Oxide Thin Films via Chemical Solution Deposition: the Roles of the Solution and the Substrate

Mark R. De Guire and Jing-Jong Shyue
Case Western Reserve University
Department of Materials Science & Engineering
10900 Euclid Avenue
Cleveland, Ohio 44106 USA

Although the majority of the research on chemical solution deposition has been directed toward the growth of sulfide, selenide, and telluride films, its use for the growth of oxide films presents exciting opportunities as well as significant challenges.

This presentation will begin with a brief review of the history of chemical solution deposition of oxides, comparing and contrasting the growth of oxides with the growth of other chalcogenides.

Two key considerations for controlling and improving chemical solution deposition processes of any specific material are the effects of the solution (pH, temperature, composition) and the effects of the substrate (surface energy, surface charge density, chemical functionality). These two aspects will be illustrated with results on the growth of vanadium oxide and titanium oxide films on organic self-assembled monolayers (SAMs), as discussed below.

Solution effects. We have performed thermodynamic calculations on the vanadium-water system to predict the ranges of pH and temperature over which the aqueous solutions will form the oxide. At 45 °C and [V] = 10 mN, solutions with initial pH of 2.5 to 3.0 are predicted to precipitate V_2O_5, with a corresponding rise in pH (to ~3.1) according to the equilibrium

$$V_{10}O_{26}(OH)_2^{4-} + 4H^+ = 3H_2O + 5V_2O_5\ (s)$$

Experimental observations, in contrast, indicate that formation of solid occurs for solutions with initial pH of 1.7 to 2.3, with the pH stabilizing at 2.3. Similar downward shifts in pH are also observed at 65 and 85 °C, and in solutions with [V] = 25 mN. The start of film formation coincides with the first appearance of solid in the bulk solution, as detected by light scattering observations.

The role of the solution is further indicated in studies of the effects of chelating agents on the formation of oxide films. The oxalate ion ($C_2O_4^{2-}$) is an effective chelating agent for vanadium, and lactate ($C_3H_5O_3^-$) for titanium. In mixed V-Ti solutions, the use of these additives allows a degree of control to be exerted over the V/Ti ratio in the resulting films. On the other hand, our results also show that V and Ti exhibit a degree of cooperativity: *i.e.*, mixed Ti-V-oxide films deposit on sulfonate SAM substrates (see below) whereas vanadium oxide alone does not.

Substrate effects. We have extensively studied the effect of substrate surface chemical functionality on the chemical solution deposition of oxide films, primarily through the use of silanol-anchored SAMs on silicon substrates. We find that certain factors that are reported to be critical for achieving the highest degree of structural order in the SAM, such as the length of the hydrocarbon chain (C11 vs. C16) in the surfactant molecule forming the SAM and the solvent (dicyclohexyl vs. toluene) in which the SAM is deposited, have little effect on the SAM's ability to promote the deposition of oxide films.

On the other hand, the acid-base character and the surface charge density of a SAM appears to have a dominant effect on its ability to promote or hinder the chemical solution deposition of an oxide film in many cases. For example, the sulfonate (SO_3H-) group is strongly acidic. X-ray photoelectron spectroscopy (XPS) suggests that sulfonate-terminated SAMs are at least 50% deprotonated in aqueous environments of $pH \geq 2$ and fully deprotonated at $pH \geq 5$. The resulting high negative surface charge density (in conjunction with a positive van der Waals interaction) promotes the deposition of oxides, such as TiO_2, ZrO_2, and SnO_2, in acidic solutions below the oxides' isoelectric points. Amine SAMs, in contrast, behave as weak bases. XPS measurements suggest that amine SAMs display a highly pH-dependent surface charge, from zero at pH=13, gradually rising to full protonation at pH=0. The resulting positive surface charge allows deposition on amine SAMs of oxides such as V_2O_5, which is above its isoelectric point (*i.e.*, negatively charged) when it forms in solutions of pH > ~2.

Alkyl ammonium salt SAMs ($-N^+(CH_3)_3$) are strongly positively charged over a wide range of pH. Vanadium oxide films grew roughly four times faster on alkyl ammonium salt SAMs than on amine SAMs under identical conditions (Figure 1). Regardless of the substrate, the films contained $V_2O_5 \bullet 1.6H_2O$ as the sole crystalline phase in the first 24 h of growth. The appearance a second crystalline phase, $V_2O_5 \bullet H_2O$, coincided with the observed increase in growth rate at ~30 h (Figure 1).

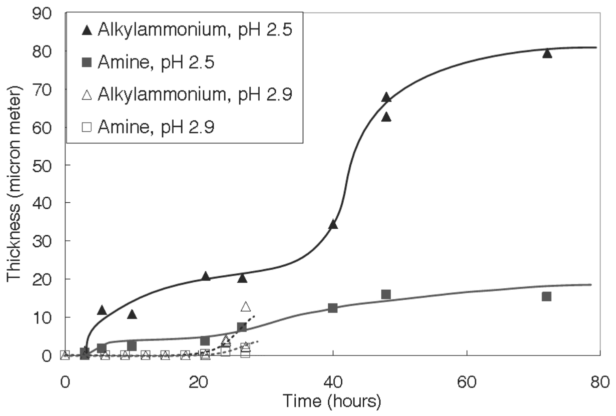

FIGURE 1. Thickness of vanadium oxide films grown from aqueous solutions ([V] = 25 mN, 45 °C) at pH = 2.5 or 2.9 on alkyl ammonium salt or amine SAMs.