Enhancing Selectivity for AS-ALD of MoO_2 through Hydrogen Treatment: Strategy of Surface Cleaning and Expanding Deactivated Areas

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Recently, in the field of DRAM capacitors, the demands for precisely depositing MoO_2 thin films for resolving the high leakage issue between high-k dielectric and TiN electrodes, onto TiN without additional patterning[1]. To meet these demands, Area selective atomic layer deposition (AS-ALD), which allows selective deposition on certain areas without undesired deposition on adjacent areas, is essential. Also accomplish the high selectivity of high-resolution films with high spatial resolution, the introduction of inhibitors is needed especially small molecular inhibitors (SMIs). SMIs consist of inert tail portions composed of single molecules, enabling them to have small sizes suitable for narrow lines at the nanometer scale. However, SMIs typically have short tail groups that cannot undergo van der Waals interactions, and they cannot densely cover the substrate surface due to steric hindrance from adjacent adsorbed SMIs during precursor adsorption[2]. Therefore, considerations regarding the treatment of unadsorbed areas and the removal of remaining reactive groups after SMI adsorption are necessary. To address this, we added a hydrogen treatment process during the AS-ALD process of MoO_2 using TCPS [$C_6H_5SiCl_3$] and DMA-TMS [$(CH_3)_3SiN(CH_3)_2$] as SMIs and analyzed the effects of hydrogen treatment on surface properties and selectivity using XPS, WCA, and AES mapping. Additionally, we calculated reaction energies for each adsorption step and final forms for each SMI-adhered surface using DFT and RSA simulations. TCPS, owing to its aromatic phenyl ring, covers a wider range of SiO_2 surfaces than DMA-TMS. However, only two out of three Cl ligands react, leaving about 1.4% of the remaining Cl ligands after TCPS adsorption, increasing the surface energy and acting as adsorption sites for Mo precursors. However, by adding a hydrogen treatment cycle during the process, all remaining Cl ligands were removed, resulting in a 13° increase in WCA and a dramatic increase in selectivity from 61% to 96%. Furthermore, hydrogen treatment not only removed residual impurities but also reduced exposed -OH groups on the surface by converting them to -H, as confirmed by the results of hydrogen treatment added during the DMA-TMS process. Despite the absence of impurities to be removed, the WCA increased by approximately 7° after hydrogen treatment, and the selectivity also increased from 84% to 94.5%. In this way, appropriate treatments during AS-ALD processes, though simple, can effectively increase selectivity, enabling precise selective deposition in desired areas even in complex structures.

References

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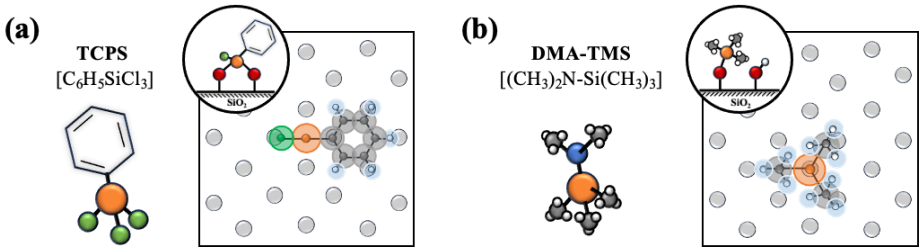

Fig. 1. The molecular structure, the form of the adsorbed SMI on the SiO_2 surface (top view), and the 2D footprint transcribed through Van der Waals area of (a) TCPS and (b) DMA-TMS.

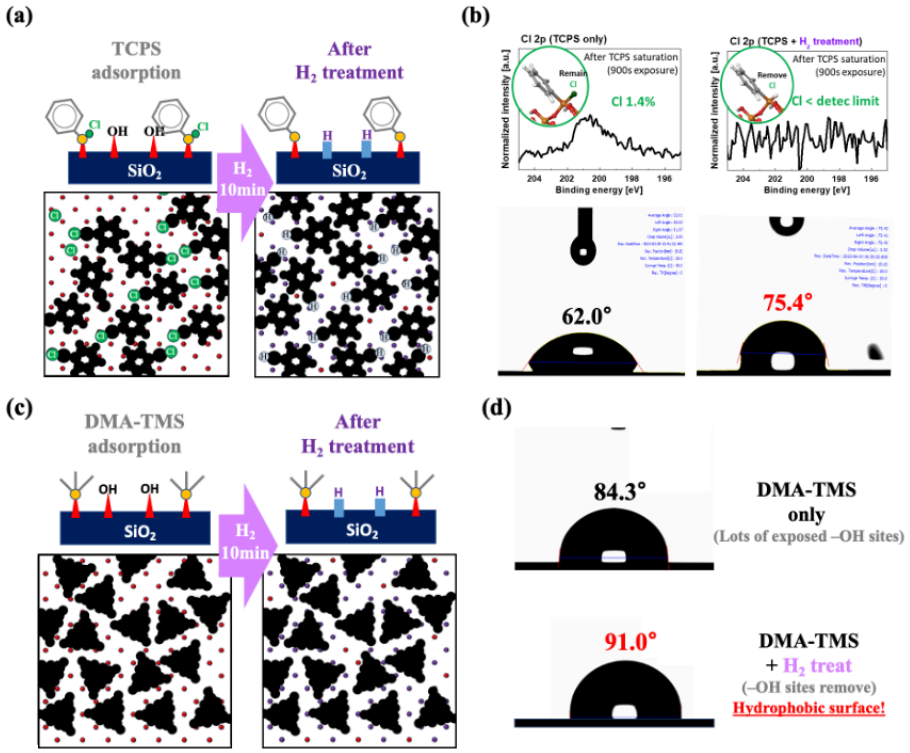

Fig. 2. (a) The hydrogen treatment mechanism and changes in surface condition, and (b) Cl 2p XPS peak and increased WCA diagram of the surface before and after hydrogen treatment for the TCPS adsorption surface. (c) The hydrogen treatment mechanism and changes in surface condition, and (d) increased WCA diagram before and after hydrogen treatment for the DMA-TMS adsorption surface.

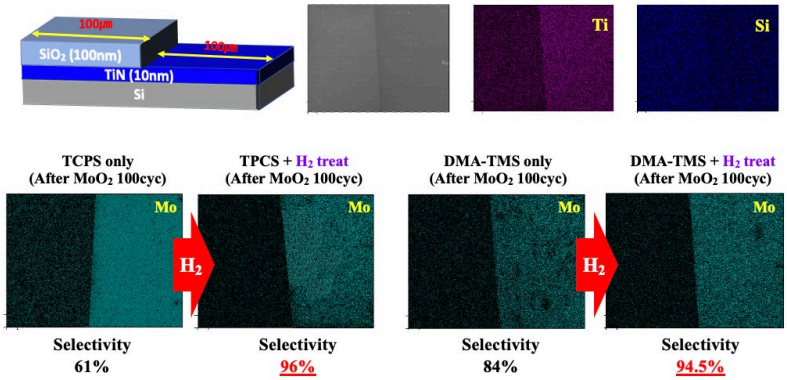

Fig. 3. AES element mapping (Ti, Si, and Mo) of SiO_2/TiN patterned substrates after 100 cycles of AS-ALD MoO_2 using TCPS and DMA-TMS before and after applying hydrogen treatment.