Area Selective ALD
Room Grand Ballroom H-K - Session AS1-TuM
Area-Selective ALD Techniques

Moderator: Adrie Mackus, Eindhoven University, Netherlands

10:45am **AS1-TuM-12 Overview of Wet And Dry Selective Processes Driven by Area Activation or Deactivation Down to Below 20nm Critical Dimensions***, Silvia Armini,* IMEC, Belgium **INVITED**

Area selective deposition (ASD) is proposed as a method for preferentially depositing a material on a specific area on the surface while the remainder is left uncoated, providing spatial control over a deposited thin film. In the context of downscaling microelectronics components below 1x nm of critical dimension, ASD by Atomic Layer Deposition (ALD), Chemical Vapor Deposition (CVD) or Electroless Deposition (ELD) offers the potential to relax downstream processing steps by enabling self-aligned patterning processes, such as self-aligned vias and tone reversal, or bottom-up metallization schemes, such as supervia or via prefill. Due to the limitations of inherent ALD selectivity, we focus our work on material surface functionalization by selective grafting thin organic films both in ALD activation and passivation mode or by plasma exposure.

For ASD ALD processes which relies on delayed nucleation on a non-growth area, defectivity and the lack of a wide portfolio of application-relevant materials are two of the main concerns for the adoption of this technology in nanofabrication. Among the strategies addressing the defectivity issue, repetitive refreshment of the non-growth surface and selective etching of undesired nuclei are particularly promising.

In this study, we review our current understanding of the relationship between structure and properties of the inhibiting/activating materials and the correspondent surface dependence of different ALD processes. Nucleation and growth behaviour of ALD on different surfaces functionalized by organic films deposited from the liquid and vapor phase on 300mm wafers or by plasmas will be analyzed and wet depassivation processes with be investigated in the attempt of removing the defects formed on top of the inhibition films.

In an attempt to understand the interaction between the ALD conditions (i.e. temperature, coreactants...) to the decomposition and modification of the organic films, in-situ XPS is exploited such as high sensitivity characterization techniques such as Secondary Ion Mass Spectrometry (SIMS).

Finally, the selectivity of the passivation and subsequent ASD process will be evaluated as a function of the patterned pitch size down to 16nm half-pitch structures. We aim at building some understanding about the relationship between the changes in surface composition due to the patterning, pitch variation and/or due to diffusion (in case of mobile species such as metals) and the ASD performance.

11:15am **AS1-TuM-14 Electron-Enhanced Atomic Layer Deposition (EE-ALD) of Cobalt Metal Films at Room Temperature***, Zach Sobell, A Cavanagh, S George,* University of Colorado - Boulder

Electron-enhanced atomic layer deposition (EE-ALD) is possible at room temperature by using electrons to stimulate the desorption of surface species. The electron stimulated desorption (ESD) process opens up free surface sites that enable the adsorption of reactants. ALD can be achieved by sequential application of electron and reactant exposures. A variety of materials have been deposited using EE-ALD at room temperature including GaN, Si and BN. Because EE-ALD is dependent on the electron flux, EE-ALD films are deposited only on surface areas illuminated by the electron beam.

In this study, Co EE-ALD was performed using sequential, self-limiting cobalt tricarbonyl nitrosyl [$Co(CO)_3NO$ (CTN)] and low energy electrons exposures at room temperature. The electron energies were varied from 75 to 175 eV. In the Co EE-ALD process, the CTN molecules first adsorb on the substrate. The electrons then induce ESD of the carbonyl (CO) and nitrosyl (NO) ligands from the adsorbed CTN. The ESD produces reactive surface sites. Subsequent CTN exposures react with the reactive surface sites and add Co to the substrate. The consumption of the reactive surface sites produces self-limiting Co EE-ALD.

In situ ellipsometry measurements observed a maximum growth rate of 0.5 Å per cycle at an electron energy of 125 eV. The in situ ellipsometry measurements also could monitor the CTN adsorption and the desorption of CO and NO ligands (see supplemental Figure 1). Quadrupole mass spectrometer (QMS) measurements confirmed the desorption of CO and NO during electron exposures. The spatial profile of the Co EE-ALD film resulting from the finite surface area illuminated by electrons was mapped by ex situ ellipsometry. This spatial profile was used to calculate an ESD cross section of $\sigma = 1x10^{-16}$ cm^2. This ESD cross section is close to the electron dissociation cross section for CTN observed in the gas phase.

There are many applications for EE-ALD because the ESD process is topographically selective. This area selectivity comes from the directionality of the electron flux. Surfaces normal to the incident electrons receive the full electron flux, whereas surfaces parallel to the incident electron path receive no electron flux. EE-ALD should be useful for the bottom-up fill of high aspect ratio structures like trenches and vias. EE-ALD may also be important for depositing ALD films on thermally-sensitive substrates. In addition, EE-ALD could be valuable for enhancing the nucleation of ALD films by creating reactive surface species on the initial substrate.

11:30am **AS1-TuM-15 Area Selective Atomic Layer Deposition on Molecular Design***, **Akihiro Nishida**, T Yoshino, N Okada, A Yamashita,* ADEKA Corporation, Japan

Area selective atomic layer deposition (AS-ALD) is promising as a self-aligned fabrication method and has become more important in recent years. Several types of AS-ALD precursors and processes have been developed all over the world so far. We recognize the importance of AS-ALD technology as well and have studied it for many years. However, it is challenging to achieve a high selectivity and hence investigation of molecule design and surface chemistry are essential factors to clarify the mechanism of selective deposition and film growth.

In this study, we have carried out the investigation on the effect of surface selectivity using several types of Co ALD precursors, and found that selectivity was affected by high steric hindrance structure, chemical surface characteristics and so on. Based on the results, new Co ALD precursors having a good selectivity have been developed. As an example, Bis(N-tert-butyl-N'-1-methyl-2-dimethylaminoethyl-acetamidinato)cobalt (II) [CBPA-1] has high selectivity and is liquid at room temperature. CBPA-1 showed a very clean TG curve without decomposition and residue at 10 Torr. Additionally, thermal ALD of thin Co metal film was demonstrated using CBPA-1 and hydrogen as the co-reactant on Ru and SiO_2 substrates, and succeeded in making shiny metallic Co films at 150-300 °C only on the Ru substrate. Regarding film quality, X-ray photoelectron spectroscopy (XPS) shows that high purity Co film was deposited. As a comparison, we also carried out thermal ALD using reference precursor Bis(N, N'-di-tert-butyl-acetamidinato)cobalt (II). However, Co was detected on both Ru and SiO_2 substrates over 275 °C by X-ray fluorescence (XRF) measurement. As a conclusion, CBPA-1 is better suited for Co AS-ALD process compared to conventional precursors such as dicobalt hexacarbonyl tert-butylacetylene (CCTBA) and Co amidinates complex. On top of that, a reducing method of isolated particles growth on SiO_2 substrate by using aminosilane was found out so it will be reported likewise.

11:45am **AS1-TuM-16 From Surface Dependence in Atomic Layer Deposition to Area-Selective Deposition of TiN in Nanoscale Patterns***, **Annelies Delabie**,* IMEC, Belgium*; D Carbajal,* UNAM*; J Soethoudt, B Chan, E Altamirano Sanchez, B Meynaerts, J Clerix, S Van Elshocht,* IMEC, Belgium

Area-selective deposition (ASD) holds potential for nano-electronic device manufacturing for bottom-up deposition in small trenches or holes, or to create nanoscale structures with great precision by self-alignment. Under certain surface and deposition conditions, material can grow selectively on a predefined pattern, while the rest of the surface remains unaffected. Nevertheless, ASD by atomic layer deposition (ALD) has been studied only for a limited number of materials. In addition, defectivity in the non-growth area is a challenge as inhibition in ALD is associated with island growth [1]. Insight into the surface dependence and growth mechanisms is needed to design highly selective ASD processes for relevant materials for nano-electronic devices.

First, we compare the inherent selectivity for a range of thermal ALD processes for oxides, nitrides and metals by investigating the surface dependence on blanket substrates. OH-terminated SiO_2 is the growth surface as all ALD processes considered here show linear growth on this surface, while CH_3-terminated SiO_2 is the non-growth surface. Both precursor and co-reagent affect selectivity (figure 1a). The selectivity for H_2O based ALD depends on the precursor in the order $TiCl_4$ > $HfCl_4$ > $Al(CH_3)_3$. The selectivity is higher for $TiCl_4$/NH_3 ALD than for $TiCl_4$/H_2O ALD in spite of the higher deposition temperature.

In view of the high inherent selectivity of $TiCl_4$/NH_3 ALD, we investigate TiN ASD in nanoscale patterns consisting of Si_3N_4 spaces and amorphous carbon (aC) lines with a critical dimension (CD) of 45nm. This material system is relevant for a tone inversion application of ASD for line-space patterning [2]. A H_2 plasma pretreatment enables ASD by passivating the aC surface by formation of methyl groups [2,3]. The selectivity for Si_3N_4 versus aC is 0.94 for 6.4 nm TiN, even higher than for OH- versus CH_3-terminated SiO_2 (blankets). The selectivity is maintained for ALD temperatures between 250 and 390° C. However, in nanoscale patterns, the selectivity is affected by impurities due to patterning. By considering surface cleans before ASD, we demonstrate ASD of 7.5nm TiN on the 45nm CD line-space patterns, with little to no TiN detected on the aC top surface and sidewalls by transmission electron microscopy (Figure 1b).

[1] J. M. Mackus et al, Chem. Mater. 2019, 31, 2

[2] E. Stevens et al, Chem. Mater. 2018, 30, 3223

[3] I. Zyulkov et al, ACS Appl. Mater. Interfaces 2017, 9, 31031

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