Conformal TiO_2 film formation on high-aspect-ratio features by supercritical fluid deposition using quasi-0th-order reaction kinetics

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Conformal TiO_2 film formation was achieved on trenches with an aspect ratio (AR) of 120 by supercritical fluid deposition (SCFD) from $Ti(O\text{-}i\text{-}Pr)_2(tmhd)_2$ with addition of methanol at 200-300°C. It was enabled by using quasi-0th-order reaction kinetics in Langmuir-Hinshelwood (LH) surface reaction mechanism. This quasi-0th-order reaction realized same growth rate everywhere even at the bottom of trenches, and therefore we could achieve perfect step coverage on such high-AR trenches. Methanol played a key role to achieve quasi-0th-order reaction; it functioned as an entrainer, a reaction suppressor, and an adsorption promoter. As an entrainer, methanol increased the available precursor concentration in TiO_2-SCFD from 0.5 to 1.5 mol/m^3. As a reaction suppressor, methanol suppressed surface reaction, whose rate constant (k_s) was 6.7 nm/min. As an adsorption promoter, methanol enhanced adsorption of precursors on the substrate, with an adsorption equilibrium constant (K) of 2.3 m^3/mol. All these effects of methanol contributed to the saturated adsorption of precursor on the substrate, enabling quasi-0th-order reaction kinetics at precursor concentrations of above 1.0 mol/m^3.

Devices with three-dimensional (3D) features have attracted a great deal of attention over the last several decades. For example, 3D-structured semiconductors for high integration density, photocatalysts with large surface/volume ratios for high photocatalytic efficiency, and terahertz metamaterials fabricated by 3D printing have been studied intensively. Coating technologies with high conformality are necessary to functionalize surfaces of these complex features. SCFD, which is an oxidation/reduction of metal organic compounds in $scCO_2$, is reported to be a promising technology for structure-independent conformal deposition and superior gap filling onto extremely high-AR features with high growth rate. A possible reason for this is due to a large precursor concentration in $scCO_2$, which realizes quasi-0th-order reaction in LH surface reaction mechanism due to surface saturation of adsorbing precursors. In this mechanism, growth rate is proportional to precursor concentration at low concentration, and saturates at high concentration (quasi-0th-order reaction), where growth rate is almost independent from precursor concentration. For deposition onto 3D features, although precursor concentration inside is lower than that outside due to deposition reaction on their inner surfaces, quasi-0th-order kinetics enables conformal deposition on the high-AR 3D features. In contrast to the vacuum-based processes like chemical vapor deposition (CVD) that utilizes high diffusivity of precursors in vacuum, in SCFD, this quasi-0th-order reaction kinetics compensate for the relatively low diffusivity of precursors in $scCO_2$. However, LH kinetics was found only for SCFD of metal films, such as Cu, Ni, Ru, Pt, and Ag, while SCFD of metal oxide films always follows first-order reaction kinetics, and LH kinetics including quasi-0th-order reaction kinetics has never been reported to date.

This is the first report to achieve quasi-0th-order reaction kinetics in SCFD of metal oxide films with the assistance of methanol. Note that it was not achieved by simply increasing the precursor concentration at high pressure condition; menthol serves as an essential contribution to achieve quasi-0th-order kinetics. Roles of methanol was clarified by kinetic analysis as mentioned above. Based on the reaction kinetics obtained, maximum step coverage to be achieved by this method is also revealed by calculating the mass balance equation of precursor within 3D features. A guideline to further improve the step coverage on 3D features is also settled. This breakthrough will expand the potential applicability of metal-oxide SCFD to features with an extremely high-AR.