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Supercritical-carbon dioxide-assisted cyclic deposition of metal oxide and metal thin films

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Thin films of aluminum oxide and palladium were deposited on silicon at low temperatures (70–120 °C) by a cyclic adsorption/reaction processes using supercritical CO₂ solvent. Precursors included Al(hfac)₃, Al(acac)₃, and Pd(hfac)₂, and aqueous H₂O₂, tert-butyl peracetate, and H₂ were used as the oxidants or reductants. For the precursors studied, growth proceeds through a multilayer precursor adsorption in each deposition cycle, and film thickness increased linearly with the number of growth cycles. © 2006 American Institute of Physics. [DOI: 10.1063/1.2181651]

Deposition of metal and dielectric films from precursors dissolved in supercritical solvents has been demonstrated for a variety of electronic and optical applications.^{1–4} Most previous work from supercritical CO₂ (sc CO₂) has been performed in a continuous growth mode (analogous to chemical vapor deposition) where all precursors are introduced simultaneously to the reactor cell. One of the limitations of this technique is that it is typically done in batch mode so that the film thickness is controlled by the amount of precursor loaded and the extent of reaction. In this work, we present the concept of sequential solvent-phase deposition, where precursors dissolved in supercritical fluid flow into the reaction chamber in a cyclic A/B exposure scheme, similar to an atomic layer deposition (ALD) process.⁵ For the precursors and conditions used in this work, the process resulted in reproducible multilayer linear growth rather than the self-limiting submonolayer film growth observed during typical ALD processes.

Because the density of sc CO₂ (critical temperature 31 °C and critical pressure 7.4×10^6 Pa) is orders of magnitude higher than any gas,⁶ it can dissolve large concentrations of organic species. The diffusivity of the dissolved species is between that for liquids ($\sim 10^{-5}$ cm²/s) and gases (~ 1 cm²/s) under typical process conditions. As a result, the precursor may be transported to the surface similarly to vacuum processes but at a significantly larger concentration. Another anticipated benefit of sc CO₂ is its high solvation energy, which can be used in promoting the deposition reaction, and facilitating the removal of reaction byproducts at low temperatures. In this work, the deposition of aluminum oxide (Al₂O₃), and palladium (Pd) using cyclic reactant exposures is described. These materials are of interest in microelectronics for potential applications in advanced metal-oxide-semiconductor transistor gate stacks as gate dielectric or metal gate materials.^{7,8}

The depositions were carried out in a hot wall, stainless steel high-pressure reaction cell (21 ml, 1.2 in. (inner diameter) $\times$ 1.2 in. depth, 1.9 in. wall thickness) shown in Fig. 1. The ends of the reaction cell used sapphire windows (~ 0.6 in. thick) sealed with compressed

teflon O rings. A similar larger cell (~ 40 ml) was used for the dissolution of the precursors. An ISCO 260D syringe pump delivered the CO₂ through 1/16 in. (outer diameter) tubing and high pressure manifold and valves. The temperature of the cells and lines were maintained with individually controlled external resistive heaters. The reaction effluent passed through an activated charcoal bed. The Si(100) substrates ($\sim 2 \times 1$ cm²) were prepared by exposing to JTB-100 Baker clean for 5 min, followed by de-ionized water rinse (10 min), and nitrogen-blow dry. Precursors for deposition included aluminum acetylacetonate (99%) [Al(acac)₃], aluminum hexafluoroacetylacetonate (minimum 98%) [Al(hfac)₃], and palladium (II) hexafluoroacetylacetonate [Pd(hfac)₂], and all were used as received. The fluorinated precursors, [Al(hfac)₃] and [Pd(hfac)₂] were stored in a well sealed desiccator to prevent reaction with the ambient.

Before each experiment, the cleaned premix cell was flushed with CO₂, and approximately 20–30 mg of precursor was loaded. The cell was then heated to 70–80 °C and pressurized with CO₂ to ~ 3500 psi, corresponding to a CO₂ density of 0.7 g/cm³, and the cell stabilized for ~ 30 min. The highly soluble fluorinated precursors dissolved completely leading to a precursor concentration ~ 0.07 – 0.1 wt % in the premix cell. The solubility limit for the nonfluorinated Al(acac)₃ precursors is estimated to be $\sim 10^{-4}$ – 10^{-5} wt %, based on similar experimental conditions.⁹ After loading a substrate, the reaction cell was flushed with CO₂ for 1 or 2 min at 40–50 °C, then pressurized with CO₂ the desired value and heated to the set point temperature.

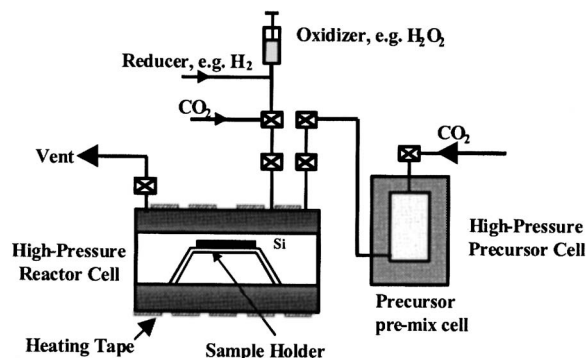


FIG. 1. Schematic diagram of the experimental setup.

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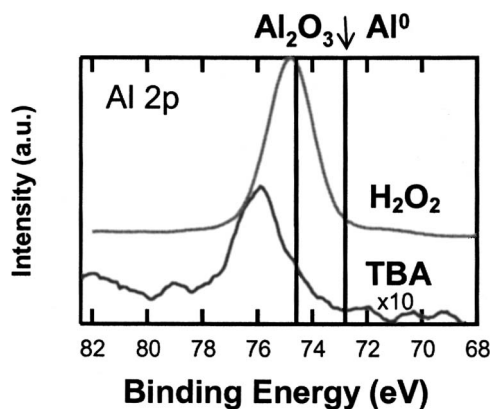


FIG. 2. High resolution XP scans for the Al 2p peaks for two aluminum based films deposited via cyclic deposition. Both films were deposited at 120 °C, and 1600 psi. Film labeled H₂O₂ was deposited from Al(acac)₃ and hydrogen peroxide, while film TBA was deposited from Al(acac)₃ and tert-butyl peracetate.

The experiments were carried out in A/B cycles similar to an atomic layer deposition process.⁵ For each cycle, a set volume (corresponding to ~0.2 g) of precursor/sc CO₂ solution (A) was injected from the premix cell to the reactor leading to a pressure rise of ~30–50 psi. The injected volume corresponded to ~0.15–0.2 mg of fluorinated precursors or ~10⁻⁴ mg of Al(acac)₃. The samples were exposed to the precursor for a time ranging from 30 s to 3 min, and then the reaction cell was vented and flushed for 1–2 min with liquid/supercritical CO₂. The reaction cell was then repressurized and an oxidizing or a reducing agent (B) was injected. For oxide films, ~0.3 ml of liquid oxidizer [30% aqueous solution of H₂O₂ or 50% tert-butyl peracetate (TBA) in mineral spirits] was injected in each cycle. For palladium deposition, ultra high purity H₂ (99.999%, ~3.5 × 10⁻⁴ mol/cycle) was used. In every case, the molar quantity of the injected oxidant/reductant was much larger than required for stoichiometric reaction. Therefore, it is expected that the growth rate would be determined by the amount of precursor adsorbed and the cycle time. After 1–3 min, the reaction cell was vented and flushed and the cycle was repeated to build up a macroscopic film thickness. A typical cycle time was ~20 min, primarily due to the use of manual hardware. Reasonably short cycle times (~1 min) can be expected for a more automated and optimized reactor system.

Films were analyzed by ellipsometry and x-ray photoelectron spectroscopy (XPS). A Rudolf ellipsometer (632.8 nm, 70° fixed angle) was used to measure the oxide thickness. XPS was conducted using a Riber LAS3000 (MAC2 analyzer, Mg Kα $h\nu$ =1253.6 eV, nonmonochromatic x-ray source) at 75° take-off-angle with 0.1 eV step size. Three different sets of precursors were studied for cyclic deposition of aluminum oxide: Al(hfac)₃ with H₂O₂, Al(acac)₃ with H₂O₂, and Al(acac)₃ with TBA. Figure 2 shows the high resolution XPS data for Al 2p core electrons for films deposited using Al(acac)₃ and either H₂O₂ or TBA at 120 °C and 1600 psi. For the film deposited with H₂O₂ a peak is observed at 74.8 eV indicative of Al–O bonds, whereas, for the film deposited using tert-butyl peracetate the peak is shifted to higher binding energy (~75.5 eV), which indicates bonding of the Al atoms with more electronegative species. The C 1s spectrum (not shown) shows adventitious

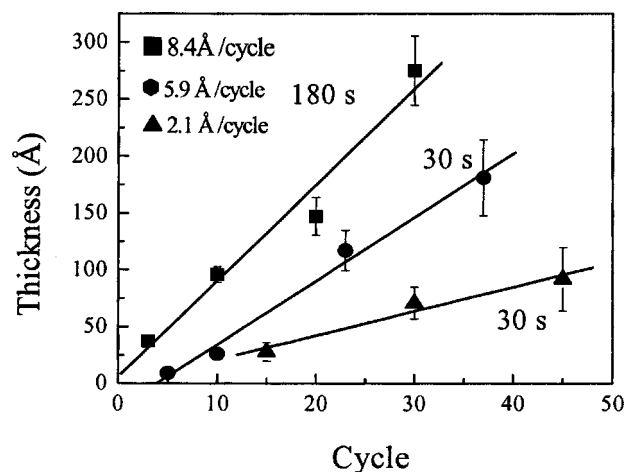


FIG. 3. Thickness data determined from ellipsometry for Al-based films deposited from Al(hfac)₃–H₂O₂ at 100 °C and ~2000 psi on native oxide of Si(100) for different precursor exposure times and sample orientations. Samples were oriented inside the reaction cell such that the deposition surface [polished surface of Si(100)] faced directly to the precursor inlet (●), or the deposition surface faced opposite to the precursor inlet (sample flipped by 180° from previous orientation) (■, ▲).

C (285 eV) for both samples, but for the sample deposited with peroxide, a second peak at 289.3 eV is observed, indicative of carbonate in the film. The intensity of the Al 2p peak indicates significantly lower growth rates when TBA was used as the oxidant. Use of the fluorinated precursor Al(hfac)₃ and H₂O₂ generally results in thicker films compared to Al(acac)₃–H₂O₂, but there is evidence for aluminum hydroxide and carbonate species present in the as-deposited films when the Al(hfac)₃ is used.⁴ Film thickness by ellipsometry versus cycle time was studied for Al₂O₃ films from Al(hfac)₃ and H₂O₂ (native silicon oxide, 100 °C, 2000 psi), and the results are shown in Fig. 3. Each data point in Fig. 3 was obtained by taking an arithmetic average of 3–7 values measured on one or more samples with identical number of cycles. Clearly, film thickness increases linearly with number of deposition cycles. However, a significant effect of Al(hfac)₃ exposure time on the film thickness per cycle is observed. For the same process conditions, an increase in precursor exposure time from 30 s to 3 min resulted in nearly fourfold increase in film growth rate (Fig. 3). Also, growth rate dependence on the sample orientation was observed, suggesting a convective flow effect in the reactor during the deposition. When the deposition surface [polished surface of Si(100)] was placed in a direct exposure to the precursor flow, a high growth rate of 5.6 Å/cycle was observed for 30 s of precursor exposure time. However, when the deposition surface was directed away from the precursor inlet, the growth rate was 2.1 Å/cycle for the same exposure time. The observed thickness per growth cycle and the convective flow dependence of growth rate are consistent with multilayer growth per cycle. Water is generally immiscible with sc CO₂, so the use of aqueous H₂O₂ peroxide in the process is expected to lead to a two-phase condition in the growth cell, which could lead to nonuniform growth. However, the Al₂O₃ film did not show evidence for discontinuous growth over the film surface, consistent with the growth being determined by the amount of precursor adsorbed during the exposure cycle, rather than the delivery of oxidizer to the surface. Alternatively, rapid diffusion and mixing of the

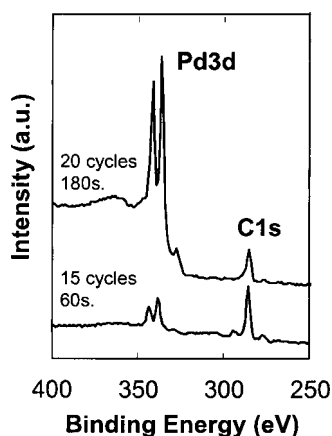


FIG. 4. Pd 3d XPS peaks for palladium films deposited on native silicon oxide using alternating exposures cycles of Pd(hfac)₂ and H₂ dissolved in sc CO₂. The film deposited with 20 cycles and 180 s Pd(hfac)₃ exposure per cycle is significantly thicker than the film deposited with fewer cycles and 60 s exposure per cycle.

aqueous-phase could result in uniform exposure of the oxidant to the sample surface.

In addition to aluminum oxide, palladium has been deposited using the cyclic deposition approach. Figure 4 shows XPS data of palladium films deposited from Pd(hfac)₂ and H₂ (70–80 °C, 2000–3200 psi) using 20 cycles [with 180 s of Pd(hfac)₃ exposure per cycle], and 15 cycles (with 60 s precursor exposure per cycle). Films generally adhered poorly to silicon and oxide surfaces, making thickness evaluation difficult. The Pd 3d peak height indicates that film deposited for 20 cycles was much thicker than that deposited for 15 cycles. The trend in film thickness suggests multilayer growth per exposure cycle and possibly nucleation inhibition during initial film growth. Some asymmetric broadening of the C 1s peak to its higher binding energy side is also observed, consistent with some C–O, C=O, CF_x, and CF₃ present in the films.^{10,11}

The observed thickness per growth cycle in the process reported here is consistent with multilayer adsorption of precursors during each deposition cycle. Liquid-phase processes with similar precursors have shown similar results where adsorption followed the Freundlich isotherm,¹² $C_{\text{solid}} = K_f C_{\text{fluid}}^n$, where C_{solid} represents the mass of precursor adsorbed/cm² on the Si surface, and C_{fluid} is the precursor concentration in the sc CO₂. K_f and n are Freundlich adsorption coefficient and Freundlich exponent, respectively. Also, our results sug-

gest time dependent precursor adsorption which is consistent with the nonequilibrium adsorption of β -diketone chelates on –OH terminated surfaces.¹² The multilayer adsorption could, for example, be initiated by forming a hydrogen bond between the precursor oxygen and surface –OH, with subsequent adsorption proceeding by intermolecular π bonding between adsorbed- and fluid-phase precursor molecules.¹²

This work demonstrates that metal oxide and metal films can be deposited from precursors dissolved in sc CO₂ using a binary deposition/exposure reaction sequence. For the precursors studied, the results indicate growth proceeds through a multilayer adsorption of precursor in each deposition cycle, and that the thickness is determined by the number of cycles used. The binary reaction scheme in sc CO₂ may allow for formation of unique material phases, for example, where the substrate material is physically modified (such as swollen or densified) in sc CO₂ allowing the deposited material to interact with the substrate to alter its material properties.

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