Inhibitor-Free Area Selective Atomic Layer Deposition based on Atomic Layer Nucleation Engineering and Surface Recovery with a Feature Size of Nearly 10 nm

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While conventional photolithography faces more and more challenges to follow the progress of aggressive semiconductor scaling, area-selective atomic layer deposition (AS-ALD) has become a promising technique that can directly reduce the number of lithography and etching processes. In this study, novel concepts including the "atomic layer nucleation engineering (ALNE)" and "surface recovery (SR)" techniques, were proposed for the realization of AS-ALD without using any inhibitors. The AS-ALD process based on ALNE and SR results in nearly 100% selectivity of the oxide (Al_2O_3) and nitride (AlN) deposition between the dielectric (SiO_2) and the metal (Pt or W). For ALNE, by directly introducing the radio-frequency (RF) substrate bias after the exposure and purging of precursors in each ALD cycle, the difference in the binding energy of the precursor adsorbed on dielectric and metal surfaces give rise to the selectivity of film deposition. The relatively lower binding energy of the precursor on the metal surface, as compared with that on the dielectric surface, opens a processing window for the local substrate plasma to remove the precursor adsorbed on metal, which contributes to the inhibitor-free AS-ALD between SiO_2 and Pt. Furthermore, for those metals that are easily oxidized during the oxide deposition, the SR technique (i.e., by introducing the RF substrate bias again) is subsequently applied to dispose of the oxidized layer on the metal surface. Accordingly, the ALNE method achieves the high-selectivity AS-ALD over 100 ALD cycles for Al_2O_3 and AlN between the SiO_2 and Pt surfaces. For tungsten (W) which is easily oxidized during the exposure of oxidant in the ALD process, the AS-ALD of Al_2O_3 without any selectivity loss over 100 ALD cycles is realized between the SiO_2 and W surfaces. In addition, the AS-ALD process based on the ALNE and SR treatments has been further demonstrated on the SiO_2/W patterned substrates with the scaling of the feature size from 75 μm to ~10 nm. In conclusion, the concept of ALNE and SR has realized the inhibitor-free AS-ALD with high selectivity, which is substantially beneficial to further extension of Moore's Law.

Keywords: Area-Selective Atomic Layer Deposition (AS-ALD), Atomic Layer Nucleation Engineering (ALNE), surface recovery (SR).

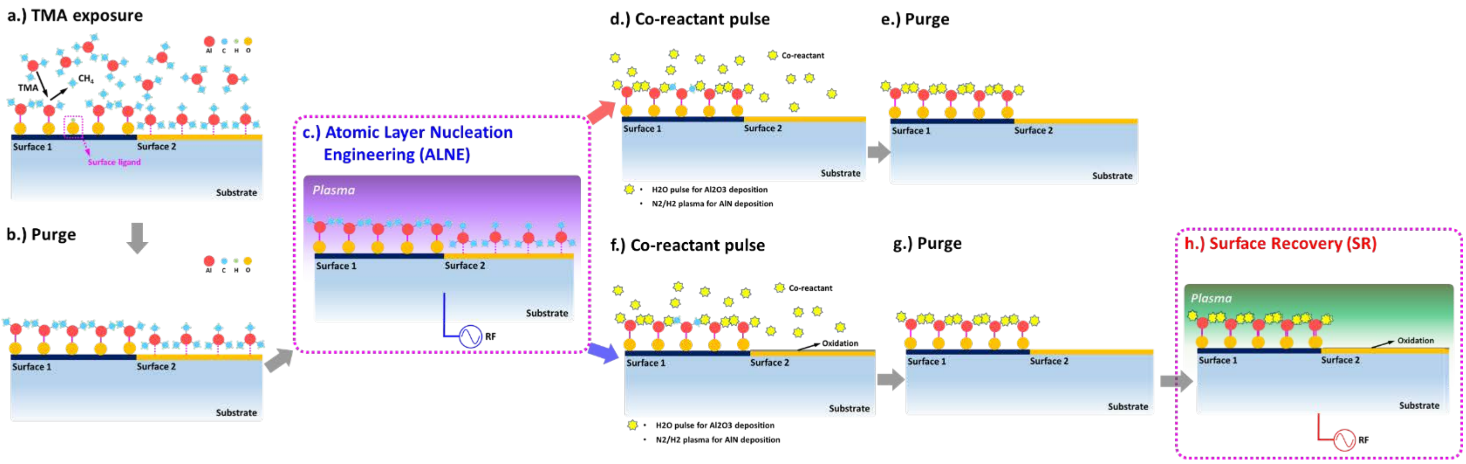

Figure 1. Schematic diagram of the inhibitor-free AS-ALD process between Surface 1 and Surface 2. Typically, the ALD cycle for the Al_2O_3 thin film deposition comprises the following steps (1) TMA pulse, (2) purge, (3) H_2O pulse, (4) purge. For the SiO_2 (Surface 1) and Pt (Surface 2), since the binding strengths of TMA precursor on SiO_2 and Pt are different, the ALNE technique, by which the local plasma is generated by introducing a RF substrate bias, can be precisely controlled to eliminate the TMA adsorbed on Pt. Thus the AS-ALD between SiO_2 and Pt is realize by the steps (a)-(b)-(c)-(d)-(e). On the other hand, although the SiO_2(Surface 1)/W(Surface 2) scenario shares identical ALNE reaction with the SiO_2/Pt surfaces, the subsequent H_2O pulse in each ALD cycle causes oxidization of the W surface. Therefore, the SR step for the removal of the surface oxidized layer is critical. As a result, the (a)-(b)-(c)-(f)-(g)-(h) steps was used to realize the AS-ALD between the SiO_2 and W surfaces.

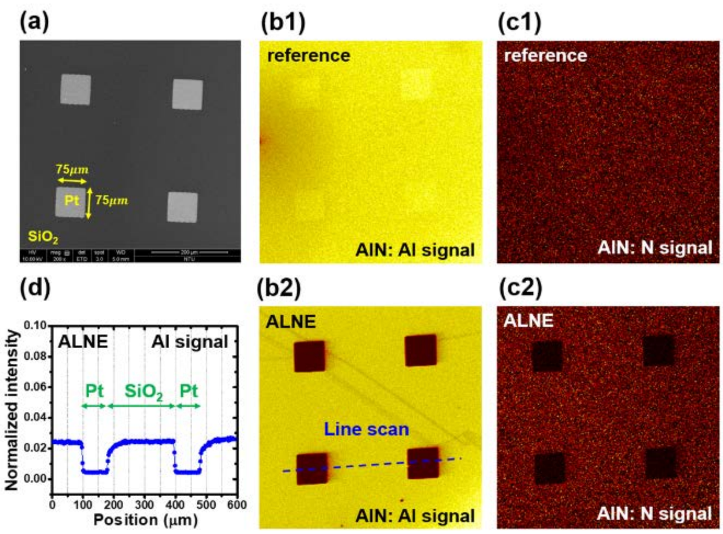

Figure 2. (a) SEM images of Pt/SiO_2 patterned substrate. The ToF-SIMS mapping image of Al^+ secondary ion for (b1) standard ALD process and (b2) ALNE constructed AS-ALD process of AlN deposition. The ToF-SIMS mapping image of N^+ secondary ion for (c1) standard ALD process and (c2) ALNE constructed AS-ALD process of AlN deposition. For the analysis, the 50 ALD cycles has been conducted for both standard and AS-ALD process. The line scan of Al^+ signals for (b2) has been further demonstrated in (d).

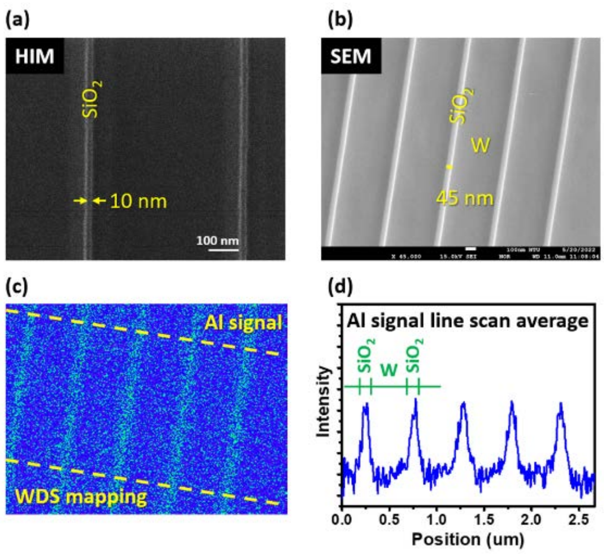

Figure 3. (a) Helium ion beam (HIM) image of the SiO_2 nanolines defined by HIM lithography on the W substrate, (b) SEM image of W/SiO_2 nanolines patterned substrate, (c) Wavelength-dispersive spectrometry (WDS) mapping of Al characteristic X-rays after 50 cycles of Al_2O_3 AS-ALD process, and (d) the average intensity of Al line scan signals from the yellow dashed lines indicated in (c). The feature size of SiO_2 nanolines is ~10 nm, which the results indicate that the inhibitor-free AS-ALD can be achieved under the ~10 nm scale.