Area Selective ALD
Room On Demand - Session AS2
Selective ALD by Area-Deactivation

AS2-1 Gradient Area Selective Deposition using Ti Precursor Inhibitor for Seamless Gap-filling in 3D Nanostructure Pattern, ***Chi Thang Nguyen,*** Incheon National University, Korea (Republic of); *E. Cho,* Samsung Electronics, Korea (Republic of); *J. Park,* Hongik University, Korea (Republic of); *B. Gu,* Incheon National University, Korea (Republic of); *B. Shong,* Hongik University, Korea (Republic of); *H. Lee,* Incheon National University, Korea (Republic of)

Atomic layer deposition (ALD) is a thin film deposition technique with excellent uniformity and conformality at nanoscale due to its unique surface self-saturated reactions of precursors and counter reactants. However, the isotropic growth of ALD is one of the bottlenecks to enable the seamless gap-filling in high aspect ratio structures, such as holes and trenches because the opening of structures is closed off at a certain thickness, resulting in formation of a void. In this work, we introduce an area-selective ALD (AS-ALD) process to realize seamless deposition in 3D nanostructures by using a gradient adsorption of a Ti source precursor inhibitor namely $TiCp^*(OMe)_3$. The $TiCp^*(OMe)_3$ inhibitor can block the growth of TiO2 ALD (using Tetrakis(dimethylamido)titanium-TDMAT precursor) up to 900 cycles (ca. 50 nm) with a high selectivity of ca. 91.3 %. For the gradient AS-ALD, the density of inhibitor adsorption inside 3D structures is controlled by exposure of the $TiCp^*(OMe)_3$ inhibitor, and the deposition of TiO_2 is inhibited in the following TiO_2 ALD depending on the surface concentration of the inhibitor. The results show the ability to control the growth of TiO_2 ALD in the hole pattern (aspect ratio =16). The gap can be filled up from bottom to determined position inside hole without any seams in the centerline. Theoretical calculations by Density functional theory (DFT), Monte Carlo (MC) simulation show high consistency with the experimental results. The concept of gradient AS-ALD could be extended to other ALD materials system for better and simplified process in many various applications.

AS2-4 Selectivity Loss Mechanisms in TiO_2 Area Selective Deposition on Dimethylamino-Trimethylsilane Passivated SiO_2, ***Rachel Nye,*** North Carolina State University; *K. Van Dongen, J. Clerix,* KU Leuven, Belgium; *G. Parsons,* North Carolina State University; *A. Delabie,* KU Leuven, Belgium

Titanium oxide (TiO_2) area-selective deposition (ASD) has been studied for applications such as hard masks for tone inversion, dielectric layers, solar cells, and photocatalysis due to the etch resistance, high dielectric constant, and high refractive index of TiO_2. While these studies[1] have successfully demonstrated several nanometers of selective deposition using various passivation, activation, and defect mitigation techniques, there is still work needed to understand selectivity loss mechanisms in order to further expand selectivity windows to reach commercial requirements. Herein we evaluate selectivity loss mechanisms of TiO_2 deposited on trimethyl-silane passivated SiO_2 substrates from $TiCl_4/H_2O$.

Dimethylamino-trimethylsilane (DMA-TMS) passivates SiO_2 substrates with a 300 s exposure at 250 °C while Si, TiO_2, TiN, and Ru surfaces remain unaffected.[2] This DMA-TMS passivated SiO_2 limits TiO_2 surface coverage to ~5% after 100 cycles (3.8 nm on the growth surface) at 150 °C, as characterized by scanning electron microscopy (SEM) and Rutherford backscattering spectrometry (RBS) (Fig. 1).

Nuclei on the non-growth surface were analyzed with SEM and atomic force microscopy (AFM) to gain insight on nucleation mechanism, adsorption kinetics, and possible impact of diffusion (Fig. 2). Particle size distributions (PSDs) reveal a high concentration of small nuclei even for high cycle numbers. This indicates new nuclei generation on the non-growth surface during deposition. Kinetic modeling[3] was employed to fit experimental data according to this information using an estimated site generation rate of 4.6×10^{-5} sites cm^{-2} $cycle^{-1}$ and a 30-cycle nucleation delay. Modeling results correspond to a thickness of ≈4 nm TiO_2 while maintaining 90% selectivity ($t_{S = 0.9}$ = 4.02 nm).* Furthermore, we compare PSDs at low (150 °C) and high (300 °C) deposition temperatures to evaluate changes in species diffusivity and loss of effectiveness in the passivation layer. Finally, this insight is applied to develop techniques for extending TiO_2 selectivity windows, including repeated passivations and periodic etching to mitigate defects. The improved understanding on TiO_2 selectivity loss identifies effective strategies to increase selectivity to reach advanced technology nodes.

AS2-7 Area-Selective Atomic Layer Deposition of Al_2O_3 on SiO_2 Vapor-Functionalized with Small-Molecule Aminosilanes, ***Wanxing Xu,*** Colorado School of Mines, USA; *P. Lemaire, K. Sharma, D. Hausmann,* Lam Research Corporation; *S. Agarwal,* Colorado School of Mines, USA

With feature dimensions of state-of-the-art semiconductor devices moving toward the 5 nm node and beyond, device fabrication based on top-down approaches is becoming ever more challenging. Recently, area-selective atomic layer deposition (ALD) has evolved as a promising method to fabricate well-defined patterns from the bottom-up with atomic-scale accuracy. Within the different approaches for area-selective ALD, the preparation of patterned substrates with material-selective organic functionalization offers a promising direction for achieving self-aligned patterns over large areas. In this study, we focus on area-selective ALD of Al_2O_3 on functionalized SiO_2 with small-molecule aminosilanes through the vapor phase. Using *in situ* optical surface diagnostics, we investigate the atomistic-scale mechanism that leads to the reaction of the ALD precursors with the functionalized SiO_2 surface.

To inhibit the ALD of Al_2O_3 on SiO_2, SiO_2 substrates were exposed to bis(dimethylamino)dimethylsilane and (*N*, *N*-dimethylamino)trimethylsilane through the vapor phase. *In situ* attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy shows that the aminosilanes react with almost all of the surface –OH groups, thereby rendering the surface unreactive toward dimethyl aluminum isopropoxide (DMAI), which was used at the aluminum precursor in conjunction with and H_2O. *In situ* ATR-FTIR spectroscopy was also used to monitor the reactions on the SiO_2 surface during Al_2O_3 ALD while film growth was monitored using *in situ* four-wavelength ellipsometry. Our experiments show that growth initiation on the functionalized SiO_2 surface may occur due to DMAI molecules that remain strongly bound to the SiO_2 surface after the purge step, suggesting that the growth on functionalized SiO_2 surface could be further inhibited by lowering the precursor dose (see Figure 1). We further show that the growth inhibition of an additional 20 ALD cycles is obtained on functionalized SiO_2 when the DMAI dose dropped from 3.2 Torr·s to 0.4 Torr·s (see Figure 2). Finally, we show that the less reactive precursor, DMAI, leads to better growth inhibition on functionalized SiO_2 compared to trimethylaluminum.

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