALD cycles with the purpose of recovering the SAM's properties. In a second approach, a "self-correcting" process is developed in which selective deposition is combined with selective etching, greatly improving the final selectivity. With both approaches, selective ALD of more than 60 nm of metal oxide dielectric material can be achieved. We also introduce a third strategy in which the substrate surface is modified by ion implantation of fluorocarbons, enabling topographically selective ALD. In this process, we demonstrate selective anisotropic deposition in which Pt deposition is inhibited on horizontal regions but active on vertical surfaces. Future directions in area selective ALD will also be discussed.

Perfectly Selective Thin Film CVD Using Inhibitor Molecules

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The nucleation and growth of thin films by chemical vapor deposition (CVD) can be strongly modified by the *continuous* addition of molecular species that adsorb on the growth surface and inhibit precursor adsorption or reaction. These species, termed *inhibitors*, have only a temporary residence time: they may adsorb intact, block precursor adsorption, and thermally desorb; or they may dissociate upon adsorption, react with adsorbed precursor or its ligands, and thermally desorb as new species. The quantity of inhibitor on the surface – and thus the degree of growth modification – is controlled by adjusting the inhibitor partial pressure, typically 0.1 – 10 mTorr, at a substrate temperature < 300 °C such that the various adsorbates do not crack into involatile products, except for the desired film growth.

We previously employed different variants of the inhibition effect in CVD to afford (i) extraordinarily conformal films in high aspect ratio structures, (ii) nearly conformal films using precursors that are give non-conformal deposits when used alone, (iii) superconformal filling of deep structures, and (iv) control over the density and size distribution of nuclei on dielectric substrates.

Here, we describe the use of inhibitors to afford perfectly selective growth of metallic materials on various substrates. Selectivity depends on strict elimination of the formation of film nuclei. A surface treatment carried out prior to film growth can greatly improve selectivity, but is subject to statistical failure. By contrast, the continuous dosing of the inhibitor during CVD provides a robust solution.

CVD of copper films is carried out using the Cu(hfac)VTMS precursor. Two sequential reactions take place: upon adsorption the VTMS ligand detaches and desorbs; then two adsorbed Cu(hfac) species react by disproportionation to deposit one Cu atom and desorb one $Cu(hfac)_2$. Disproportionation is rapid on metal substrates, because they facilitate charge exchange, but is slow on dielectrics. We add excess VTMS as the inhibitor to provide selectivity; it recombines with adsorbed Cu(hfac) to reconstitute the Cu(hfac)VTMS precursor which desorbs. On metal substrates the inhibitor reduces the copper growth rate by a factor of ~ 4. But on dielectrics, the VTMS scours Cu(hfac) off the surface prior to disproportionation and halts all nucleation. This approach works even on challenging substrates such as carbon-doped SiO_2.

We also describe emerging work on the CVD of metal carbides and nitrides for which the use of an inhibitor can controllably switch the nucleation behavior – and thus the selectivity – on various substrates.

Insight in nucleation mechanisms of semiconducting 2D metal sulfides and application to area selective deposition

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Semiconducting 2D transition metal dichalcogendes (TMDs) like MoS2 and WS2 are attracting interest for ultra-scaled nano-electronic devices because of their monolayer thickness, large band gap values, low dielectric constants, lack of dangling bonds and structural stability. Enabling integration in devices requires the development of deposition techniques that provide TMDs with good structural quality and monolayer growth control on large area substrates. In addition, some applications require a low thermal budget due to the presence of temperature sensitive structures. 2D TMDs can be synthesized by Chemical Vapor Deposition (CVD) or Atomic Layer Deposition (ALD) in top-down or bottom-up approaches (with or without transfer). Achieving high quality structures and good semiconductor properties remains challenging for direct deposition at low temperature. 2D TMDs deposited at low deposition temperature are polycrystalline in the absence of a template for epitaxial seeding, and grain boundaries can degrade the carrier mobility. In this respect, bottom-up synthesis approaches based on selective deposition are attractive. The idea is to grow the single crystal 2D TMDs only where needed in the device structure and keep the grain boundaries or defective structures outside the electrically active region by controlled seeding and selective lateral growth. However, the design of such processes requires a thorough understanding of the growth and nucleation mechanisms of 2D TMDs.

This presentation will review our insights in the nucleation and growth mechanisms of semiconducting 2D metal sulfides by CVD and ALD, and the insights are applied to demonstrate selective deposition. We focus on metal halide precursors ($SnCl_4$, WF_6) and H_2S in view of the potential for high purity films, mild deposition temperatures and selectivity. WS_2 and SnS_2 have a layered hexagonal structure, while SnS has a double layered orthorhombic structure. WF_6 is an interesting precursor for area selective deposition as the WS_2 CVD is surface mediated at low deposition temperatures. This enables area selective deposition based on conversion of sacrificial patterns, a new concept for area selective deposition. Careful control of the growth kinetics in SnS and SnS_2 CVD enables directional growth. Due to the higher reactivity of the crystal edges as compared to basal planes, the crystals can grow mainly in the lateral direction. As a consequence of the lack of reactive sites on the basal planes, the vertical growth rate can be several orders of magnitude lower.

Design and synthesis of catalytic nanoparticles via area selective atomic layer deposition

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Supported metal nanoparticles are among the most important catalysts for many practical reactions. The catalytic performance strongly depends on the size, composition, and structure of the metal nanoparticles, as well as the surrounding supports. A promising new method of catalyst synthesis is atomic layer deposition (ALD). ALD is a variation of chemical vapor deposition wherein materials are deposited on targeted surfaces via a sequential self-limiting reaction. The self-limiting nature ensures highly conformal and uniform deposition over high aspect ratio surfaces. Combined with surface modifications, it is possible to achieve 3D control of metals, oxides, and other compound materials growth via area-selective ALD. Hence, design and synthesis of advanced catalysts at the nanoscale becomes possible through precise control over the size and composition of nanoparticles, the catalytic active surfaces, and the structure of protective layer. In this presentation, the application of area-selective ALD to synthesize selective oxide overcoats through both area deactivation and inherent selectivity will be described. With atomically-precise thickness control and unique structure of oxides overcoats to stabilize metal nanoparticles, enhanced catalytic activity and stability could be achieved.

Understanding Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions

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Selectivity in etching is required to remove one material in the presence of other different materials. Selectivity in atomic layer etching (ALE) is important for advanced semiconductor fabrication. Selective ALE, together with area selective atomic layer deposition (AS-ALD), could be useful for maskless fabrication of advanced devices. ALE could help AS-ALD achieve better selectivity by removing unwanted ALD nucleation from the material that is being selected against. Unlike plasma-based ALE processes, thermal ALE can also be accomplished using chemical reactions that enable selectivity without surface damage.

This talk will examine the etching of a number of important semiconductor materials including Al_2O_3, HfO_2, ZrO_2, SiO_2, Si_3N_4, and TiN. Thermal ALE can be defined by sequential, self-limiting fluorination and ligand-exchange reactions.[1] Fluorination is achieved using HF as the fluorine reactant. Different metal precursors provide various ligands that may transfer during ligand-exchange. Etching occurs when the transferred ligands produce stable and volatile metal products that may leave the surface. The metal precursors are tin(II) acetylacetonate ($Sn(acac)_2$), trimethylaluminum (TMA), dimethylaluminum chloride (DMAC), and $SiCl_4$.[2] These metal precursors provide acac, methyl, and chloride ligands for ligand exchange. Spectroscopic ellipsometry and quartz crystal microbalance (QCM) were used to investigate the etch rates and the reaction mechanism.

The spectroscopic ellipsometry measurements together with QCM studies revealed that HfO_2 was etched by all of the metal precursors. Al_2O_3 was etched by all of the metal precursors except $SiCl_4$. ZrO_2 was etched by all of the metal precursors except TMA. In contrast, SiO_2, Si_3N_4, and TiN were not etched by any of these metal precursors. These results can be understood by the stability and volatility of the possible etch products. Temperature can also be used to obtain selective thermal ALE. The combination of different metal precursors with various ligands and different temperatures can provide multiple pathways for selective thermal ALE.

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Advanced Process Technologies for sub-10nm Patterning

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For the past half-century the semiconductor market has expanded continuously along with drastic reduction in bit cost, mostly driven by continuous scaling of semiconductor devices. Historically, advancement of lithographic technology was the major enabler for the regular cadence of areal shrinkage. For the past decade, multi-patterning technologies were introduced to assist lithography for continuous scaling and concepts for atomic scale process control were introduced to further advanced patterning of complex device structures. It is expected that multi-patterning along with atomic scale process technologies will continue to be required to complement EUV when it is introduced as the next generation lithographic light source[1].

Key patterning challenges for future nodes include edge placement accuracy for multiple patterning, edge roughness of lines and holes, alignment of multiple layers, implementation of new materials, adoption of new lithographic technologies like EUV and overall low cost and high yield solutions. To address the key patterning challenges, atomic scale process technologies based on concepts that are self-limiting, self-aligning and self-directing are all being developed in concert. Area selective deposition represents a special class of processes where material is deposited only on a specific desired surface or material. This allows integrators to position dielectrics and metals only where they are needed in a 'bottom-up' scheme and thus avoiding cost or performance limitations of traditional 'top-down' patterning methods. Indeed area selective atomic layer deposition and etch processes are being developed that are self-limited, self-aligned and self-directed. Such processes can not only simplify existing manufacturing flows, but may also enable new integration schemes that will help to continue system performance and cost scaling into the future[1-3].

In this presentation, we will provide an overview of the latest integrated process technologies and how atomic scale processes including area selective deposition may be used to overcome patterning limits at sub-10nm generation.

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2) *A. J. M. Mackus, A. A. Bol and W. M. M. Kessels, Nanoscale, 2014, 6, 10941-10960*
3) *K. Tapily, K. Yu, S. Consiglio, R. D. Clark, D. O'Meara, C. Wajda, and G. Leusink, AVS Focus Topic Selective Deposition, San Jose 2015*

Effects of Hydroxyl Density and Metal Oxide Composition on Inherent Substrate Selective ALD of Tungsten

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Area-selective thin film deposition is expected to be important for advanced sub-10 nanometer semiconductor devices, enabling feature patterning, alignment to underlying structures and edge definition. Several atomic layer deposition (ALD) processes show inherent propensity for substrate-dependent nucleation. This includes tungsten ALD (W-ALD) which is more energetically favorable on Si than on SiO_2. However, the selectivity is often lost after several ALD cycles. We investigated the causes of tungsten nucleation on SiO_2 and other "non-growth" surfaces during the WF_6/SiH_4 W-ALD process to determine how to expand the "selectivity window." We propose that hydroxyls, generated during the piranha clean, act as nucleation sites for non-selective deposition and show that by excluding the piranha clean or heating the samples, following the piranha clean, extends the tungsten selectivity window. We also assessed how the W-ALD precursors interact with different oxide substrates though individual WF_6 and SiH_4 pre-exposures prior to W-ALD deposition. We conclude that repeated SiH_4 pre-exposures reduce the tungsten nucleation delay, which is attributed to SiH_4 adsorption on hydroxyl sites. In addition, oxide surfaces were repeatedly exposed to WF_6, which appears to form metal fluoride species. We attribute the different tungsten nucleation delay on Al_2O_3 and TiO_2 to the formation of nonvolatile and volatile metal fluoride species respectively. Finally, using our understanding of the W-ALD nucleation and substrate selectivity, we briefly show how the process pressure and temperature can be adjusted to widen the selectivity window.

Area-selective ALD of silicon oxide using acetylacetone as inhibitor in a three-step cycle

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Area-selective ALD (AS-ALD) is currently attracting renewed attention because of its potential application in self-aligned fabrication flowcharts. In this work, a new AS-ALD approach is introduced, which exploits inhibitor molecules, dosed in a three-step (ABC) cycle, to prevent precursor adsorption only on certain surfaces. This approach is inspired by previous work in which similar inhibitor molecules were used to enhance the doping efficiency of ALD-grown films by blocking adsorption sites,[1] and by the use of inhibitor molecules in area-selective CVD.[2] AS-ALD can be obtained using an ABC ALD process, in case the inhibitor molecule selectively adsorbs on specific materials (step A), thereby blocking the precursor adsorption in the subsequent pulse (step B).

AS-ALD of SiO_2 has been demonstrated for an ALD process consisting of acetylacetone (Hacac) inhibitor (A), $H_2Si[N(C_2H_5)_2]_2$ precursor (B), and O_2 plasma (C) pulses. This process resulted in immediate growth with a rate of 0.09 nm/cycle on GeO_2 and SiO_2, and significant nucleation delays on Al_2O_3, HfO_2, and TiO_2 (see Figure 1), as determined from *in-situ* spectroscopic ellipsometry measurements and corroborated by XPS analysis (for GeO_2 and Al_2O_3). Density functional theory (DFT) simulations suggest that Hacac adsorbs readily on Al_2O_3, while the adsorption on SiO_2 itself is an endothermic reaction with a high activation energy barrier. *In-situ* Fourier transform infrared spectroscopy (FTIR) studies confirmed that Hacac chemisorbs on Al_2O_3 and blocks $H_2Si[N(C_2H_5)_2]_2$ precursor adsorption. Conversely, only a small amount of Hacac adsorption was detected on SiO_2. To further prove the feasibility of this process, AS-ALD growth of SiO_2 was demonstrated on samples with patterned Al_2O_3 on GeO_2.

A unique feature of this new approach for AS-ALD is that it distinguishes between the growth on different metal oxide surfaces (e.g. GeO_2, SiO_2 versus Al_2O_3, HfO_2, TiO_2). Moreover, in contrast to most other AS-ALD approaches, it is compatible with plasma-assisted or ozone-based ALD. Both of these features open up new application opportunities for AS-ALD. It is expected that the approach can be extended to other materials, and potentially allows for tuning the selectivity by selecting suitable inhibitor molecules.

[1] A. Yanguas-Gil, J.A. Libera, and J.W. Elam, Chem. Mater. **25**, 4849 (2013).
[2] S. Babar, E. Mohimi, B. Trinh, G. S. Girolami and J. R. Abelson, ECS J. Solid State Sci. and Technol., **4** N60-N63 (2015).

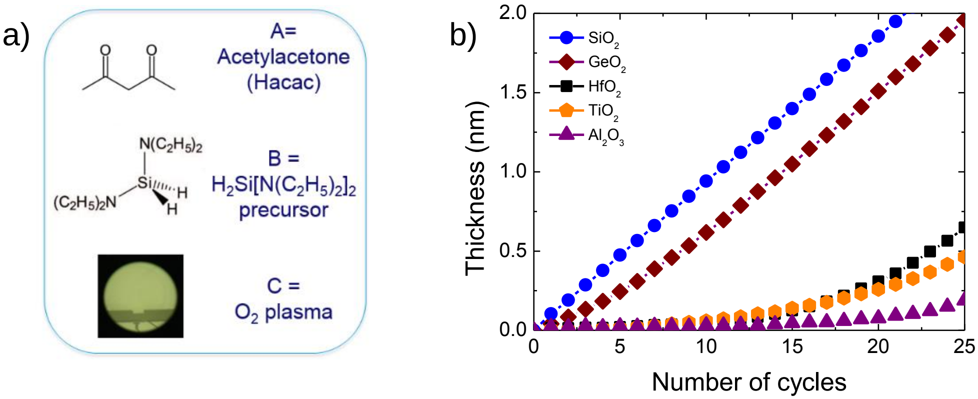

Figure 1. (a) The ABC cycle for area-selective ALD of SiO_2. (b) Nucleation curves for SiO_2 ABC ALD cycles on different substrate materials.

Investigating the difference in nucleation of silicon-based materials Si, Si_3N_4, SiO_2 and C-doped SiO_2 during PECVD/PEALD for future selective area deposition (S-ALD)

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Area-selective atomic layer deposition (S-ALD) allows nanostructures of arbitrary shape and composition to be built with atomic precision. Most current approaches for S-ALD are based on local inhibition (e.g. with self-assembled monolayers) or activation. However, these blocking/activation layers have limited lateral resolution. For this reason, exploiting inherent differences in nucleation on different substrates is of crucial importance for developing future S-ALD processes. We are focussing on the silicon-based materials Si, Si_3N_4, SiO_2 and C-doped SiO_2, which are low-permittivity dielectrics used in electronics for various barrier applications.

It has been found that the Si-NH_x surface of Si_3N_4 is inert with respect to dissociative adsorption of Si precursors in thermal and NH_3-plasma ALD, but reactive after treatment with N_2-plasma[1], whereas the Si-OH surface of SiO_2 is reactive. We are using *ab initio* modelling to examine more closely the reasons for this selectivity. We investigate the difference in nucleation on Si-OH and Si-NH_x substrates during exposure by amide ($SiH_3(NR_2)$) and chloride ($SiCl_4$) precursors by calculating their adsorption and activation energies.[2] We explain that the lower reactivity of the amide precursor on the NH_2-Si_3N_4 surface compared to the OH-SiO_2 surface is due to the orientation of the hydrogen atoms, where incoming precursors approach the OH group vertically and approach the NH_2 group side-on.

It seems counter-intuitive to expect selectivity in plasma deposition processes, but the computational evidence suggests that it may be possible. We compute the reaction mechanism and kinetic parameters of silane plasma species (SiH_2 and SiH_3) with surface sites in order to see if there is selectivity towards H-Si or H-C. We find that both SiH_3 and SiH_2 show selectivity that favours insertion into the Si-H surface bond, rather than the C-H bond. In fact, SiH_2 is computed to show no barrier for insertion into the Si-H bond. The reason seems to lie in the formation of an Si(surface)-H-Si(silylene) 3c2e bond, maintaining a near-singlet spin state throughout. This reaction therefore leads to unlimited growth of Si-Si bonds and so is not self-limiting in the ALD sense. By contrast, we find that a barrier of 0.41 eV exists for the SiH_3 radical to strip the H from the Si-H bond and produce silane, which seems to be due to homolytic cleavage of Si-H. The barriers are much higher for C-H cleavage. We conclude that this could facilitate area-selective PECVD of Si onto Si-H, and not onto the C-H of C-doped oxide.

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2. Murray, Ciaran A. ; Elliott, Simon D.; Hausmann, Dennis; Henri, Jon; LaVoie, Adrien, *ACS Applied Materials and Interfaces* **2014,** 6, 10534-10541.

Selective CVD metal deposition for nano device fabrication

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Selective chemical vapor deposition of metal such as Tungsten has been evaluated in semiconductor device fabrication for more than 30 years (1) . Recently, the use of metallic caps has emerged as a key requirement to improve electromigration reliability in sub-20 nm Cu-Low k interconnect. For Cu wiring, metallic capping has been achieved by using a Cu alloy seed layer which includes a minority component such as Manganese or Aluminum. During various thermal cycles, these components diffuse to the Cu-dielectric interface, acting as an enhanced interface adhesion and Cu surface diffusion suppressor layer (2) . This layer subsequently improves Cu electromigration and overall device reliability. Another simple, controllable and more precise method is to use a selective metal deposition process to place an ultrathin metal capping layer on top of Cu wiring metal prior to dielectric capping.

In this paper, we will present our recent IBM development, evaluation and implementation of selective deposition of Cobalt, Manganese and Ruthenium metal caps (3-7) in nano Cu-Low k interconnect wiring. The in-situ selectively deposited Cobalt metal cap, especially with Cobalt metal wrapping around the Cu interconnect, produces the best copper wiring electromigration reliability data as shown in figure 1. Currently, this selectively deposited Cobalt cap is one of the first selective metal deposition approaches being used in industry for Cu interconnect reliability enhancement.

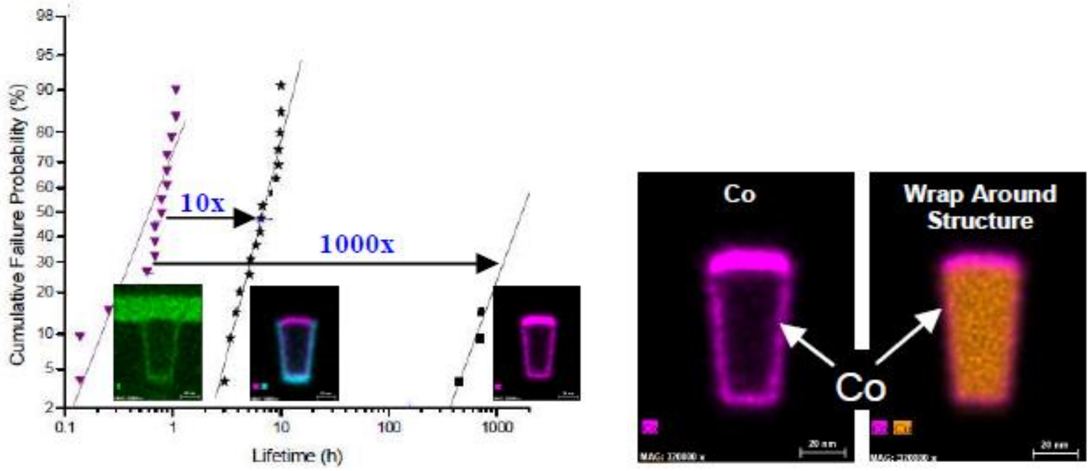

Figure 1- Cu Electromigration reliability improvement with selective Cobalt metal cap (10x) and Cobalt wrap around (1000X) Cu metallization.

Acknowledgments: This work was performed by Alliance Teams in various IBM Research and Development Facilities and at Albany Nanotech. The contribution of many members of BEOL metals and FA analysis teams in this evaluation are acknowledged

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Area selective Ru ALD for sub 7 nm bottom-up metal interconnects

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For the past two decades, microelectronic components such as transistors and interconnects were aggressively downsized in accordance with Moore's law and ITRS [1]. Conceptually, a dielectric replacement (DR) is being considered to avoid dielectric etch step by patterning a dummy dielectric, which is removed after metallization and replaced by non-damaged low-k material. In a DR scheme, the inter-line dielectric is a sacrificial resist material, such as an amorphous carbon (a-C:H). When line half-pitch approaches 7 nm, filling of the structures becomes very challenging and even with conventional ALD, defects like voids and seams are likely to be formed due to trench pinch-off. As a solution, area selective deposition (ASD) can be exploited, allowing bottom-up and void-free filling of high aspect ratio structures. Bottom-up metal growth, used for standing metal lines, can be achieved on the SiCN dielectric barrier at the bottom of the trench with selectivity to a-C:H.

In this work, thermal ALD Ru using an ethylbenzene-ethyleyelohexadiene (EBECHRu) precursor was used. In this precursor, the Ru(0) is enclosed in the organic frame, which decomposes in the presence of O_2 at the temperature above 225 ^{0}C. We observed Ru inhibition on a 3s H_2 plasma-treated a-C:H surface, which we explain by an unfavourable interaction between the methyl group passivated a-C:H surface and electron-donating groups, such as the alkyl-modified cyclohexadienyl ligands, of the EBECHRu precursor [2]. A weak Van der Waals force may be the only interacting force between the ligand and the methyl group. On the contrary, electron-deficient silanol or amino groups on the SiCN surface tend to interact with the electron-donating precursor groups.

The achieved ASD of ALD Ru catalyst enables ELD metal bottom-up fill. In order to validate our approach, ELD Cu ASD on SiCN from an in-house model chemistry was grown on 42 cycles of ALD Ru deposited at 275 ^{0}C with 7s H_2/N_2 followed by 3s H_2 plasma treatment. The post-etch plasma treatment triggers ALD Ru selectivity. According to XSEM and EDX analyses after the ELD process, a ~ 46 nm Cu film has been deposited on SiCN, while no Cu is detected on the a-C:H. Further, the ASD Ru catalyst approach has also been successfully tested on ~ 45 nm half-pitch lines followed by ELD Cu bottom-up trench filling. Morphological study and electrical measurements of patterned structures will be presented.

[1] International Technology Roadmap for Semiconductors (2013) 1–51
[2] J. Heo et al., Electrochem. Solid-State Lett. (2013) H210

Area-selective Deposition of Metal Films

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In this work, we employ nanoimprint lithography and directed self-assembly of block copolymers to define features on various oxide substrates and demonstrate the area-selective atomic layer deposition (A-SALD) of metal oxides on exposed regions of the substrate. The ALD oxide films are grown at temperatures below 200 °C and produce carbon-free oxide features, such as lines and cylindrical disks. The polymer film can be etched away using O_2/Ar plasma processing and then the metal oxide feature can be reduced to the metal thermally with hydrogen or by employing an oxygen scavenging layer, such as aluminum. The ALD process employs (bis(N-tert butyl, N'ethylpropionamidnato) cobalt (II), bis(N,N'-di-t-butylacetamidinato) nickel(II), bis(N,N'-di- t-butylacetamidinato) iron (II) and tetrakis(dimethylamino)tin(IV), and water as the co-reactant to deposit CoO, NiO, Fe_2O_3 and SnO_2, respectively.

In this talk, Co is taken as the exemplary metal; however the process works for other transition metals, including Fe, and Ni. Magnetic materials are used in a wide variety of devices ranging from microelectronics to RF technology to energy. Previous efforts to deposit Co metal using bis(N-tert butyl, N'ethylpropionamidnato) cobalt (II) and H_2 in ALD have suffered from carbon and nitrogen incorporation into the film and nucleation on polymer- and alkylsilane-coated surfaces. Therefore a route to impurity-free CoO deposition in the defined areas followed by reduction from CoO to Co is selected. The approach is illustrated with a 110-nm pitch nanoline pattern of 40 nm-wide trenches and 120 nm-high cured-imprint polymer lines created by nanoimprinting. After O_2/Ar plasma-etching to remove a 10 nm residual layer at the trench bottom, CoO ALD occurs only at the bottom of the trenches. Following deposition at 180 °C and removal of the polymer lines with etching, the CoO is reduced to form Co metal. With this A-SALD approach, we are able to pattern large-area uniform and parallel Co metal nanolines with a 110-nm pitch. The nanoline width can be tuned by the O_2/Ar treatment of imprinted pattern and the height of nanolines can be adjusted by the number of ALD cycles. X-ray photoelectron spectroscopy is used to determine the composition and oxidation state of nanolines at various steps in the process. Scanning electron microscope and atomic force microscope are used to determine the pitch, width and height of the nanolines. Using I-V measurement and vibrating sample magnetometer, we explore the electrical and magnetic properties of the Co nanolines.

Selective Deposition: A Materials Supplier's Perspective

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In its various forms, selective deposition is not new and has been observed, studied and even used in epitaxial processes for many years. The novelty is the diversification of the processes (deposited materials and their selectivity to certain substrates) that are now demanded by the industry to alleviate the sky-rocketing costs of lithography and enable simpler process flows.

For instance, while never adopted for mass production, selective W-CVD has been extensively studied as early as the 80's. Similarly, what is now described as inherently selective deposition of Co or Ru CVD/ALD processes used to be reported as undesirable and surface specific "induction time". As such, the development of inherently selective deposition processes (mostly for metallization) often consists for materials supplier in revisiting the utilization of previously developed molecules or molecule families, in an attempt to amplify the selectivity. Better understanding of surface preparation, of the precursor-surface interaction, of the effect of certain impurities, and of the impact of alternative co-reactants, are thus the key axes of developments for material suppliers.

For surface protection based selective deposition of dielectric films (typically using SAMs), a large library of processes do exist, and growing selectively a metal oxide film from a metal alkylamide / H_2O-based ALD process is no longer a challenge in itself. What remains a challenge however is the metrology to assess the absence of parasitic growth on protected areas (TEM not being an appropriate day to day quality control tool), whether from SAM layers defects or at sharp edges in 3D structures. The need for matching the SAM chemical structure (and the way it is layered on the wafer), with the precursor design itself is also calling for high productivity combinatorial studies. The identification of critical impurities in the SAM material and their correlation with unwanted deposition on protected areas remains also vastly un-explored so far, but will be critical to make such process industry worthy.

Finally, the capability to gently etch-back unwanted deposits to suppress in situ nucleation centers forming over SAM layers or at the interface of SAM coordination to substrate surface can also enable the adoption of such processes by providing more tolerance to imperfect selectivity, and ALE should be considered as an integral part of the selective deposition quiver.

Strategies for Area Selective Atomic Layer Deposition

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Area selective deposition by CVD is well known from epitaxy of Si, SiGe layers in semiconductor devices. ALD has now been adopted as well in a variety of applications in semiconductor device manufacturing but only as a non-area selective process. Area selective ALD potentially has a variety of benefits for process integration and could solve several critical problem in further down scaling of devices. The ALD mechanism of well-defined sequential self-limiting reactions with specific chemical groups on the surface also maybe provide new pathways to design unique area selective ALD processes.

In this paper selected results of our work on different approaches for area selective ALD will be presented and reviewed. This includes clever ALD precursor selection to obtain selectivity but also use of various surface treatments. Results for deposition on and selectivity towards different surfaces such as metals, oxides and block-copolymers will be presented and also various learnings from patterned structures with small dimensions. Challenges and opportunities for area selective ALD will be reviewed.

Selective deposition using the inherent substrate-dependent growth initiation based on nucleation delay and on the joint use of plasma etching mode

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At advanced nodes, lithography starts to dominate the wafer cost (EUV, managing multiple mask passes per layer and pattern placement error….). Therefore complementary techniques are needed to continue extreme scaling and extend Moore's law. Selective deposition and etching is one of them because they can be used to increase and enhance patterning capabilities at very low cost. From all the different deposition processes, Atomic Layer Deposition (ALD) is maybe the most suitable technique to develop a selective process due to its very good coverage property and its high surface sensitivity. This process is then called SeALD (Selective ALD) or AS-ALD (Area Selective ALD). It is usually based on a specific surface passivation or protection treatment in order to limit/inhibit chemical reactions with the ALD precursor/reactant. This surface deactivation is usually obtained by using organic groups such as Self-Assembled Monolayers (SAM). The idea is to chemically and locally bond a molecule directly to the surface in order to block reactive sites and then prevent further reactions between the precursor molecules and the surface. Deposition of SAMs prior to ALD is not straightforward, since it may induce defects localized at uncovered sites. Surface preparation is the key issue with SAMs and it generally requires specific advanced cleaning techniques in combination with extended SAM deposition times. Another pathway for selective area deposition with ALD is to take advantage of the inherent substrate-dependent growth initiation, based on nucleation delay and on the joint use of a PEALD mode and plasma etching mode, by adding a chemical plasma etching step to the ALD ones. Here, we propose a selective ALD process, without surface treatment before deposition with SAMs but using a Plasma assistance ALD process. We used this process for the deposition of two oxides that are currently under study for non-volatile resistive memories applications: Ta_2O_5 and TiO_2. The intention for memory application is to realize a crosspoint memory in backend level from a pattern area or a trench area without the photolithography step.

Figure 1a is illustrating our selective plasma ALD process for the growth of Ta_2O_5. Three different substrates (Si, SiO_2 and TiN) have been patched onto a Si wafer and introduced simultaneously into the ALD reactor. After the selective plasma ALD deposition (80 cycles), the three samples have been analyzed by X-ray reflectivity (XRR) in order to determine the Ta_2O_5 thickness deposited on top. As can be seen figure 1b there is no Ta_2O_5 layer on Si or SiO_2 substrate while XRR confirms the presence of a thick 7 nm layer of Ta_2O_5 layer on top of TiN in figure 1c(smaller arches after selective deposition). This is confirmed also by XPS with the study of the O1*s*, Ta4*f* and F1*s* spectra (not shown here). We are currently extending this selective plasma ALD process for TiO_2 growth. The process and its potential application will be described in more details in the conference.

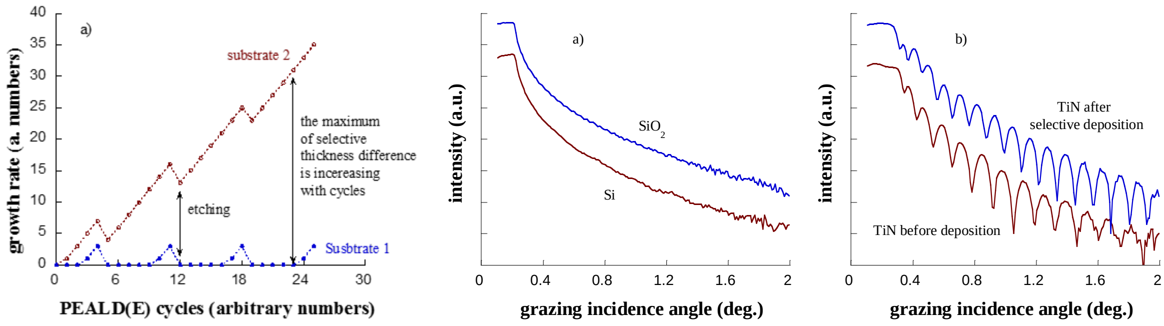

Figure 1a): selective process principle, b) XRR on Si and SiO_2 substrate after Ta_2O_5 deposition, and c) XRR on TiN after Ta_2O_5 deposition in the same batch.

Applications of Area Selective Deposition

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With the wide variety of materials now in use for semiconductor processing there are many examples of integration environments that present interesting combinations of exposed surfaces where selective chemistry and surface reactions can be exploited to simplify device processing.

While there many creative concepts in academic and patent literature suggesting that selective processing is a new space, there are examples of processes that have been developed and are in high volume manufacturing today. As examples, selective epitaxy and Co capping will be discussed and presented in the context of what is needed for a selective process to yield in a manufacturing environment.

Different new proposed applications of selective deposition for patterning, minimizing resistance and lowering aspect ratios will also be reviewed and evaluated in terms of how challenging the environment is with respect to the performance required of the selective deposition process.

ASD17

2^{ND} AREA SELECTIVE DEPOSITION WORKSHOP

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1. Novel reactive chemistries for in-situ surface functionalization: new tools for area selective deposition

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Several efforts have begun to explore novel methods for Area Selective Deposition (ASD). These utilize surface blocking agents, plasma based films, as well as emerging ALD/ALE combinations. Though this field is in its infancy, tremendous progress has been made with limited tools. The use of the novel reactive molecules, anhydrous hydrogen peroxide and hydrazine, has been largely ignored. This is partly due to a lack of literature precedent, and also because only very recently did these materials become readily available in a form conducive to Semiconductor development. We previously reported novel membrane based delivery systems for gaseous hydrogen peroxide and hydrazine which allow for *in situ* surface preparation. This paper summarizes known properties and reports on recently discovered reactivity characteristics of these reactive molecules on several material surfaces with the objective of showing potential utility in ASD.

Hydrogen Peroxide has similar oxidation properties to Ozone (oxidation potential O_3 = 2.1V versus 1.8V for H_2O_2) while simultaneously having slightly stronger proton transfer properties than water (H_2O_2 pKa = 6.5 versus pKa = 7.0 for water). Key to our early discoveries is the fact that H_2O_2 has a very weak O-O bond, where Bond Energy = 36 kcal/mole.

We have demonstrated the low temperature, highly dense nucleation/functionalization of Si-H and SiGe surfaces under conditions where water reactivity is very limited. More unexpected has been the self-limiting nature of hydroxide (-OH) functionalization on Si, Si-H, and SiGe surfaces with the use of anhydrous hydrogen peroxide gas. In these instances, oxygen penetration into the surface can be carefully controlled to 1-2 monolayers, thus leaving the remaining substrate undamaged. This leads to tremendous versatility for potential use in ASD where (-OH) functionality may be easily converted to blocking species, used to grow additional oxide films by ALD, or removed fairly easily by known methods to leave a pristine surface with little or no substrate damage/material loss.

Similarly, hydrazine has a very weak N-N bond (BE = 55kcal/mole) and therefore has been shown to be much more reactive toward Silicon surfaces than gaseous NH_3. In addition, hydrazine efficiently nucleates SiGe surfaces at sub 300C temperatures to yield a thinly passivated surface that can be further functionalized or removed.

This presentation will provide additional details on the newly discovered reactivity of both hydrazine and anhydrous hydrogen peroxide on several surfaces as well as outline some potential ASD pathways.

2. Area-selective deposition of ruthenium using an ABC-type process combined with selective etching

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In area-selective atomic layer deposition (AS-ALD) by area-activation, ALD is locally activated using a method such as electron beam induced deposition (EBID) to deposit a seed layer. This seed layer "activates" the surface by catalyzing subsequent ALD growth. In an ideal scenario, the remainder of the substrate experiences a long nucleation delay before any growth occurs,[1,2] such that deposition only takes place on the seed layer pattern.

In this work, we investigate three methods to improve the selectivity of AS-ALD by area-activation of Ru metal. In the first method, we show how by adding a H_2 step to our Ru ALD process (ethylbenzen-cyclohexadiene Ru(0) precursor, O_2 gas), we can deposit Ru metal at lower temperatures and thus use temperature to achieve differences in growth rates of the Ru metal on different substrates. It is found that if the temperature of this three-step (ABC) ALD process is decreased to 150 ^{0} C, area-selective Ru deposition can be obtained with high selectivity on patterned Pt-containing seed layers deposited using EBID. For applications that require thicker layers of Ru, it is found that residual islands that start to appear on the non-growth areas can be eliminated by performing an O_2 plasma etch as a post-deposition treatment (See Figure 1a). This combination of area-selective ALD and selective etching can yield a high selectivity for growth on EBID Pt. Finally, we explore whether supercycles in which short O_2 plasma pulses are performed at key intervals, can lengthen the nucleation delay of the Ru ALD process on SiO_2 (See Figure 1b).

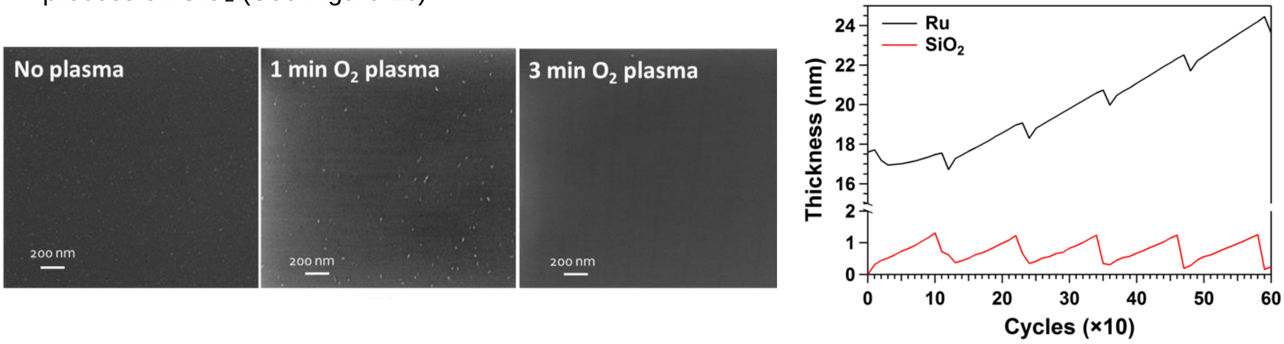

Figure 1. (a) Scanning electron microscopy images showing the effect of O_2 plasma post-deposition treatment at 225 °C on residual Ru islands. (b) In-situ spectroscopic ellipsometry measurements during supercycles consisting of 100 Ru ABC ALD cycles, and 1 cycle of 15s O_2 plasma and 15s H_2 gas exposure. The supercycle deposition was carried out at 150 °C.

(1) Mackus, A. J. M.; Dielissen, S. A. F.; Mulders, J. J. L.; Kessels, W. M. M. Nanopatterning by Direct-Write Atomic Layer Deposition. *Nanoscale* **2012**, *4*, 4477–4480.
(2) Mackus, A. J. M.; Bol, A.A.; Kessels, W. M. M. The Use of Atomic Layer Deposition in Advanced Nanopatterning. *Nanoscale* **2014**, *6*, 10941–10960.

3. Feasibility study of single and multi-layered graphene as plasma-compatible deactivation layers for selective deposition of III-nitride materials

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Plasma-assisted atomic layer deposition (PA-ALD) is a promising method for low-temperature growth of III-nitride materials. However, selective film deposition using PA-ALD is quite challenging mainly due to the plasma-incompatibility of conventional deactivation/blocking layers including SAMs and polymers. The main motivation of this work was to explore alternative growth inhibition materials which could withstand plasma environment.

Towards this goal, we investigated single-layer graphene (SLG) and multi-layered graphene (MLG) as an effective lift-off mask for AlN, GaN, and InN grown via low-temperature PA-ALD. We achieved crystalline III-nitride thin films on graphene blocking layer and Si substrate surface. As far as SLG and MLG possess relatively weak Van der Waals forces between (1) graphene/substrate and (2) graphene/graphene interfaces, here, we gauge the importance of those forces for selective deposition of III-nitride materials. This strategy could be mainly used as an alternative patterning approach based on the graphene-assisted lift-off technique.

To evaluate the selective deposition studies, GaN, AlN, InN, and graphene have been removed from Si surface and were characterized using SEM and XPS. Spectroscopic ellipsometry measurements were performed to measure the film thickness on Si substrate surface and graphene-masked area. An extensive comparative study has been carried out with some successful results for certain binary III-nitride alloys. Possible blocking, nucleation, and graphene-penetration mechanisms will be discussed in conjunction with possible future strategies to further develop selective deposition methods for plasma-assisted film growth recipes.

4. Nanoscale patterning of C_4F_8 plasma polymer blocking layers via femtosecond pulsed laser processing for selective deposition of noble metals

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In this study, we show that by using the pulsed-laser processing technique it is possible to achieve nanoscale patterned surfaces for AS-ALD of nobel metals. To develop this alternative methodology, we have used: an ultrafast Yb-fibre laser, operating at a central wavelength of 1,030 nm which has a 170-fs pulse duration, 1 MHz repetition rate with adjustable laser power levels. For Pt ALD growth, we used trimethyl (methylcyclopentadienyl) platinum (IV) and ozone as Pt and O_2 precursors, with N_2 as the carrier gas. Samples have been characterized using HR-SEM, contact angle measurements, EDX-analysis, and XPS for elemental composition analysis.

Our study consists of the following steps:

- C_4F_8 plasma polymerization on Si(100) substrate surface in an ICP etch reactor;
- Micro- and nanoscale patterning of C_4F_8 plasma polymer by femtosecond (fs) laser pulses;
- Si surface patterning by nonlinear laser lithography (NLL);
- AS-ALD of Pt thin films on patterned C_4F_8/Si interface;
- Plasma polymerization of C_4F_8 on Pt thin film;
- Hydrophobicity study of dielectric/metal/substrate stack.

We will present our experimental results on surface patterning via *fs* laser pulses and NLL for Pt AS-ALD. Here we speculate about the transparency of C_4F_8 polymer to ~1 µm wavelength. In this regardsTherefore, due to substrate heating, polymer can be removed from specific areas. Patterned structures with diameters as small as 250 nm have been achieved.

This new capability could pave the way for cost-effective lithography-free patterning technique. For future work, (1) surface patterning with smallest possible features; (2) super-hydrophobic surfaces with metal contacts underneath are under development of which the latest results will be presented as well.

5. *In situ* study of the nucleation of noble metal ALD processes using synchrotron-based grazing incidence small angle X-ray scattering

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The increasing interest in nanopatterning of noble metals by area-selective atomic layer deposition (ALD) demands an in-depth understanding of the nucleation-controlled growth behavior. In this work, we demonstrate that synchrotron-based X-ray fluorescence (XRF) and grazing incidence small-angle X-ray scattering (GISAXS) are uniquely suited for *in situ* monitoring of the amount of deposited metal atoms and nanoscale surface morphology during the initial growth stages of noble metal ALD processes. The evolution in key scattering features observed in the 2D GISAXS images provides insights in the growth kinetics of the metal deposits, from isolated nuclei to coalesced wormlike structures. In particular, GISAXS can provide direct information on the role of atom and cluster surface diffusion during ALD growth. Quantitative analysis of the scattering patterns yields average values for the shape, size and spacing of the metal nuclei and islands.

Using a custom-built synchrotron-compatible high-vacuum ALD setup facilitating *in situ* XRF and GISAXS measurements [1], we investigated the effect of several deposition parameters on the nucleation of Pt ALD with the $MeCpPtMe_3$ precursor on planar SiO_2 substrates. The results indicated a diffusion-mediated island growth mode for the O_2-based Pt ALD process at 300 °C, marked by a decreasing average areal density and formation of laterally elongated Pt clusters. Secondly, it was found that a decrease in Pt precursor dose slows down the nucleation and island growth. However, GISAXS patterns acquired at the same surface density of Pt atoms revealed the same Pt morphology, independent of the precursor dose. This is again a consequence of the Pt atom and cluster surface mobility during O_2-based Pt ALD. Thirdly, we investigated the effect of the reactant type (O_2 gas, O_2 plasma, N_2 plasma, NH_3 plasma [2]) on the nucleation of Pt ALD and observed a clear difference in island growth behavior for the oxygen- vs. nitrogen-based processes. The latter processes showed a higher density of initial nuclei and were marked by a constant average center-to-center distance between neighboring Pt islands during the growth process. Analysis of the Pt cluster dimensions furthermore revealed vertically elongated clusters for the N_2 and NH_3 plasma-based Pt ALD processes. Therefore, it is concluded that atom and cluster surface diffusion phenomena are suppressed during the nitrogen-based processes.

[1] J. Dendooven et al., Rev. Sci. Instrum. 87 (2016) 113905.
[2] D. Longrie et al., ECS J. Solid State Sci. Technol. 1 (2012) Q123-Q129.

6. Nucleation of 2D WS_2 by Plasma Enhanced Atomic Layer Deposition from WF_6, H_2 plasma and H_2S

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To exploit the semiconductor properties of two-dimensional (2D) transition metal dichalcogenides in ultra-scaled nano-electronic devices, a highly crystalline structure with controlled number of monolayers is required. In Atomic Layer Deposition (ALD), these structural properties are determined by the nucleation behavior of the layers. However, the nucleation mechanisms of 2D materials by ALD have so far not yet been investigated. Therefore, we investigate the nucleation mechanisms of WS_2 from a PEALD process from WF_6, H_2S and H_2 plasma using a complementary set of characterization techniques including Rutherford Backscattering Spectroscopy, Atomic Force Microscopy, and Time-of-Flight Secondary Ion Mass Spectrometry. We have grown WS_2 on 300 mm Si substrates covered with either a 30 nm ALD amorphous Al_2O_3 layer or a 90 nm thermally grown SiO_2 (1000 C), and 2” c-plane bulk sapphire.

The substrate and deposition temperature influence the nucleation behavior and determine the crystallinity and domain size of the WS_2 layers. At a deposition temperature of 300 °C, the growth of WS_2 is strongly enhanced on the Al_2O_3 surface (Figure 1). The high nucleation density of 10^{14} /cm^2 promotes fast closure of the first WS_2 layer. On the other hand, the combination of the high nucleation density with lateral and vertical growth contributions limits the crystal domain size to 5-30 nm. By choosing a substrate that has a lower reactivity towards the PEALD precursors, e.g. SiO_2, the nucleation density decreases to $3{\cdot}10^{11}$ /cm^2. An even lower nucleation density of $5{\cdot}10^{10}$ /cm^2 is obtained on SiO_2 by increasing the deposition temperature to 450°C due to the increasing mobility of the ad-atoms on the surface. This leads to WS_2 crystals that grow primarily in a lateral direction, which increases the WS_2 crystal domain size to 100 nm.

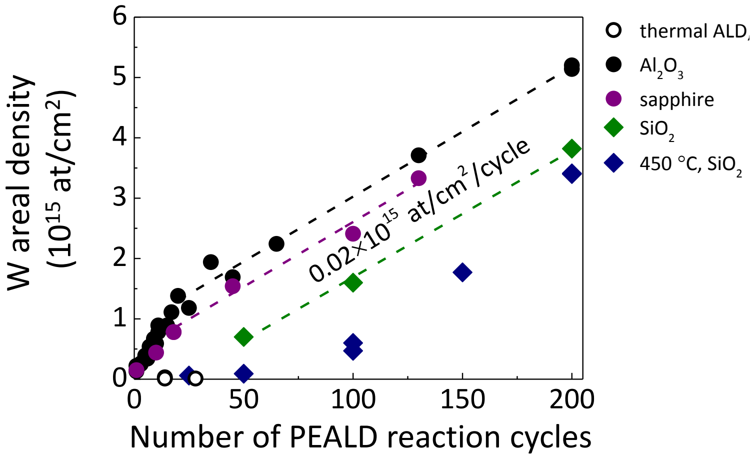

Figure 1: Growth curves of WS_2 PEALD on amorphous ALD Al_2O_3, SiO_2 by thermal oxidation, and sapphire at 300 °C and 450 °C. The W areal density (RBS) is plotted as a function of number of PEALD reaction cycles. A crystalline WS_2 layer consists of $1.16{\cdot}10^{15}$ W at/cm^2.

7. Area-selective atomic layer deposition using polymer growth inhibition layers: a case study for metal-oxides and noble metals

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Nanoscale process integration demands novel nano-patterning techniques in compliance with the requirements of next generation devices. Conventionally, top-down subtractive (etch) or additive (deposition/lift-off) processes in conjunction with various lithography techniques is employed to achieve film patterning, which become increasingly challenging due to the ever-shrinking misalignment requirements. To reduce the complexity burden of lithographic alignment in critical fabrication steps, self-aligned processes such as selective deposition and selective etching might provide attractive solutions.

Here, we demonstrate a methodology to achieve area-selective atomic layer deposition (AS-ALD) by using inductively couple plasma (ICP) grown fluorocarbon polymer film as growth inhibition layer. The fluorocarbon layer was grown using C_4F_8 feed gas in a conventional ICP-etch reactor. Our approach has been tested for metal-oxides and metals including ZnO, Al_2O_3, TiO_2, HfO_2, Pt, and Pd. Additionally, we investigate the poly(methyl methacrylate) (PMMA) and polyvinylpyrrolidone (PVP) as growth inhibition layers for AS-ALD of TiO_2. Contact angle, X-ray photoelectron spectroscopy, spectroscopic ellipsometer, energy dispersive X-ray spectroscopy, and scanning electron microscopy measurements were performed to investigate the blocking ability of polymer layers against ALD-grown films. Characterizations carried out revealed that effective blocking on fluorocarbon layer is achieved for ZnO, Pt, and Pd films with different blocking cycle numbers before nucleation initiates. Remarkably, Pt grown using an ozone based process shows significant growth inhibition (upto 200 growth cycles) on C_4F_8. On the other hand, a rather slow nucleation has been observed for HfO_2 growth on fluorocarbon coated surfaces, while TiO_2 and Al_2O_3 growth showed almost no delay with a growth rate equal to the ones on conventional substrate surfaces. For TiO_2, PMMA revealed successful growth inhibition upto the maximum inspected growth cycles while PVP was able to block TiO_2 growth upto 300 growth cycles. By exploiting this inhibition feature, thin film patterning has been demonstrated by growing ZnO, Pt, and Pd films on photolithographically patterned fluorocarbon/Si samples. We also demonstrate nanoscale patterned deposition of TiO_2 using a PMMA masking layer that has been patterned using e-beam lithography.

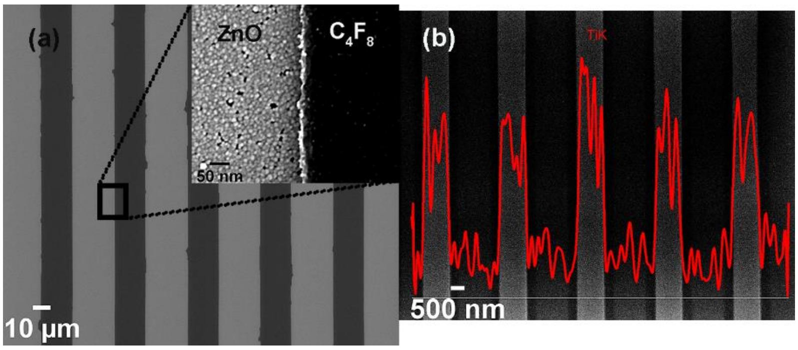

Figure 1. (a) SEM image of patterned ZnO line features on lithographically defined fluorocarbon patterns, (inset) High resolution SEM image from the interface of ZnO and fluorocarbon confirming successful pattern placement, (b) EDX Ti K line scan obtained from nm scale TiO_2 line features

8. Multi-dimensional Nano- and Micro-patterning through Self-Templating Assembly

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Creating multi-dimensional hierarchical structures in nano- or micrometer scale are a requisite for the fabrication of various functional devices in all fields of science and engineering. Conventional lithography techniques (i.e., photolithography, e-beam lithography, dip-pen nanolithography, nanoimprint lithography, and etc.) have been utilized to fabricate various devices for electronics, mechanics, and biomedical engineering. Despite their remarkable attributes and capabilities, those fabrication processes often require complicate procedures as well as considerable labors and expenses. However, in nature many hierarchically organized nanostructures (i.e., diatoms, abalone shell, butterfly wing, and moth eyes) possess exquisite structures and functions, which surpassing the capability achievable by current top-down and bottom-up fabrication methods. Moreover, many of these structures are made of a simple basic building block.

Herein, inspired by nature's self-templated assembly processes, we developed a novel biomimetic micro-patterning technique to create well-defined three-dimensional hierarchical structures by using instability phenomena of helical nanofibers at the air/liquid/solid interfaces. We utilized M13 bacteriophage (phage) as a model helical nanofiber building block, due to its' monodispersity, liquid crystalline property, and genetic flexibility to display functional peptides. By controlling meniscus forces, we could induce formation of the smectic nanofilament phases of the phage and tune the adhesion properties between the nanofilaments-to-nanofilament and nanofilament-to-solid substrates. The resulting structures possess hierarchically organized two- and three-dimensional periodic structures with exquisite optical properties. These self-assembled multi-dimensional hierarchical structures were tunable by varying parameters that affect the kinetics and thermodynamics of assembly such as pulling speed, pulling time, and ionic concentration. The resulting microstructures could enhance the power of phage-based piezoelectric energy generations. Our facile bio-inspired self-assembly strategy may provide the way to fabricate large-scale advanced micro electronic or optical devices and biomedical applications in the future.

9. Area-selective atomic layer deposition of In_2O_3 based on the Si doping level

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Many electronic devices comprise regions of highly *p*- or *n*-type doped silicon (in brief, p^+ and n^+ Si). In this work, we report on the atomic layer deposition of mixed-phase polycrystalline/amorphous In_2O_3 films, which selectively takes place depending on the doping level of the crystalline silicon. Specifically, In_2O_3 growth was found to take place at p^+ Si regions, whereas no deposition takes place at n^+ Si regions. Figure 1 shows an example of such area-selective deposition of In_2O_3[1] at the rear surface of interdigitated-back contact silicon solar cells, where p^+ and n^+ Si surfaces are adjacent.

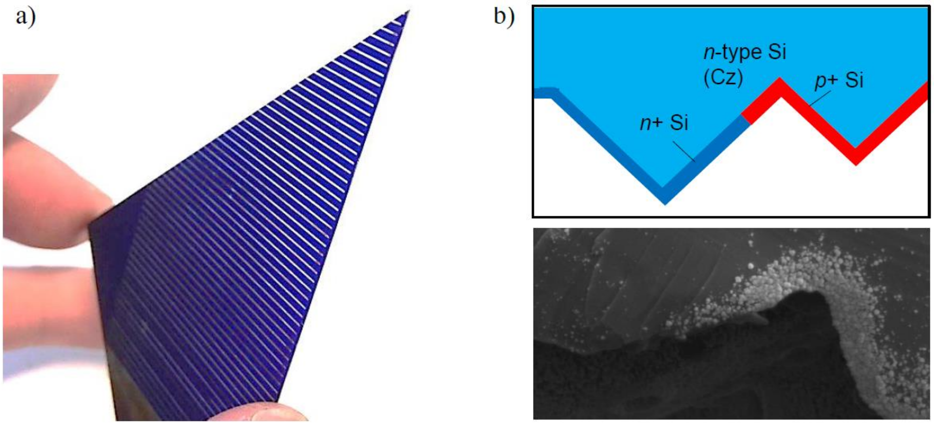

Figure 1 (a) A photograph of an IBC solar cell structure where ~75 nm of In_2O_3:H has selectively been deposited by ALD on p^+ Si (the blue stripes), whereas no In_2O_3:H has been deposited on n^+ Si (white stripes). (b) Cross-sectional scanning electron microscopy (SEM) image of the *pn*-junction at the rear side of the IBC solar cells. The cross section was exposed to the ALD of In_2O_3:H. In this way, the diffused p^+ Si highly doped region, (which is approximately ~0.4 um wide) is visible in the cross-section SEM image, as only on top of this p^+ Si region the polycrystalline/amorphous In_2O_3 layer was locally grown.

The ALD of In_2O_3 was carried out using InCp and H_2O at 100 ºC in an Oxford Instruments OpAL reactor. The n^+ and p^+ highly-doped Si regions are formed by diffusion from $POCl_3$ and BBr_3 into random-pyramid textured silicon in a horizontal tube furnace (Tempress Systems). After removal of phosphorus and boron silicate glasses, the samples were subjected to diluted hydrofluoric (HF) acid prior to the deposition of In_2O_3. Although p^+ Si remains hydrophilic (even after a prolonged HF dip), n^+ Si rapidly becomes hydrophobic. X-ray photoelectron spectroscopy analysis revealed that in both cases the native oxide was completely removed after the HF-dip.

Apart from the deposition of a continues In_2O_3 film on p^+ Si, deposition of isolated In_2O_3 grains occurs at the n^+ Si (111) facets. It is postulated that such deposition is initiated by the presence of defect sites. For area-selective deposition on substrates which comprise multiple materials, undesirable deposition can thus take place at edges and defects sites. In this case, scanning electron microscopy reveals that the growth rate of In_2O_3 at defect sites was lower than at p^+ Si. Therefore, a short (material selective-) etch can possibly be used to remove the isolated In_2O_3 grains.

[1] A. Mameli *et al.*, *Chem. Mater*, **29**, 921-925 (2017)

10. Direct-write ALD of transparent conductive oxides: micro- and nanoscale patterned In_2O_3:H and ZnO

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To date, several approaches have been developed for achieving area-selective atomic layer deposition (AS-ALD), which can be classified as either area-activation[1] or area-deactivation.[2] The former is referred to as direct-write ALD when no subtractive steps are employed. In this contribution, we report on direct-write ALD of two transparent conductive oxides, In_2O_3:H and ZnO. The method exploits the difference in nucleation delay on two differently terminated surfaces: OH- and H-terminated Si surfaces.

Previously, we have demonstrated that microscale In_2O_3:H patterns can be fabricated by local activation of the surface using a micro-plasma printer, followed by a second step in which AS-ALD takes place on the activated surface only.[3] In this contribution we extend the idea to ZnO AS-ALD, while aiming at nanoscale dimensions. In this case an ultra-thin SiO_2 seed layer was deposited to activate the H-terminated surface (i.e., a-Si:H) for ALD growth. 500-by-500 nm^2 SiO_2 seed layers were deposited by electron beam induced deposition (EBID) using tetraethyl orthosilicate (TEOS) and H_2O as the precursors. For the ALD of ZnO, diethylzinc (DEZ) and H_2O were used as the precursor and the co-reactant, respectively, in a thermal ALD process at substrate temperatures ranging from 100 to 250°C. Selective deposition of ZnO was obtained using 80 ALD cycles. The selectivity was demonstrated by in-situ ellipsometry, SEM, cross-sectional TEM and energy dispersive X-ray spectroscopy (EDX) analysis. The influence of the ALD process temperature and EBID patterning parameters on the extent of selectivity have been investigated in detail. First principle density functional theory calculations corroborate the selectivity of the ALD process by revealing a kinetically hindered surface reaction between DEZ and H-terminated Si surfaces.

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[1] A. J. M. Mackus *et al.*, J. Phys Chem. C, **117**, 10788-10798 (2013)
[2] R. Chen *et al.,* Adv. Mater., **18**, 1086-1090 (2006)
[3] A. Mameli *et al.*, *Chem. Mater Comm.*, **29**, 921-925 (2017)

11. Selective Deposition in STM Lithography-defined Patterns

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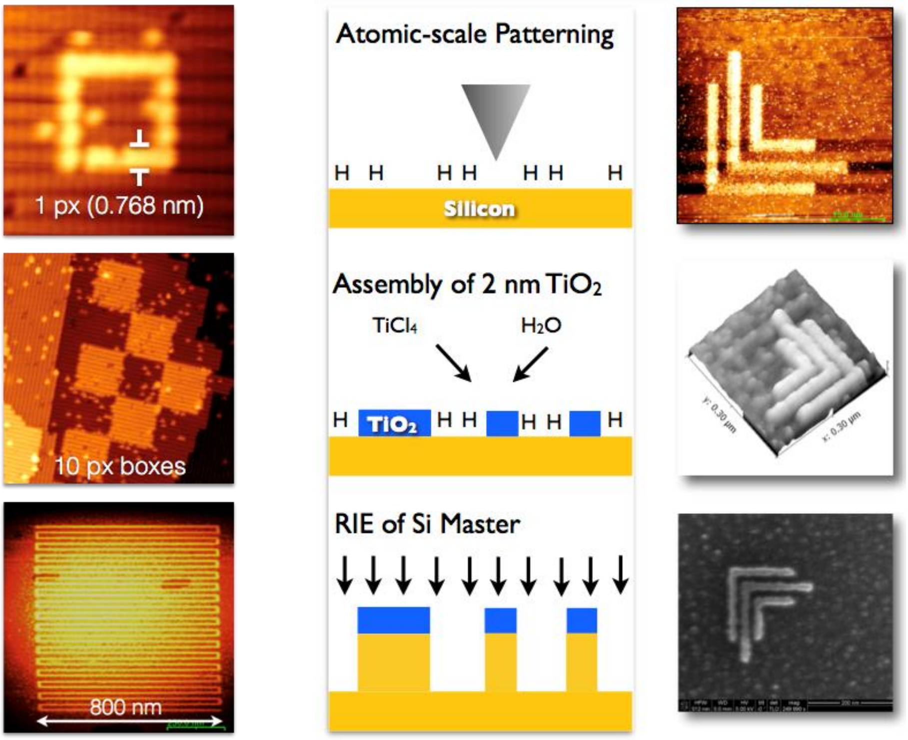
Hydrogen Depassivation lithography(HDL), in which the electrons from an STM tip excite surface Si-H bonds until they break[1], has the proven ability to remove single atoms from a surface, and thus can be used to pattern a surface with sub-nm resolution. By varying the lithography conditions, different size patterns, from removal of single H atoms to bond pads on the micron scale, can be created.

Selective deposition of various species onto the reactive dangling bonds is required to transfer these patterns into nanoscale 2D and 3D structures, with the eventual goal of using HDL-defined patterns for Atomically Precise Manufacturing.
The degrees of selectivity found for various types of adsorbate species, including hydrides, hydrocarbons, metal atoms and metalorganic precursors have been explored [1]; the implications for broader applications of HDL are discussed. The two main applications of this patterning developed thus far are the P-in-Si dopant patterning process developed at UNSW to fabricate a quantum computer, and formation of patterned thin films of TiO_2 to act as hard masks for RIE. These hard masks can potentially be useful as templates for Nanoimprint Lithography, or for other molecular stamp processes. We are exploring other possible selective adsorption chemistries, including the patterning of acceptor dopants for bipolar atomic-scale devices, and selective deposition of a noble metal for a variety of applications.

[1] M. A. Walsh and M. C. Hersam, *Annu. Rev. Phys. Chem.*, vol. 60, pp. 193–216, Jan. 2009.



Left: Examples of STM Lithography. The lithography pixel (px) is defined as two Si dimers on the same dimer row, giving a square 0.768 nm pixel containing 4 H atoms. The dimers where H has been removed appear brighter in the STM image due to electronic contrast.
Right: Schematic of Patterned ALD process. First, STM Lithography is used to create an atomic-scale pattern. Then a hard mask is formed by selective ALD of TiO_2, which is then used to create a taller structure using standard RIE processes.

12. Vertically aligned patterned diamond-graphite hybrid nanorod arrays with superior field electron emission properties

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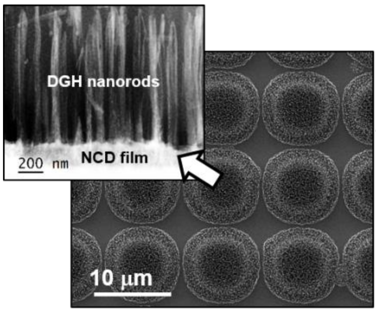
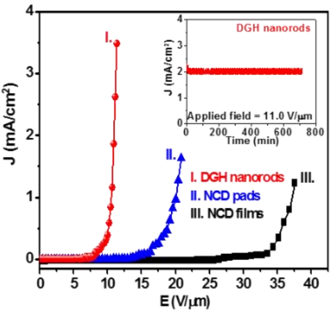
One-dimensional (1D) nanostructures have attracted a great deal of interest not only from a fundamental point of view but also as potential candidates in electronic and photonic nanoscale based systems and devices. Field electron emission (FEE) process, in which electrons are extracted from the material surface by quantum mechanical tunneling, is extensively applied in field emission displays FEDs, back-light units, and electron guns. For a material to be used as a good field emitter, the requirements are low turn-on field, high emission current density, and good stability. To achieve low threshold field, the material should possess low work function and/or high field-enhancement factor (β). The β in turn can be increased by increasing the aspect ratio of the material as in the case of 1D nanostructures. Fabrication of 1D nanostructure arrays for the diamond films is a reliable approach. Not only do the FEE emitters have effective lower turn-on fields but also the stable operation of FEE is prolonged. The various approaches to nanostructure fabrication such as templated etching, random maskless etching, and metal-hard mask etching have been used to make diamond nanostructures such as nanohoney comb, nanocones and nanopillars. However, these nanostructuring fabricating approaches involve complex and expensive multi-step processes~~,~~ resulting in low yields and low efficiency.

In this study, we study an approach to fabricate diamond-graphitic hybrid (DGH) nanorod arrays *via* a combination of a novel “patterned-seeding” technique by selective area growth of nanocrystalline diamond (NCD) films and “nanodiamond-masking” technique for reactive ion etching of NCD films to avoiding possible metallic contamination. The resulting DGH nanorods have diameters of ~15–20 nm and heights of ~800–1200 nm. The DGH nanorod arrays possess the superior FEE behaviors with low turn-on field (5.26 V/μm), long lifetime stability (700 min) and high β (3270). The enhanced FEE properties are attributed to the nanocomposite nature of the DGH nanorods composed of *sp*^{2}-graphitic phases in the boundaries of nano-sized diamond grains. The simplicity in nanorod fabrication process renders DGH nanorods of greater potential for the applications as cathodes in FEDs and microplasma display devices.





13. Substrate dependence of ruthenium atomic layer deposition

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As the dimensions of future nano-electronic devices scale down to sub-10 nm, ruthenium is presented as a promising candidate to replace copper in interconnect structures [1]. At these dimensions, the Ru interconnect resistance is anticipated to be lower than that of Cu. However, filling vias or trenches of sub-10 nm dimensions with Ru through physical vapor deposition (PVD) and conformal atomic layer deposition (ALD) can result in void formation, leading to increased resistance and poor electromigration performance. A possible solution is a bottom-up fill approach. However, this requires the selective deposition of Ru on the bottom of the feature, typically a metal, and deposition on the dielectric sidewalls should be avoided. Therefore, in this work we investigate the surface dependence and nucleation behavior of Ru deposition, as the obtained insight can be applied to design a selective deposition process for Ru. We focus on the (ethylbenzyl)(1,4-cyclohexadienyl)-ruthenium and oxygen (EBECHRu/O_2) ALD, that yields Ru layers with low resistivity (19 µΩcm for 15nm film thickness) and low impurity content.

The growth rate of Ru ALD is enhanced on TiN substrates (0.06 nm/cycle on TiN as compared to 0.03 nm/cycle on other substrates, Figure 1). The enhanced growth rate has been attributed to Ti surfactants which remain on the Ru top surface during the deposition. On SiO_2 with high surface -OH concentration, Ru ALD shows immediate linear growth and rapid Ru film closure (Figure 1, 2). On dielectric surfaces with lower -OH concentration, an inhibition period is observed, and the Ru film closure proceeds slower. Both are related to a lower nucleation density, whereas the growth rate of nuclei appears the same on each surface.

An organosilicate glass surface with Si-CH_3 surface termination is identified a promising no-growth surface for selective Ru ALD, as it shows a long inhibition period for Ru ALD (Figure 1). The initial nucleation density on this surface is low (10_{10} nuclei/cm$_{-2}$, figure 3), which explains the long inhibition period and slow layer closure (figure 2). New Ru nuclei are continuously generated during the ALD process, as the nucleation density increases with ALD cycle number between 50 and 200 cycles. The Ru nuclei grow at a rate of 0.03 nm/cycle, resulting in a broad nucleus size distribution. Coalescence of Ru nuclei explains the decrease in nucleation density at 300 ALD cycles.

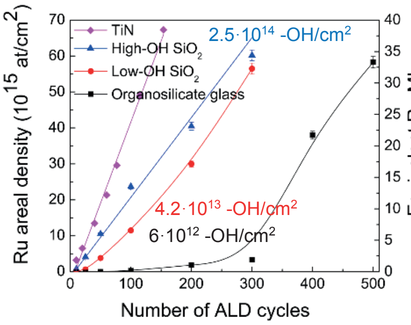

Figure 1: Ru areal density as determined by Rutherford Backscattering Spectrometry (RBS) on different dielectrics as a function of the Ru ALD cycle number.

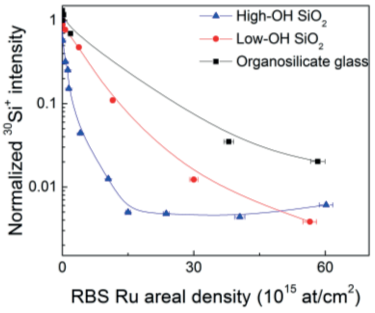

Figure 2: Decay of the normalized Time-of-Flight Secondary Ion Mass Spectrometry (TOFSIMS) intensity of $^{30}Si^+$ from different dielectrics as a function of the amount of Ru deposited on these dielectrics.

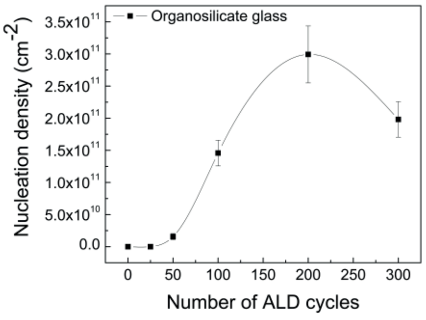

Figure 3: Ru nucleation density on organosilicate glass as a function of the Ru ALD cycle number.

[1] L. G. Wen et al. (2016). "Ruthenium metallization for advanced interconnects". Paper presented at the Interconnect Technology Conference / Advanced Metallization Conference, San Jose, CA, May 23-26 2016.

14. μ-Plasma assisted ALD at atmospheric pressure of thin TiO_2 layers

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The interest in area selective deposition of thin films has been growing extensively in the past years, for example in the manufacturing of printed micro-electronics, labs-on-chips devices, etc. Besides for nano-scale patterned thin films, area selective deposition is also a challenge in applications, where μ-meter patterned thins films are required. In this work plasma-enhanced chemical vapor deposition (PE-CVD) and spatial plasma assisted atomic layer deposition (PA-ALD) of titanium dioxide (TiO_2) thin films was achieved at atmospheric pressure and low temperature by using a modified μ-PlasmaPrinter (μPP) designed by Innophysics B.V.

The μPP combines the benefits of digital printing technique with atmospheric pressure plasma processing via multi needle-to-plane dielectric barrier discharges (DBDs). The system allows patterned plasma treatment with a resolution of few hundreds micrometers and consists of a high-voltage substrate table, a dielectric layer and a print head. The print head is integrated in a XYZ platform and consists of 24 grounded needle electrodes, which can be individually displaced towards the high voltage substrate table. The system has been already used to deliver amino-group containing patterned polymer thin films, however the μPP has never been used for deposition of thin film metal oxides.

Achieving high quality oxide films with low levels of impurity in atmospheric pressure and low temperatures has always been a challenge. The μPP was used as a plasma source for a PE-CVD and PA-ALD process of TiO_2 on silicon substrate by using TTIP as precursor. Plasma-assisted ALD was achieved by the integration of a precursor dosing head and thereby modified the system into a spatial PA-ALD system. The precursor head moves together with the plasma print head and consists of an in- and outlet. The plasma print head is used as an oxidant stage through O_2 μ-plasma exposure. ALD reactions are achieved by the alternate shifting of both deposition heads (i.e. plasma and precursor) over the substrate. Hence, both deposition heads serve each as one half-cycle in the ALD process. The PE-CVD TiO_2 layers contained large amount of carbon (+7.5%) and the refractive index was only 1.81. The PA-ALD TiO_2 layers contained less than 1% of carbon and the refractive index increased to 1.97, provided sufficient plasma exposure time. Saturation of the growth was achieved at 0.15 nm/cycle at 500 ms of TTIP exposure and 400 μs of O_2 μ-Plasma exposure. Since the plasma exposure occurs in a patterned manner, selective ALD would be possible.

15. Selective ALD of metal-oxides on noble metals through catalytic oxygen activation

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Thin films and nanoparticles of iron oxide (Fe_2O_3) and nickel oxide (NiO) find many applications in catalysis, magnetic/spintronic devices and solar cells. Furthermore, these materials are often combined with noble metals to further improve their magnetic or catalytic properties. For example, Fe/Pt alloys are commonly used for magnetic storage as well as synthesis of carbon nanotubes.

In this work, we demonstrate area-selective ALD of Fe_2O_3 and NiO on catalytically active Pt and Ir substrates, using *t*-butyl ferrocene and nickelocene as precursors in combination with O_2 gas as the reactant. While these precursors typically require strong oxidizing reactants such as ozone or O_2 plasma, the catalytic activity of Pt and Ir allows the ALD surface reactions to take place even with O_2 gas. Specifically, the Pt and Ir substrates enable dissociative chemisorption of the O_2 molecules, which has previously been exploited for area-selective ALD of Pt[1]. Non-catalytic substrates such as Si, SiO_2 and Al_2O_3 do not provide this catalytic activity, therefore deposition on these substrates does not occur.

Using this novel area-selective ALD process, we have successfully prepared both thin films as well as core-shell nanoparticles. The process is studied in detail using a combination of *in-situ* spectroscopic ellipsometry (SE), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Surprisingly, the growth does not stop even after the catalytic substrate has been covered, which may indicate some mixing of the materials.

Finally, we exploit this area-selective ALD process to prepare catalytic Pt-Fe_2O_3 core-shell nanoparticles for the synthesis of single-walled carbon nanotubes (CNTs). The use of ALD for both the Pt particles as well as the Fe_2O_3 shells ensures that the particle diameters (and therefore the CNT diameters) are very well-controlled.

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