Area Selective ALD
Room Arteveldeforum & Pedro de Gante - Session AS-TuP
Area Selective ALD Poster Session

AS-TuP-1 A Novel Cobalt Precursor for Area-Selective Deposition*, **Hiroyuki Oike**, Y Yamamoto, T Hayakawa, T Furukawa, K Tokudome,* TOSOH Corporation, Japan*; K Tada,* Sagami Chemical Research Institute, Japan

Cobalt thin films have attracted much attention for a wide variety of technological applications, such as $CoSi_2$ contacts, capping layers and liners of copper interconnects in integrated circuits.[1-3] Lately, area-selective deposition of cobalt thin films, especially by means of CVD/ALD, has been one of the hot topics in this field.

In this work, we developed a novel cobalt complex, [(2-dimethylamino-1,1-dimethylethyl)(trimethylsilyl)amino](2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt [**Co1**], as a precursor for area-selective deposition of cobalt thin films (metal-on-metal).

Co1, a deep green liquid at room temperature, has excellent physicochemical properties suitable for use in CVD/ALD processes, so its TG curve showed a single-step weight loss with almost no residue. In the DSC measurement, the exothermic peak due to thermal decomposition was observed around 210°C. The vapor pressure of **Co1** was determined to be 0.1 Torr at 88°C by the Clausius-Clapeyron plots. These results indicate that **Co1** has sufficient vapor pressure and thermal stability for CVD/ALD processes.

Area-selective behavior was examined by CVD of **Co1** with formic acid (HCO_2H) as a co-reactant at 200 °C on ruthenium, copper, platinum and SiO_2 substrate, respectively. After a deposition time of 90 min, cobalt thin films were deposited on ruthenium, copper and platinum substrates, while no cobalt thin film was formed on SiO_2 substrate. The excellent selectivity between these metal substrates and SiO_2 substrate was clearly observed. In addition, it was confirmed that the cobalt thin film on ruthenium substrate has a thickness of 33 nm and a cobalt content of 93% by XPS analysis.

We propose that **Co1** is a promising precursor for selective cobalt film deposition processes.

References

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AS-TuP-3 Thermally Assisted Area Selective Atomic Layer Deposition*, **Bart de Braaf**, K Storm,* Eindhoven University of Technology, The Netherlands

We explore a new method for area selective ALD by modifying the temperature profile on the

substrate. The technique keeps the majority of the substrate at a low temperature, suppressing the chemical reaction, while a small, local area is heated to allow the reaction to proceed. Controlling the size and the position of the heating spot on the substrate allows for 'writing' on the surface, with potential applications in the bottom-up fabrication of electronic devices like solar panels and OLED displays. We study the feasibility and window of opportunity of this technique by computational modeling. We first model the control of the temperature by various illumination protocols, and then model and simulate the nucleation and growth of spatially localized layer given an inhomogeneous temperature profile, to show that the site and the extent of nucleation can in theory be localized and controlled.

AS-TuP-5 Simple Fabrication of Patterned MOF Thin Films via Area Selective Deposition of ZnO by Spatial ALD*, **Chiara Crivello**, D Muñoz-Rojas,* LMGP Grenoble INP/CNRS, France*; V Nguyen,* Phenikaa University, Vietnam*; O Hassan,* Grenoble INP/CNRS, France

Metal-Organic Frameworks (MOFs) constitute a class of hybrid materials that have received a lot of attention due to their versatility in physical and mechanical properties and by the many possibilities that can be used to synthesize them. Given their particular properties and the possibilities to integrate them into devices, it has become important to synthesize MOFs as thin films. The initial methods to deposit MOF thin films were based on the same approaches used for the bulk synthesis, which involve the use of solvents and thus are not ideal for integration in nanofabrication processes [1]. More recently, solution-free approaches have been proposed based on Atomic Layer Deposition (ALD). [2] Thanks to the surface-limited, self-terminating nature of ALD reactions, the deposition of films with precise control over the thickness and with high conformity even on high-aspect-ratio or porous substrates is possible. Thus, the combination of oxide layers made by ALD with vapors of organic linkers has been reported and it is indeed a very appealing route towards achieving device integrated MOF thin films. [3]

SALD is a variation of ALD that has the advantage to be faster compared to ALD and that can work at atmospheric pressure and even in the open air. [4,5] We have also demonstrated that by adjusting the deposition parameters of our home-made SALD system we can perform area selective deposition in a direct way, i.e. without the need for patterning or masking steps [6].

In this communication, we will present the synthesis of Zeolitic Imidazolate Frameworks (ZIFs) obtained from ZnO films deposited by SALD and using less toxic ligands with respect to the classical 2-Methylimidazole. We will also demonstrate that area selective deposition of MOF thin films can be easily achieved by converting ZnO patterns deposited with our SALD.

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AS-TuP-7 Topographic Area Selective Deposition: A Ccomparison Between PEALD/ALE and PEALD/Sputtering Approaches*, **Moustapha Jaffal**, T Yeghoyan, V Pesce, A Chaker, D Sylvain, G Lefevre,* LTM-UGA, France*; R Gassilloud, N Posseme,* CEA-Leti, France*; M Bonvalot,* LTM-UGA, France*; C Vallée,* CNRS LTM, France

Multiple patterning for advanced 3D nano-electronic devices largely relies on plasma processes. For instance, conformal deposition of spacers on pitches and mandrels is carried out by Plasma Enhanced Atomic Layer Deposition (PEALD), with subsequent anisotropic plasma etching steps of top and bottom deposits, so as to keep only vertical coatings on 3D feature sidewalls. Such a technological route is well-established, although it suffers from several drawbacks, such as deposition-related trench corner accumulation, or etch-related foot formation, spacer sidewall trimming and trenching. These can be potentially avoided thanks to a so-called super-cycle approach, as developed previously by our group, whereby a complete coating of 3D structure sidewalls is achieved by multiple and alternating deposition and etch cycles [1,2].

The proof of concept for this lateral 3D structure coating by in-situ super-cycle deposition was published last year for the specific case of Ta_2O_5: super-cycles were composed of Ta_2O_5 standard PEALD steps intercalated by Ar^+ plasma sputtering steps with ions of approximately 260 eV incident kinetic energy [3]. Although this process appears to be suitable at the macroscopic scale, its transfer to the nanoscale for spacer definition with appropriate critical dimension (CD) control is not trivial, as illustrated in Figures 1 and 2. Indeed, the Ar^+ sputtering step may induce significant damages to exposed substrate surfaces, such as roughness, amorphization, redeposition or ion implantation.

In this work, we have investigated the possibility of using a so-called quasi-Atomic Layer Etching step (q-ALE) instead of an Ar^+ sputtering step, for the definition of a 3D ASD process with true nanoscale control. The q-ALE step consists in a self-limited fluorine-based passivation followed by a low-energy soft Ar^+ plasma removal of the thus-modified uppermost surface layer and can be easily performed within the same ALD reactor chamber.

The optimization of this PEALD-q-ALE super-cycle process will be presented for the topographic selective deposition on vertical surfaces only, with the objective of minimizing any drift and cross contamination. The occurrence of etch-related defects and the overall process throughput will be discussed in view of previously published results obtained from PEALD – Ar^+ sputtering processes.

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AS-TuP-10 Molecular Rearrangement of a MLD Thin Film by Electron Beam Irradiation*, **GeonHo Baek**, S Lee, J Lee, J Park,* Hanyang University, Republic of Korea

Recently, to increase the transistor density of logic and memory devices, the structure of device has to be technically developed and it requires the process which decreases cost of process and increases process yield with simplifying device process. Area selective deposition can be one of the methods to simplify process. Among conventional selective deposition methods, there is an electroless deposition (ELD) method which is useful for Cu metallization[1]. However, as smaller size of device is developed, the resistivity of Cu electrodes increases drastically, so the metal electrodes such as Mo, Co and Ru can be selected as a candidate for fine nano-pattern[2]. Furthermore, due to issues of particle and contamination in the ELD process, another methodology is required to fabricate defect-free nano pattern[3]. Area selective atomic layer deposition (ASALD) is a promising future technology to realize 5nm scale memory device and apply on industry. The ASALD is a key process which is one of “bottom-up” technology to reduce cost of fabrication and complement positional error alternative to conventional “top down” technology.

In this paper, the authors researched an inhibitor for the ASALD using molecular layer deposited (MLD) film annealed by electron beam irradiation (EBI). The authors studied the effect of EBI on an indicone film which is fabricated by using INCA-1 (Bis(trimethysily) amidodiethyl Indium) and HQ (hydroquinone) and an alucone film which is fabricated by using TMA (Trimethylaluminum) and 4MP (4-mercaptophenol). The EBI effect on MLD films was evaluated by investigating change of thickness, composition and structure. In the annealed indicone (HQ), there are only carbon and oxygen, but various elements of aluminum, carbon, oxygen and sulfur in the annealed alucone (4MP) film. The various elements act as impurity and inhibit reconstruction of graphitic carbon. The graphitic carbon of annealed indicone (HQ) film can be used for inhibitor of ASALD due to deficiency of hydroxyl group on the surface. In order to observe selectivity of the annealed indicone film, atomic layer deposition of ZnO was performed on annealed indicone / silicon line pattern and the surface of annealed indicone can inhibit 20 cycle of ALD ZnO as compared to Si surface.

AS-TuP-11 Inherent Area-Selective Atomic Layer Deposition of Ruthenium Thin Film with Novel Ru Precursor*, **Hye-Mi Kim**, J Lee, S Lee,* Hanyang University, Republic of Korea*; R Harada, T Shigetomi, S Lee,* Tanaka Kikinzoku Kogyo K.K., Japan*; B Shong,* Hongik University, Republic of Korea*; J Park,* Hanyang University, Republic of Korea*; T Tsugawa,* Tanaka Kikinzoku Kogyo K.K., Japan

Ruthenium (Ru) thin films are deposited by atomic layer deposition (ALD) using novel precursor, $Ru_2\{(CH_3)_3CNCHCCH_2CH_3\}(CO)_6$ (T-Rudic), and two different co-reagents, H_2O and O_2. Ru films are deposited as 0.1 Å/cycle at 150 ^{o}C with H_2O and 0.8 Å/cycle at 200 ^{o}C with O_2. Different reaction behavior was observed between two reactants, especially film growth rate depending on growth temperature. O_2 shows only CVD growth behavior, on the other hand, H_2O co-reactant set shows ALD saturation between 150 to 200 ^{o}C. We find that film growth preference exists among the various substrates (Si, SiO_2, Al_2O_3, graphitic carbon) when H_2O applied at 150 ^{o}C. Ru film selectively grown on various substrates and except for Si substrate, nucleation delays were detected. To identify the selective deposition mechanism, density functional theory (DFT) calculation of half-reaction was progressed. Due to the difference in chemisorption energy, nucleation delay occurred on hydroxyl-terminated SiO_2 surface. Both experimental data and DFT calculation indicates that prefer growth on hydrogen-terminated surface (Si). We also infer the reaction mechanism of precursor and reactant from other precedent researches in addition to our results, remained carbonyl ligand after chemisorption of precursor reacts with H_2O by WGSR method and forms Ru film. Overall, this work shows that the ALD deposition of novel Ru precursor and its film properties, selective deposition and the reaction path of the precursor. Our study suggests that through precursor designing and selecting proper reactant ASD could be achieved using ALD technique.

AS-TuP-12 Selective Atomic Layer Deposition of Nickel on the Molybdenum Oxide Supported on γ-Al_2O_3 for Enhanced Hydrodesulphurization of Dibenzothiophene at Lower Temperatures and Pressures*, A Khodadadi, S Bahrani, Y Mortazavi, **Fatemeh Gashoul Daresibi,*** University of Tehran, Iran

It is believed that components such as Ni promote the hydrodesulfurization (HDS) activities of Mo- and W-based sulfide catalysts. Till now, various investigations have been done in order to understand the synergy mechanism between promoter (as Ni) and sulfided Mo(W), the structure of the active catalytic sites and HDS reaction mechanisms. Generally, the mechanism for the HDS reaction is proposed to be based on the requirement of anion vacancy for the S-containing molecule being adsorbed through S-heteroatom. In the promoted transition metal sulfides as Ni-Mo catalysts the presence of Ni promoter may accompanied the formation of anion vacancies as a result of promoter atom substitution with Mo atoms in S-Mo-S slabs of Ni-Mo-S phase which is known as the catalytic active site in the HDS catalysts. So, intimate contact of Ni and Mo species and edge decoration by the Ni promoter is believed to be necessary for formation of Ni-Mo-S active phase while the NiS_x is not reactive [1-3].

In this study, Ni(acac)$_2$ was selectively deposited on MoO_3 by atomic layer deposition (ALD) at 180 ^{o}C. The selective deposition was confirmed by monitoring Hacac as the reactive chemisorption product in the ALD reactor effluent gases using a gas cell in FTIR. There is 30 ^{o}C temperature window, at which the Ni(acac)$_2$ is selectively deposited on MoO_3 but not on γ-Al_2O_3, as shown in **Fig.1** .In this way, the determined contents of Ni (by ICP technique) showed 0.07 and 0.64 wt% deposition of Ni on MoO_3/γ-Al_2O_3 and γ-Al_2O_3, respectively during first ALD cycle for 20 minutes at 180 ^{o}C. The MoO_3, seems to catalyze the reactive chemisorption of Ni(acac)$_2$ [4]. The FTIR spectra of MoO_3/γ-Al_2O_3 and the one after reactive adsorption of Ni(acac)$_2$ shown in **Fig. 2**. confirms the successful ALD and possible formation of acac-Ni-O-MoO_x species.

3 wt% Ni on 6, 9 and 14 wt % Mo/ γ-Al_2O_3 catalysts were prepared by both S-ALD and conventional impregnation (IMP) methods and their dibenzothiophene (DBT) sulfur removal efficiencies were evaluated and presented in **Fig. 3** at 300 ^{o}C and 1 and 5 bar pressures. The S-ALD prepared catalysts show up to about 80% higher S-removal efficiency, compared to the ones prepared by IMP method.

In conclusion, the selective ALD can provide an intimate contact of Ni and Mo, which results in the formation of Ni-Mo-S reactive phase required for effective desulfurization.

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AS-TuP-13 Area Selective Atomic Layer Deposition of Molybdenum Films on Nanoscale Metal and Metal Nitride Patterns*, **Se-Won Lee**, M Kim,* Merck Performance Materials Ltd. Korea, Republic of Korea

Deposition of conductive metal in super-narrow lines and vias represents significant challenge for scaling semiconductor devices. Cu interconnect lines show significant increase in resistivity below 10 nm and can’t be used without a barrier due to electromigration. Tungsten inherently has higher resistivity compared to copper while precursor choice is often limited to tungsten hexafluoride which also requires a relatively thick barrier film to protect dielectric layer. Molybdenum (Mo) is considered as an attractive material for future devices. Mo has almost same level of low bulk resistivity comparing to W, but it has smaller EMFP (Electron Mean Free Path), so the effective resistivity, a product of bulk resistivity and EMFP, is expected to be lower compared to W for films less than 10nm. While Mo films can be deposited by traditional CVD or ALD processes, area selective deposition of metal films can significantly reduce process steps and provide new options for device integration.

Here, we report area selective thermal ALD of Mo films on metal and metal nitride substrates using high purity molybdenum pentachloride ($MoCl_5$) and molybdenum dichloride dioxide (MoO_2Cl_2). Deposition of Mo films was investigated by thermal ALD process with hydrogen reactant gas at 350-500^{o}C on various substrates, such as aluminum oxide, silicon oxide, titanium nitride and ruthenium metal. Both Mo precursors showed higher deposition rate on TiN substrate compared to SiO . However, MoCl showed significantly higher process selectivity toward TiN and Ru. The dependence of selectivity on process conditions, such as precursor ampoule temperature, chamber pressure and deposition temperature was investigated. Higher selectivity was attributed to MoCl ability to self-etch deposited Mo film.The films were characterized by XRF, 4-point probe, XPS, SIMS and XRD. Molybdenum films deposited from $MoCl_5$ on Ru substrate at 450^{o}C showed no detectable chloride by XPS and << 0.01 at % by SIMS.

High resolution TEM of Mo films on patterned TiN/SiO_2 and Ru/LowK wafers shows a seamless bottom-up molybdenum fill on highly challenging structures with CD < 30 nm and feature height > 80 nm, with very minor defects on SiO_2 and LowK dielectric. Over 10 times enhancement of effective deposition rate was observed inside the features compared to blanket film. For example, selected process conditions provided 4.2 nm Mo film on blanket Ru film while the same conditions deposited over 80 nm Mo film inside of ~ 20 nm via. The result may suggest that ASD mechanism on nanoscale is different from the macroscale mechanism.

AS-TuP-14 300 mm-Wafer Characterization of Ruthenium Area-Selective Deposition in Nanoscale Line-Space and Hole Patterns*, Jan-Willem Clerix,* *A Delabie,* KU Leuven – University of Leuven/IMEC, Belgium*; J Hung,* Nova MI/IMEC, Belgium*; L Warad, K Shah,* Nova MI, Belgium

Area-Selective Deposition (ASD) will become more and more important for nano-electronic device fabrication. It is an approach that relies on the selective growth of materials, based on differences in precursor adsorption and diffusion on varying surfaces. The promise of both vertical and horizontal growth control, simplified production flows and elimination of edge placement errors make Area-Selective Atomic Layer Deposition (AS-ALD) an ideal technique to complement top-down patterning. Yet, unintentional island growth on the non-growth surface is a major challenge for AS-ALD, and defect mitigation strategies are being developed. Crucial to this development is the availability of characterization techniques that map selectivity and defectivity on large area substrates containing nanopatterns.

In this work, we investigate the growth rate and selectivity of Ru ASD on nanoscale TiN/SiO_2 line-space and hole patterns on 300 mm wafers. The process consists of a N,N-dimethylamino-trimethylsilane surface passivation step, (ethylbenzyl)(1-ethyl-1,4-cyclohexadienyl)Ru/O_2 ALD and an O/Cl plasma defect etch; and has been used previously to create a Ru hardmask for block patterning [1]. In this work, we investigate defect mitigation strategies based on particle size control or selective etch. We therefore use a full-wafer in-line characterization approach based on Optical Critical Dimension Metrology (OCD), X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). XPS provides information about both growth and non-growth patterns simultaneously without the need for cross-section imaging. Additionally, each XPS measurement probes 10^4 structures, while SEM probes ~10, which benefits XPS sensitivity. Attenuation of the Ti and Si signals is used to monitor Ru coverage on the TiN growth and SiO_2 non-growth surfaces. The Ti3s signal shows how over a 120s etch all Ru is removed from the growth surface (figure 1), not all Ru is removed from SiO_2. Our preliminary findings indicate that further optimization is needed to obtain an ASD window through etch selectivity. Alternatively, particle size control can be used when using an etch-based defect mitigation strategy.

Area Selective ALD
Room Baekeland - Session AS-WeM
Selective ALD I

Moderators: Dennis Hausmann, Lam Research, Hanjin Lim, Samsung Electronics Co., Inc.

10:45am **AS-WeM-1 Promixity Effect of Selective Co ALD on the Nanoscale*, Michael Breeden,* ***S Wolf, A Anurag, V Wang,* University of California San Diego*; D Moser, R Kanjolia, M Moinpour, J Woodruff,* EMD Performance Materials*; A Kummel,* University of California San Diego*; M Li, M Bakir,* Georgia Institute of Technology

The use of selective-area Co ALD is desired both for bottom-up fill of Co in interconnect and vias, as well as in forming connections between stacked dies in packaging. The cobalt ALD process using $Co(DAD)_2$ and formic acid (HCOOH) or tertiary-butyl amine (TBA) is known to have nearly infinite selectivity (>1000 cycles) on metal vs. insulator (SiO_2 or low-k SiCOH) planar surfaces [1,2]. However, when the spacing between the metal and insulator regions is less than 100 nm, there can be a reduction in selectivity under identical ALD conditions, due to the diffusion of molecularly-adsorbed metal precursor from reactive to non-reactive surfaces [3].

In this report, Co ALD was performed using $Co(DAD)_2$ + TBA at 180°C on 85 nm wide Cu stripes on SiO_2, as well as on suspended Cu stripes with a 200 nm spacing between the Cu growth surfaces. The planar structure of these stripes enables top-down scanning electron microscopy (SEM) imagery and x-ray photoelectron spectroscopy (XPS) quantification to be used to monitor the presence of unwanted Co nuclei on insulator (SEM) and the growth rate on Co (XPS). To control precursor dose, multiple precursor pulses were employed in each cycle to limit the maximum pressure when dosed through a turbomolecular pump to minimize background contamination. XPS is performed without breaking vacuum to prevent oxidation of Co. The Cu stripes were tested for open- or short-circuit connection between surfaces due to Co ALD growth. Finally, cross-sectional transmission electron microscopy of the alternating strips was performed.

Four strategies have been found to improve Co ALD selectivity: adding a passivant to remove insulator defect sites, increasing the purge time, decreasing the precursor dose, and periodic annealing at 260°C in vacuum. SEM of the striped pattern with a longer purge time shows decreased unwanted nucleation; while the periodically annealed stripe pattern shows a removal of all unwanted nuclei on SiO_2, along with a densified film and edge buildup of Co. This is consistent with reabsorption of the Co nuclei from the insulator surface to the growth surface in a low-temperature nanoscale reflow process. It is possible the low temperature nanoscale reflow process would enable further scaling of the diffusion barriers to SiCOH. For packaging, this low temperature ALD process has the potential to induced selective Cu bump bonding as shown by the results on the suspended Cu stripes.

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2. S. Wolf, et al. Appl. Surf. Sci., 2019, **510**, pp. 144804

3. F. Grillo, et. al. ALD Conference Proceeding, Seattle, WA 2019

11:00am **AS-WeM-2 Cobalt Electron-Enhanced Atomic Layer Deposition (EE-ALD) Using High Electron Flux Hollow Cathode Plasma Electron Source (HC-PES): Rapid Growth and Bottom-Up Fill*, Zachary Sobell,*** *A Cavanagh,* University of Colorado - Boulder*; S George,* University of Colorado - Boulder

Electron-enhanced atomic layer deposition (EE-ALD) facilitates low temperature ALD using an electron beam that can remove surface species by electron stimulated desorption. Previous work has demonstrated BN [1] and Co [2] EE-ALD using an electron gun. Higher electron fluxes by a factor of > 3000 can be produced by a hollow cathode plasma electron source (HC-PES). In addition, the HC-PES is more resistant to chemicals and has significantly faster ON/OFF times. This HC-PES has been used to grow Co films with area selectivity using cobalt tricarbonyl nitrosyl [CTN, $Co(CO)_3NO$] exposures together with electron exposures.

Rapid Co EE-ALD is observed with cycles times of ~40 s/cycle. In situ ellipsometry measurements reveal that nucleation is rapid on the native oxide of silicon wafers (Figure 1). Co EE-ALD displays growth rates of ~2.5 Å/cycle over an area of > 4 cm^2. The uniform film thickness over this area also argues that the electron exposures are able to obtain saturation behavior by desorbing all the ligands from the adsorbed CTN species. The high electron fluxes have also led to new growth phenomena. At small electron exposures <0.05 C/cm^2, normal "ALD like" Co growth is observed versus sequential CTN and electron exposures. At higher electron fluxes >0.1 C/cm^2, the Co growth enters a new regime where the growth can continue for many precursor doses following only one electron exposure. Co film thickness as large as 1000 Å have been grown using multiple CTN exposures following only one electron exposure.

The directionality of the electrons is also useful for area selective EE-ALD. Because the electron flux is normal to the surface, the horizontal surfaces are exposed to higher electron fluxes than the vertical surfaces. Consequently, EE-ALD on vias should occur primarily from the bottom up. Co EE-ALD films were grown on high aspect vias and then examined using transmission electron microscopy (TEM). Co EE-ALD was performed using 45 CTN/electron cycles with electron energy at 140 eV and electron exposure at 10 mA for 10 s. For the vias with an aspect ratio of ~4, the TEM images revealed a film thickness of ~5 nm on the sidewall (Figure 2) and ~30 nm on the bottom (Figure 3). The six times larger deposition on the bottom could facilitate bottom-up fill of the via.

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11:15am **AS-WeM-3 Probing the Selectivity of Area-Selective Spatial ALD + Etch-Back Supercycles for SiO_2 by Low Energy Ion Scattering*, Alfredo Mameli,*** TNO/Holst Center, Netherlands*; P Brüner,* IONTOF GmbH, Germany*; F Roozeboom,* TNO/Holst Center, Netherlands*; T Grehl,* IONTOF GmbH, Germany*; P Poodt,* TNO/Holst Center, Netherlands

Area-selective ALD interleaved with etch-back steps in a supercycle fashion has recently been reported as very effective in achieving high selectivity. Such supercycles can result in lower defectivity on the non-growth area and thicker layers on the growth area, as compared to solely area-selective ALD.[1, 2] The complementarity of deposition and etching techniques can therefore offer great potential for reaching the ultimate requirements in advanced device manufacturing.

Here we use low energy ion scattering (LEIS) to probe the selectivity of the first supercycle, consisting of plasma-enhanced selective spatial-ALD of SiO_2 and conventional CF_4-based reactive ion etching (RIE). Given its extreme sensitivity to the top monolayer(s) of a thin film, LEIS can reliably quantify the selectivity and defectivity on the non-growth areas in terms of surface coverage and derived thickness.

For the selective spatial ALD a three-step approach was adopted,[3] consisting of successive inhibitor, silicon precursor (BDEAS) and O_2 plasma exposures. Silicon wafers (growth area) with large ZnO patterns (non-growth area) were used as substrates. After 20 spatial ALD cycles, no silicon was detected on the non-growth area by LEIS (detection limit 2 % SiO_2 surface coverage), implying excellent process selectivity. The selectivity is however gradually lost by increasing the number of ALD cycles up to 110. On the non-growth area, the SiO_2 layers now had an averaged thickness of 3.5 nm as measured by spectroscopic ellipsometry (SE) and corroborated by LEIS measurements (86% Si surface coverage). At the same time on the growth area, a SiO_2 thickness of 11 nm was measured. In order to correct for the selectivity loss, a 3 seconds RIE step was applied, which restored the Si coverage and reduced the SiO_2 thickness on top of the non-growth area back to zero, as demonstrated by LEIS. Concurrently, 8 nm thick SiO_2 was left on the growth area.

The data presented in this work demonstrate the effectiveness of combining selective spatial ALD + etch-back corrections to achieve extreme SiO_2 selectivity while retaining high deposition rates. Furthermore, we will discuss how LEIS can provide useful information on selectivity as well as defect formation on the non-growth area. Finally, we have extended the plasma-enhanced selective spatial ALD of SiO_2 to other non-growth areas.

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[3] A. Mameli et al., *ACS Nano*, 11, 9303-9311 (2017).

Area Selective ALD
Room Baekeland - Session AS-WeA
Selective ALD II & III

Moderators: Adrie Mackus, Eindhoven University, Netherlands, Christophe Vallée, LTM/CNRS-UJF, France

1:00pm **AS-WeA-1 Area-Selective Atomic Layer Deposition of 2D WS₂ Nanolayers using Inhibitor Molecules***, **Shashank Balasubramanyam**, M Merkx,* Eindhoven University of Technology, Netherlands*; M Verheijen,* Eurofins Materials Science Netherlands B.V., Netherlands*; E Kessels, A Mackus, A Bol,* Eindhoven University of Technology, Netherlands

Due to the continued downscaling of device dimensions, ultra-thin two dimensional (2D) semiconductors like WS_2 are considered as promising materials for future applications in nanoelectronics. At these nanoscale regimes, device fabrication with precise patterning of critical features is challenging using current top-down processing techniques. In this regard, area-selective atomic layer deposition (AS-ALD) has emerged as a promising technique for bottom-up processing to address the complexities of nanopatterning.[1] To date, AS-ALD of metals and dielectrics have been successfully demonstrated.[1] However, AS-ALD of 2D materials has remained elusive. In this contribution, we demonstrate area-selective deposition of 2D WS_2 nanolayers by using a three-step (*ABC-type*) plasma-enhanced ALD process.

AS-ALD of WS_2 was achieved by using acetylacetone (Hacac) inhibitor (A), bis(tertbutylimido)-bis(dimethylamido)-tungsten precursor (B), and H_2S plasma (C) pulses at a low deposition temperature of 250 °C. This process resulted in immediate growth on: (1) SiO_2 (commonly used substrate for the growth of 2D TMD layers), (2) 2D TMDs such as MoS_2, NbS_2, and TiS_2 and (3) metal oxides such as MoO_3, Nb_2O_5 and WO_3 while effectively blocking growth on Al_2O_3 and HfO_2 surfaces, as determined from *in situ* spectroscopic ellipsometry and *ex situ* X-ray photoelectron spectroscopy measurements. The surface chemistry of this selective process was analysed by *in-situ* Fourier transform infrared spectroscopy. The analyses revealed that the inhibitor adsorbed on the non-growth surfaces (Al_2O_3), blocking precursor adsorption, while little or no inhibitor adsorption was detected on the growth surface (SiO_2) where WS_2 was readily deposited. As WS_2 grows readily on several TMD surfaces, our process can be also used to selectively grow 2D TMD vertical heterostructures (*e.g.* WS_2 on MoS_2) in presence ofthe non-growth areas (*i.e.,* Al_2O_3 and HfO_2).

To improve the crystallinity, the AS-ALD WS_2 films were annealed at temperatures within the thermal budget of industrial semiconductor processing (≤ 450°C). The annealed films exhibited sharp Raman peaks, which is a fingerprint of highly crystalline WS_2. Furthermore, Raman line scans over the patterns showed very sharp peak intensity transitions at the SiO_2-Al_2O_3 interface which confirmed that annealing had no impact on selectivity.

To summarize, this work pioneered the combination of two key avenues in atomic-scale processing: area-selective growth and ALD of 2D materials. It is expected that the results of this work will lay the foundation for area-selective ALD of other 2D materials.

Reference:

[1] Mackus *et al.*, *Chem. Mater.***31,** 2–12 (2019).

1:15pm **AS-WeA-2 Kinetic Modeling of Ru Area-Selective Atomic Layer Deposition on Nanopatterns***, **Jan-Willem Clerix**,* KU Leuven, Imec, Belgium*; E Alonso Marques,* KU Leuven, Imec, TU Delft*; J Soethoudt,* KU Leuven, Imec, Belgium*; F Grillo,* ETH Zurich, Switzerland*; G Pourtois,* Imec, Belgium*; R van Ommen,* Delft University of Technology, Netherlands*; A Delabie,* Imec, Belgium

Area-Selective Deposition (ASD) is emerging as a promising bottom-up approach for nano-electronic device fabrication. However, unintentional growth on the non-growth area is a major challenge during ASD by atomic layer deposition (ALD). In addition, processes at the interface between growth and non-growth areas remain poorly understood. Insight into the growth mechanisms during ALD on nanoscale patterns can contribute to the development of ASD processes.

First, we investigate the mechanism of (ethylbenzyl)(1-ethyl-1,4-cyclohexadienyl)Ru/O_2 (EBECHRu) ALD on different blanket non-growth surfaces by experimentally parametrized mean field and kinetic Monte Carlo models (KMC) [1]. We compare two hydrophobic methyl-terminated surfaces: SiO_2-$Si(CH_3)_3$ and organosilicate glass (OSG). The extent of growth inhibition during Ru ALD differs for these two cases. We identify a growth mechanism that describes the Ru areal density, surface coverage and particle size distribution and their evolution during ALD. Ru nanoparticles initially grow mainly by surface diffusion and aggregation. Precursor adsorption on the Ru nanoparticles occurs only when they reach a critical diameter of 0.85 nm, as smaller particles do not catalyze O_2 dissociation. The initial precursor adsorption is faster on SiO_2-$Si(CH_3)_3$ and the diffusion length of Ru adatoms and nanoparticles is larger. This explains the higher Ru content and larger particle size for a given number of cycles (Figure 1).

Informed by such insights, we use KMC simulations to study the impact of surface diffusion near the interface between growth and non-growth areas. We use the model parameters as determined for Ru ALD on blanket substrates and assume the growth area to act as sink for Ru nanoparticles. The simulations indicate a depletion zone with low nanoparticle density on the non-growth surface near the interface with the growth area (Figure 2).

We conclude that the interface between growth and non-growth areas plays an important role during ASD, and that the growth mechanisms critically depend on the surface properties and functionalization.

[1] J. Soethoudt et al., Adv Mater. Interfaces **5**, 1800870(2018).

1:30pm **AS-WeA-3 Area-Selective Atomic Layer Deposition on Chemically Similar Materials***, **Tzu-Ling Liu**, S Bent,* Stanford University

Traditional top-down semiconductor fabrication processes are facing more challenges as a result of the scaling down of devices. Multiple processing steps not only increase the process complexity and cost but also introduce more process errors, such as with two-dimensional overlay and edge placement. Area-selective atomic layer deposition (AS-ALD), which allows direct deposition of materials on desired regions, is considered to be one promising solution and has been attracting more attention recently. One common way to selectively inhibit ALD growth on specific regions is to use self-assembled monolayers (SAMs), which form spontaneously on specific surfaces, depending on the reactivity of the SAM headgroup with substrates.

Despite the apparent simplicity of using SAMs as inhibitors for AS-ALD, the approach requires the starting substrate to have materials with sufficiently different chemical properties to allow selective SAM adsorption. This can present challenges when the desired substrate pattern has chemically similar materials present on the surface at the same time, such as dielectric/dielectric systems. Hence, it is important to expand selective deposition to more general systems. In this study, we describe new area selective ALD systems in which the above challenge is addressed. We have performed area selective ALD on chemically similar materials by selective deposition of alkylsilane and phosphonic acid SAMs on different dielectric surfaces. By taking advantage of the distinct reactivity of SAMs on various surfaces, we can choose SAMs that pack differently, affecting the ALD blocking ability. We show that a relatively well-packed SAM which is able to block ALD can be formed on Al_2O_3, HfO_2, TiO_2 and TaN substrates, while a poor SAM is formed on SiO_2 surfaces, after optimization of the SAM deposition. Selectivities greater than 90% are reached for 50 cycles ZnO ALD on SAM-treated Al_2O_3, TiO_2 and TaN compared to the SAM-treated SiO_2 surface, while a selectivity above 90% can be achieved for HfO_2 versus SiO_2 after 25 cycles ZnO ALD. In addition to MO_x/SiO_2, more general selectivity in MO_x/MO_x systems is also studied and we demonstrate AS-ALD in the Al_2O_3/HfO_2 system where Al_2O_3 is the non-growth surface. With our strategy, we demonstrate the ability to perform AS-ALD on patterns with chemically similar materials such as TaN/SiO_2, Al_2O_3/SiO_2 and Al_2O_3/HfO_2. This study gives insight into achieving more general selectivity and opens up the possibility for new applications in next generation electronic devices.

1:45pm **AS-WeA-4 Area-Selective Atomic Layer Deposition Al_2O_3 using a Small Thiol Inhibitor and Effects of Precursor Size***, H Lee, **Bonwook Gu**,* Incheon National University, Republic of Korea

Area-selective atomic layer deposition (AS-ALD) is attracting increasing interest because of its ability to enable both continued dimensional scaling and accurate pattern placement for next-generation nanoelectronics. Self-assembled monolayers (SAM) have been used as inhibitor to change the surface property in AS-ALD. The conventional SAMs, however, were relatively long and big in the range of 2~3 nm, so they are not suit for AS-ALD in few nanometer scale 3D patterns. In this work, we investigated ethanethiol (ET) for a small size inhibitor of AS-ALD on metal substrates, Co and Cu. We used two Al precursors with different molecular size, trimethyl-aluminum (TMA) and dimethyl-aluminum-isopropoxide (DMAI) for blocking property, with H_2O counter reactant. ET was selectively absorbed on Cu and Co, but not on SiO_2 and showed better inhibition property against ALD

Al_2O_3 using DMAI than that using TMA. In order to investigate the different blocking property of ET to TMA and DMAI, we calculated the adsorption kinetics and dynamics of Al precursors on Cu and Co surfaces inhibited by ET using density-functional theory (DFT) and realized physical adsorption behavior based steric hindrance using Monte-Carlo (MC) simulation. DFT results showed that DMAI forms dimers during adsorption on surfaces, and TMA preferably reacts even on the CH_3-terminted ET surfaces. Consistently, the steric hindrance simulation by MC showed a reasonable difference in Al precursor adsorptions on ET-inhibited Co and Cu surfaces. From the results and knowledge, we could extend the degree of freedom to obtain better AS-ALD property to selection of ALD precursors, and it could be applied to other AS-ALD materials systems.

3:15pm **AS-WeA-10 Effect of Copper Surface Condition on Passivation Characteristics for Applications to Area Selective Atomic Layer Deposition***, **Su Min Hwang**,* University of Texas at Dallas*; H Kim, J Kim,* The University of Texas at Dallas*; Y Jung,* University of Texas at Dallas*; L Pena, K Tan, J Veyan,* The University of Texas at Dallas*; D Alvarez, J Spiegelman,* RASIRC*; K Sharma, P Lemaire, D Hausmann,* Lam Research Corp.*; J Kim,* University of Texas at Dallas

Recently, area-selective atomic layer deposition (AS-ALD) by locally passivating the copper surface has garnered attention by reducing the number of processing steps as well as by alleviating key challenges associated with lithography and layer alignment at the sub-5 nm node.[1–3] However, despite the enormous scientific effort in recent years, lack of surface science during cleaning and passivation of Cu surfaces impede the development of AS-ALD. Specifically, the effect of the copper surface on the quality of passivation materials, such as self-assembled monolayers (SAMs) has been rarely reported.

Herein, electroplated Cu films were treated using glacial acetic acid (CH_3COOH) and anhydrous N_2H_4, respectively.[4] After cleaning, the Cu samples were immersed in a 1 mM solution of octadecanethiols (ODTs) in ethanol for 20 h. To elucidate the surface chemistry and stability of ODTs, the passivated Cu samples were loaded into an *in-situ* reflectance absorption infrared spectroscopy (RAIRS) system equipped with an ALD chamber, then ALD of AlO_x process was performed using TMA and H_2O at 120 °C. During surface cleaning, CH_3COOH removes surface adventitious contaminants (e.g., $–CH_x$, $–CO_3$, and –OH), and most importantly, reduces the surface oxide (Cu_2O) to metallic copper by forming copper acetate as an intermediate material. In the *ex-situ* XPS and RAIRS, the SAMs on the CH_3COOH-treated Cu sample gives poor selectivity of ALD-AlO_x compared to the SAMs on the as-is Cu and N_2H_4-treated Cu, respectively. It implies that the residual copper acetate on the surface can affect the chemisorption of ODTs during passivation, eventually attributing a relatively lower surface coverage, poor thermal stability of ODTs, and poor selectivity during ALD process. To circumvent the issue, the effect of post-treatment after surface cleaning with CH_3COOH was investigated. Vacuum treatment of the sample under the UHV condition ($\sim 10^{-8}$ Torr) can partially reduce the copper acetate by forming $-CH_x$ and -OH species. However, a post-annealing at 75 °C effectively removes the copper acetate and residual contaminants on the surface, which can improve not only ODTs quality in the passivation process but also the increase of nucleation delay during the consecutive ALD process. The detailed experimental results will be presented.

The authors acknowledge Lam Research Foundation for the partial financial support and Rasirc Inc. for providing the Brute N_2H_4 as well as their partial support.

[1] N.F.W. Thissen et al., 2D Mater. **4**, (2017)

[2] L.F. Pena et al., ACS Appl. Mater. Interfaces **10**, 38610 (2018)

[3] M. He et al., J. Electrochem. Soc. **160**, D3040 (2013)

[4] S.M. Hwang et al., ECS Trans. **92**, 265 (2019)

3:30pm **AS-WeA-11 Top and Bottom Ta_2O_5 Topographical Selective Deposition on 3D structures by Plasma Enhanced Atomic Layer Deposition***, **Taguhi Yeghoyan**, V Pesce, M Jaffal,* LTM-UGA, France*; R Gassilloud, N Posseme,* CEA-Leti, France*; M Bonvalot, C Vallée,* LTM-UGA, France

Advanced nanoelectronics technologies, e.g. FinFETs or DRAM deep trench capacitors, are made of active 3D objects. This 3D structuration of matter increases integration complexity, adding multiple nanopatterning steps that affect the fabrication cost. Part of the patterning cost could be reduced if thin films could be selectively deposited on specific surfaces of the 3D structures, like pillars or trenches. Such Topographical Selective Deposition (TSD) processes can be achieved using an anisotropic deposition technique based on a standard Plasma Enhanced Atomic Layer Deposition (PEALD) coupled with directional plasma ion bombardment that induces a local modification of material properties [1].

Recent reports of TSD on 3D structures have two main objectives. The first objective is to deposit thin films only on sidewalls of 3D structures, for which several methods have been already reported, including pre-growth surface deactivation [2], post-growth in-situ plasma etching or ex-situ wet etching processes [1,3]. The second objective is to deposit thin films only on horizontal (top and bottom) surfaces of 3D structures, for which process routes have been scarcely reported and remain challenging [4,5]. R. A Ovanesyan *et al*. used a three-step ALD process composed of two conventional thermal steps, followed by a subsequent N_2 plasma step in order to reduce carbon contamination in the top and bottom SiN_x deposit, hence, densifying it. The obtained film was then wet etched to achieve the desired top and bottom topography [4].

In this work, we present an original approach leading to only top and bottom Ta_2O_5 densification, based on a standard two-step PEALD cycle, followed by a post-growth wet etching step with an effective selectivity of 10 to 1. As evidenced from SEM imaging, as-grown Ta_2O_5 thin films deposited on 3D trenches (aspect ratio 13:1) show approximately 70% conformity from bottom to top and middle to top, whereas post-growth wet etched structures do not exhibit any vertical coating while maintaining initial bottom to top conformity. We think that the methodology established here could be easily extended to most PEALD deposited materials.

[1] Faraz T. et al., ACS Appl. Mater. Interfaces 2018, 10, 15, 13158-13180

[2] Kim, W.-H et al, ACS Nano 2016, 10 (4), 4451–4458.

[3] Chaker A. et al., Appl. Phys. Lett. 114, 043101 (2019)

[4] Ovanesyan, R. A et al., Plasma. 2017, 29 (15), 6269–6278.

[5] ASM International Analyst and Investor Technology Seminar, Semicon West 2018

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