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Low Temperature Deposition of Metal Oxide Thin Films in Supercritical Carbon Dioxide using Metal-organic Precursors

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ABSTRACT

A novel chemical route in thin film formation that includes the use of inorganic and organic peroxides and metal organic complexes soluble in supercritical carbon dioxide has been investigated for the deposition of alumina, titania and zirconia thin films at low temperatures (<150°C). The metal organic precursors used include: $Al(acac)_3$, $OTi(tmhd)_2$, and $Zr(acac)_4$. Tert-butyl peroxide, and a 30% aqueous solution of hydrogen peroxide were used as oxidants. Depositions were carried out in a 25 ml hot wall reactor at pressures ranging from 2100 to 3900 psi at 80-140°C. The deposited thin films were investigated by using X-ray photoelectron spectroscopy (XPS) and transmission Fourier transform infrared spectroscopy (FTIR). XPS and FTIR results indicate the formation of metal oxides thin films with some bonded carbon. The deposition temperatures achieved in this process are substantially lower than those used in conventional vacuum deposition techniques making feasible the deposition on temperature sensitive substrates and organic materials required for the development of hybrid organic/inorganic devices. Processing at low temperatures in supercritical carbon dioxide may provide the basis for the development of an alternative, environmentally friendly, thin film deposition technique for the processing of nanostructures.

INTRODUCTION

Metal oxide materials have many important applications, such as, gate oxides in Complimentary Metal Oxide Semiconductor (CMOS) devices, [1,2] magnetic tunnel junctions, [3] and optical coatings.[4] Conventional deposition techniques including chemical vapor or atomic layer deposition are chemical reaction based and are driven by the energy provided by a heated substrate. Both these vacuum-based techniques require relatively high substrate temperatures even when used in conjunction with plasma excitation, to assist in the precursor adsorption, oxidation and by-product desorption. [5] Use of solvation energy may provide a viable alternative for the deposition of thin films when high temperature processing is undesired.

The use of solvation forces to assist in the chemical reaction on a substrate has already been applied to solvent based techniques such as electroplating, [6,7] electroless deposition, [8,9] and in supercritical carbon dioxide for the deposition of thin films. [10,11,12] Supercritical fluids have very intriguing properties: liquid-like density but gas-like transport properties, low viscosity, and high diffusivity. Additionally, they exhibit zero surface tension that allows diffusion in high aspect ratio trenches and microporous structures, and enhanced solvent ability near or above the critical point. In this project we use the enhanced solvent ability of supercritical CO_2 to deliver large concentrations of metal organic precursor and oxidizers to a substrate, and make use of the energy provided by the solvation forces to complete the oxidation of the metal atom and the ligand removal at low temperature. Supercritical CO_2 is safe to handle and exhibits easily accessible critical points (critical temperature 31°C and critical pressure 1070 psi). [13]

EXPERIMENT

The depositions were performed in a ~25 ml high-pressure stainless steel cell with sapphire windows purchased from Thar Technologies. A schematic of the reactor system is shown in Figure 1. Pressurized CO_2 was delivered using an ISCO 260D syringe pump through a high-pressure manifold. Resistive heaters with feedback control were used to maintain the temperature of the reaction cell within ±1 °C of the set point value. Before each experiment, the cleaned cell was flushed with CO_2 and a piece of Si was placed inside the cell along with approximately 20-30 mg of precursor. The cell was then sealed, heated to 45°C and pressurized with CO_2 at 1250 psi. Then, the temperature was raised to the desired reaction temperature, and the precursor was observed to dissolve. The oxidizer solutions were introduced to the cell in two different ways: (1) loaded to the deposition cell in a quartz thimble simultaneously with the precursor; and (2) injected inside the deposition

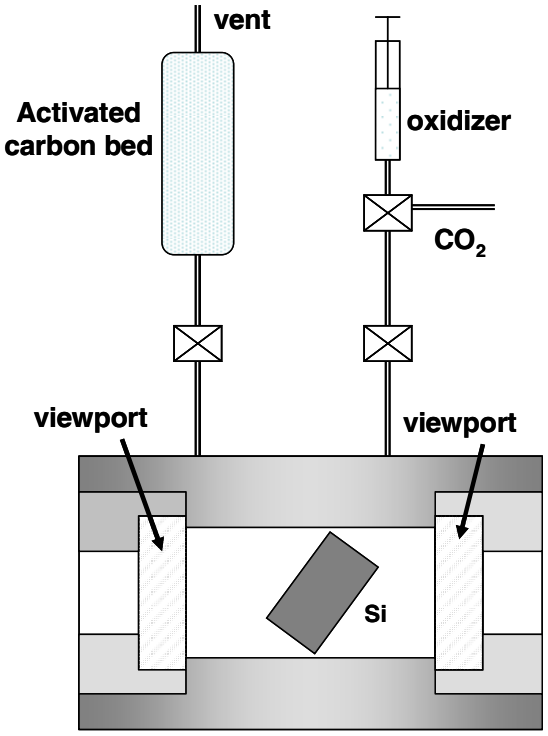

Figure 1. A schematic of the deposition system.

cell after the temperature reached the desired reaction temperature. After a set reaction time (typically 30 min), the cell was purged with CO_2 and the effluent was filtered in an activated charcoal bed before venting. The samples were then rinsed in acetone in a sonic bath for 1 min to remove the precipitated precursor and reaction byproducts from the surface. The films were deposited on native oxide Si (100) surfaces. Precursors included aluminum acetylacetonate (99%) ($Al(acac)_3$), zirconium acetylacetonate (99%) ($Zr(acac)_4$) and Bis(2,2,6,tetramethyl-3,5-heptane dionato) oxotitanium(IV) ($OTi(tmhd)_2$) purchased from Strem Chemicals. All precursors were used as received. The precursors were stored in a well-sealed desiccator to prevent any reaction with ambient moisture. Coleman-grade CO_2 with 99.99% purity was used for all the experiments. The oxidizers tested in the course of this work were: a 30% aqueous solution of hydrogen peroxide, and tert-butyl peroxide. The chemical structure of the precursors and tert-butyl peroxide is shown on Figure 2 .

The samples were characterized by X-ray photoelectron spectroscopy (XPS) and transmission Fourier transform infrared spectroscopy (FTIR). The XPS measurements were performed ex situ with a Kratos AXIS 165 (Mg Kα, $h\nu$=1253.6 eV, mono-chromatic X-ray source) at 90° takeoff-angle at 0.5 eV step size. A ThermoNicolet IR bench was used in the transmission mode. For each spectrum we collect 256 scans at 4 cm^{-1} resolution. The instrument was purged using purified air with low concentrations of moisture and CO_2. A background spectrum was collected after each measurement using a substrate fragment that originated from the same wafer as the deposited substrate.

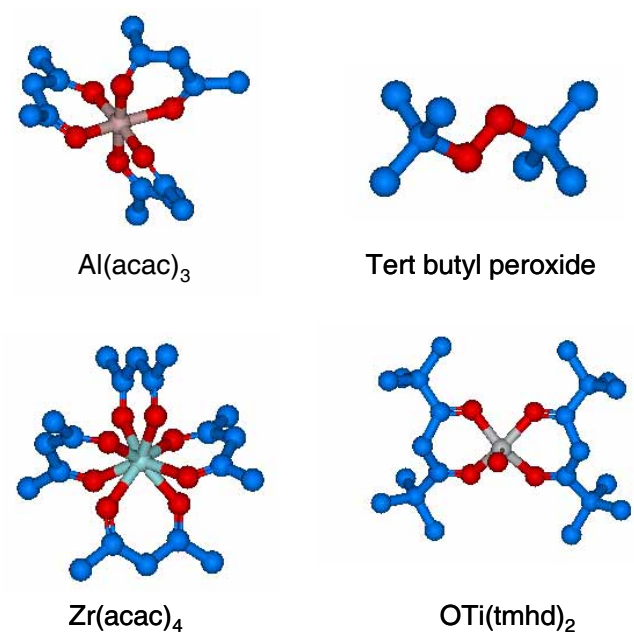

Figure 2. A stick and ball model of the structure of the precursors and the organic peroxide used.

RESULTS

Zirconium oxide films were deposited on Si substrates using $Zr(acac)_4$ and tert-butyl peroxide at temperatures ranging from 120 to 140°C and pressures from 2100 to 3600 psi. The oxidizer was injected into the cell after the temperature reached the set point temperature. Figure 3a shows a survey XPS scan for a film deposited at 140°C, 3900 psi. The presence of Zr, O

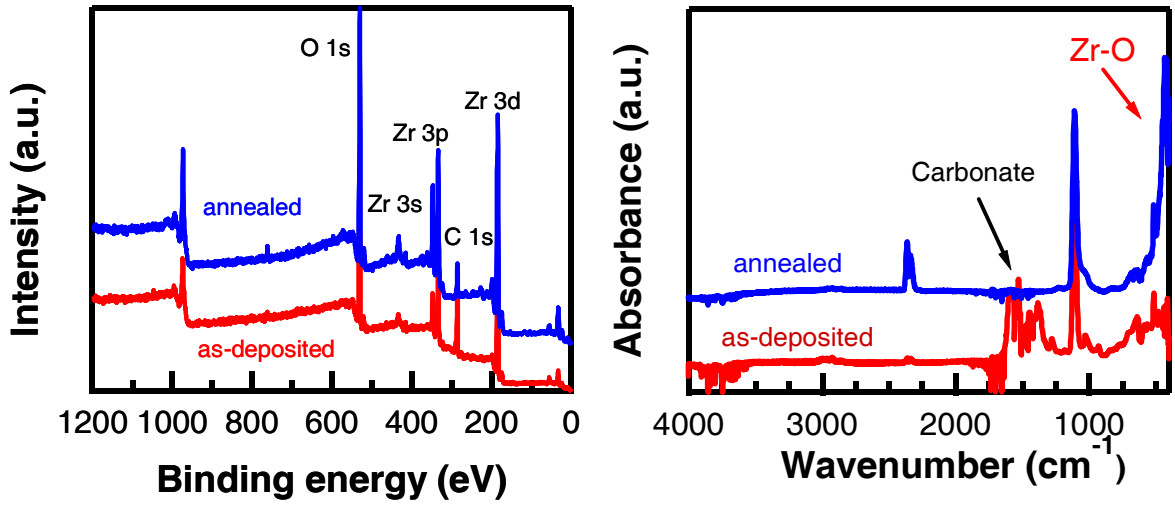

Figure 3. (a) XPS survey spectra for the as-deposited and annealed (4 min 700°C in Ar) film from $Zr(acac)_4$ and tert-butyl peroxide at 140°C (b) mid-IR spectra for the same films.

and C in the film is evident. Carbon is present in the film in two forms, adventitious carbon with a binding energy at 285.0 eV that is due to surface contamination from the ambient, and bonded carbon in the form of carbonate species that has 3-5 eV chemical shift. Figure 3b shows mid IR spectra for the same film. The formation of ZrO bonds is verified by the broad peak at 400-700 cm^{-1}.[14] The absorptions in the 1200-1700 cm^{-1} range indicate the presence of carbonate type bonding in the film. [14] The infrared signature of the carbonate species practically disappears after anneals at 700°C in inert atmospheres.

Aluminum oxide films were deposited on Si substrates using $Al(acac)_3$ and tert-butyl peroxide at temperatures ranging from 80 to 140°C and pressures from 2100 to 3600 psi. The oxidizer was injected into the cell after the temperature reached the set-point value. We

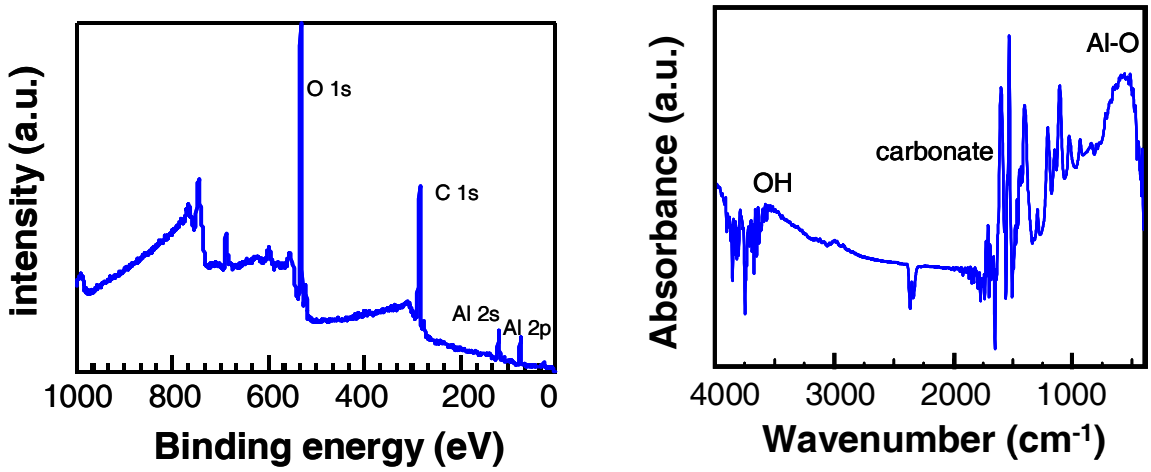

Figure 4. a) XPS survey spectrum for a film deposited from $Al(acac)_3$ and tert-butyl peroxide at 110°C, 2900 psi. b) mid-IR spectrum for the same film.

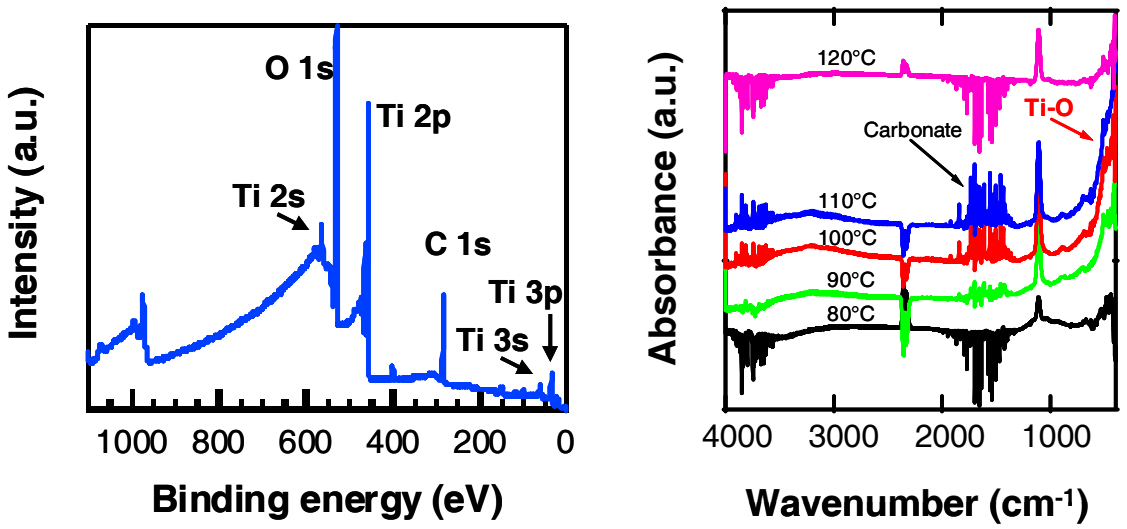

Figure 5. a)XPS survey spectrum for a film deposited from $OTi(tmhd)_2$ and H_2O_2 at 110°C, 2860 psi. b) mid-IR spectra for a series of films deposited at temperatures from 80-120°C.

found a very narrow processing window for film formation at 110-120°C. Figure 4a shows a survey XPS scan for a film deposited at 110°C. The presence of Al, O and C in the film is evident. Figure 4b shows a mid IR spectrum for the same film. The formation of AlO bonds is verified by the broad peak at 400-900 cm^{-1}.[15] Similarly to the ZrO_2 films the infrared spectrum indicates the presence of carbonate type bonding in the film, disappears after mild anneals.

Titanium oxide films were deposited from the reaction of $OTi(tmhd)_2$ and H_2O_2 in a broad temperature window ranging from 80 to 120°C and pressures around 3000 psi. The XPS spectrum verifies the presence of Ti, O, and some adventitious carbon in the thin film formation. This conclusion is corroborated by the IR spectra that show Ti-O absorptions.[16] For this material we observe only minimal carbonate formation, but there is some absorption in the 3600-3000 cm^{-1} range that is associated with the presence of H_2O and H-bonded OH in the film.

CONCLUSIONS

The formation of metal oxide thin films (alumina, zirconia, titania) thin films from the reaction of metal organic precursors with tert-butyl peroxide or hydrogen peroxide using supercritical carbon dioxide as the delivery medium has been demonstrated at temperatures below 140°C, which is significantly lower than the temperature required for conventional chemical vapor deposition methods. Carbonate type impurities are detected in all films but they are desorbed after mild anneals. The process related carbon content of the film is difficult to analyze by ex-situ XPS due to the adventitious carbon from the environment, and post-deposition

carbonate formation due to reactions of the film with atmospheric CO_2. These results demonstrate the potential of the technique for low-temperature deposition of metal oxide thin films.

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