MATERIALS SCIENCE

Low-Temperature Thin-Film Deposition and Crystallization

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Crystalline oxide films are important components in a wide array of electronic and optical devices, and their study and manufacture involve major aspects of current science and technology. A plethora of methods, such as sputtering, chemical vapor deposition, pulsed laser deposition, and sol-gel, are commonly used to deposit these films, and many new techniques are being developed (*1*). In each of these methods, however, the deposited film is amorphous. For those applications requiring a crystalline film, an additional high-temperature processing step is required. This high-temperature step can lead to considerable constraints in combining the desirable characteristics of a crystalline oxide film with those of thermally unstable substrates and other device components. High-temperature processing also adds considerable costs to manufacturing. We describe a simple method that provides a general means for both low-temperature deposition and crystallization of oxide films. To demonstrate the generality of the method, we describe here the production of Zn_2SiO_4, ZrO_2, and MnO_2 films, which are of interest for applications in displays, electronics, and energy storage, respectively.

The present method derives from our report on the preparation of oxide powders by a method of precipitation and hydrothermal dehydration (*2*). In this process, a hydroxo precipitate is dehydrated under hydrothermal conditions to yield an anhydrous, crystalline oxide at temperatures as low as 400 K. We have now combined this dehydration and crystallization process with the successive-ionic-layer-adsorption-and-reaction (SILAR) deposition method (*3*) to produce fully crystalline oxide films at low temperatures. In the SILAR process, the cation constituent is first adsorbed onto the substrate surface, followed by a rinsing step in water to produce an approximate monolayer of coverage. The substrate is then transferred to a solution containing the anionic constituent, wherein a precipitation reaction occurs at the surface of the substrate; the process is completed with an additional water rinse. This cycle of coating and rinsing is repeated many times under robotic control to achieve a desired film thickness. For the examples given here, substrates were immersed in ~0.1 M solutions and rinse baths for 10 s each, and 700 cycles were used to develop a film thickness near 250 nm. Dehydration was performed overnight (~12 hours), although crystallinity in some systems has been observed after a 30-min treatment.

Films of Zn_2SiO_4 were produced on glass and nitrided silicon (Si_3N_4/Si) substrates by using the SILAR process with Zn^{2+}(aq) and

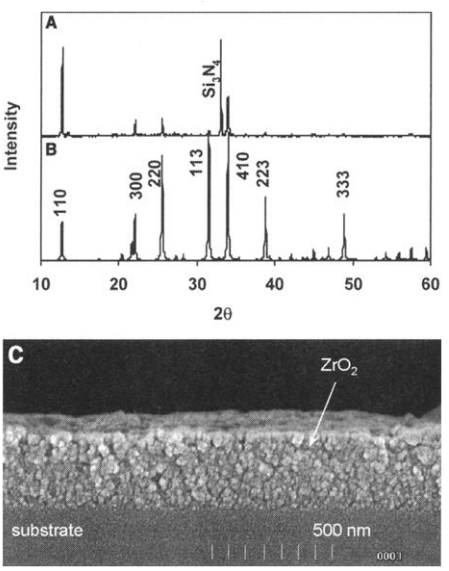

Fig. 1. (**A**) X-ray diffraction pattern of Zn_2SiO_4 film on Si_3N_4/Si. (**B**) Simulated powder x-ray diffraction pattern of Zn_2SiO_4. (**C**) Electron micrograph of ZrO_2 film on Si_3N_4/Si substrate.

SiO_4^{4-}(aq) as the cationic and anionic constituents, respectively. The SiO_4^{4-}(aq) species undergoes extensive hydrolysis, so the as-deposited film is an amorphous hydrated hydroxide salt. The film was crystallized by heating at 378 K in a sealed 23-ml Teflon-lined Parr reactor containing 0.15 ml of water (pressure ~ 12 atm). From consideration of the x-ray diffraction patterns in Fig. 1, A and B, the resulting film is a highly crystalline form of Zn_2SiO_4. For comparison, annealing the amorphous, as-deposited film near the softening point of the glass substrate (temperature = 923 K) does not produce a crystalline product.

Crystalline films of ZrO_2 have been deposited on Si_3N_4/Si substrates. Again, SILAR deposition with the aqueous solutions Zr^{4+}(aq) and OH^-(aq) results in an amorphous, hydroxylated film. After hydrothermal dehydration at 473 K, the resulting diffraction pattern reveals the formation of the expected monoclinic form of ZrO_2; an electron micrograph of the resulting film is given in Fig. 1C. Curiously, direct annealing of the amorphous film in air at 923 K results in the production of an oxygen-deficient tetragonal form of $ZrO_{2-\delta}$, whereas under normal conditions, this phase exists only at temperatures above 1273 K (*4*). Annealing the monoclinic film at 923 K results in no structural change.

MnO_2 and Mn_2O_3 have been deposited on SiO_2/Si substrates by using the solutions Mn^{2+}(aq) and OH^-/H_2O_2(aq). The as-deposited material is amorphous. After a hydrothermal anneal at 473 K, the film is crystalline, forming the tetragonal, rutile form of MnO_2 (*5*). Annealing the as-deposited film at 773 K results in loss of oxygen and production of the cubic, bixbyite structure of Mn_2O_3 (*6*). These processing methods thus provide facile control of product formation and oxidation states of the Mn cation.

A simple and general method has been demonstrated for both low-temperature thin-film deposition and crystallization of refractory oxides. It provides opportunities for development of manufacturing methods, generation of unusual composite materials, and application of high-temperature materials to low-cost substrates, as shown by the deposition of a green-emitting phosphor on a flexible, plastic substrate (fig. S1) (*7*).

References and Notes

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7. See supplementary information available on *Science* Online.
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Supporting Online Material

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Methods
Fig. S1

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