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$_2$H) 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.

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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$_2$O$_5$: super-cycles were composed of Ta$_2$O$_5$ 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 °C with H_2O and 0.8 Å/cycle at 200 °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 °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 °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 °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 °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 °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 °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°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°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.

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