In-Situ Analytical Study on Atomic Layer Deposition of Metal Silicate Thin Films Using Hexachlorodisilane and Water

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Atomic layer deposition (ALD) is a critical process in the fabrication of modern electronic devices due to its ability to precisely grow thin films through the chemical adsorption of precursors.[1] Various metal oxide films can be deposited at low temperatures using metal precursors such as alkoxides or halides, along with water as the oxygen precursor. However, when using hexachlorodisilane (HCDS) and H_2O for SiO_2 ALD, challenges arise at low temperatures or with limited precursor exposure, often necessitating higher deposition temperatures or the use of Lewis base catalysts like pyridine or ammonia.[2] Through in-situ analyses using Fourier transform infrared spectroscopy (FTIR) and quartz crystal microbalance (QCM), we propose that metal hydroxyl groups (M-OH, where M represents Al, Ti, or Zn) located near silanol (Si-OH) groups facilitate the chemisorption of HCDS and H_2O at low temperatures, eliminating the need for catalysts. To elucidate the role of these metal hydroxyl groups, we conducted in-situ analyses of the ALD processes for metal silicate using trimethylaluminum, $TiCl_4$, or diethylzinc with FTIR and QCM. The hydrogen bonding between M-OH (or M-O-Si) and silanol groups may enhance the nucleophilicity of the oxygen of silanol, thereby promoting SiO_2 ALD. Although the M-OH groups promote the growth of silica, they gradually become covered by silica layers as ALD cycles repeat, reducing their effectiveness as promoters. Since the basicity of M-OH affects the strength of hydrogen bonding with silanol, we investigated the basicity of these M-OH groups using acetylacetone (Hacac) as a probe molecule. Among the M-OH groups studied, Zn-OH exhibited the highest basicity, followed by Al-OH and Ti-OH. We also discuss the correlation between the basicity and the effectiveness of the M-OH promotor.

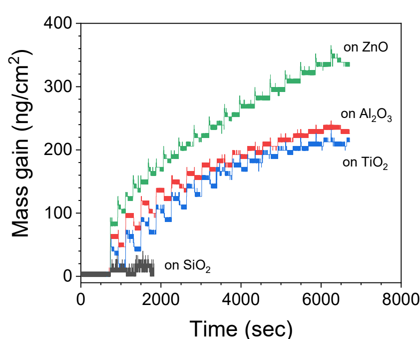

Figure 1. Comparison of mass gain by QCM showing the promotion effect on SiO_2 growth across different oxide surfaces.

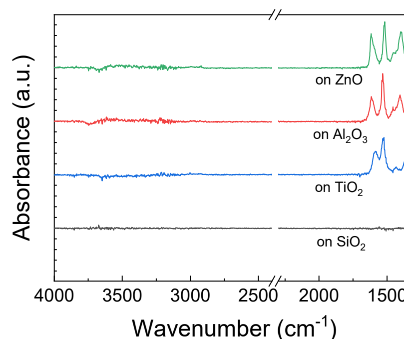

Figure 2. In-situ FTIR spectra of acetylacetonate adsorbed to probe the basicity of different oxide surfaces.

[1] S. M. George, Chem. Rev. **110**, 111 (2010).

[2] J. Hyun, H. Kim, B. Shong, and Y. -S. Min, Chem. Mater. **35**, 4100 (2023).

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