

Low temperature metal oxide film deposition and reaction kinetics in supercritical carbon dioxide

Qing Peng^a, Daisuke Hojo^a, Kie Jin Park^b, Gregory N. Parsons^{a,*}

^a Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695, USA

^b Novellus Systems, Inc., 4000 North First Street, San Jose, California 95134, USA

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Abstract

An effective method is developed for low temperature metal oxide deposition through thermal decomposition of metal diketonates in supercritical carbon dioxide (scCO₂) solvent. The rates of Al(acac)₃ (Aluminum acetyl acetonate) and Ga(acac)₃ (Gallium acetyl acetonate) thermal decomposition in scCO₂ to form conformal Al₂O₃ and Ga₂O₃ thin films on planar surfaces were investigated. The thermal decomposition reaction of Al(acac)₃ and Ga(acac)₃ was found to be initialized at ~150 °C and 160 °C respectively in scCO₂ solvent, compared to ~250 °C and 360 °C in analogous vacuum-based processes. By measuring the temperature dependence of the growth rates of metal oxide thin films, the apparent activation energy for the thermal decomposition of Al(acac)₃ in scCO₂ is found to be 68±6 kJ/mol, in comparison with 80–100 kJ/mol observed for the corresponding vacuum-based thermal decomposition reaction. The enhanced thermal decomposition rate in scCO₂ is ascribed to the high density solvent which effectively reduces the energy of the polar transition states in the reaction pathway. Preliminary results of thin film deposition of other metal oxides including ZrO_x, FeO_x, Co₂O₃, Cr₂O₃, HfO_x from thermal decomposition of metal diketonates or fluorinated diketonates in scCO₂ are also presented.

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1. Introduction

Metal oxide thin films have important applications including dielectrics for semiconductor devices, thermal insulation, filtration, catalyst supports, coatings, sensors and others [1–4]. A wide range of processes have been developed to deposit metal oxide thin films, including chemical vapor deposition (CVD) [5–7], spray thermal decomposition [8], atomic layer deposition (ALD) [3,9], and others. However CVD usually requires high reaction temperature ($T > 400$ °C) to enable the metal-containing precursor to thermally dissociate at or near the growth surface, even in the presence of oxidizing agents such as O₂, O₃ and H₂O [5–7]. Atomic layer deposition can provide very conformal and uniform coatings, but it is not always amenable to low temperature processing, and deposition rates are relatively slow [3,9]. Spray pyrolysis techniques are also of

interest, but they typically suffer from an inherent inability to coat high aspect ratio structures [8].

Supercritical fluids have unique properties including zero surface tension, low viscosity and high diffusivity (analogous to vapors) and high density (similar to liquids) [10]. These unique properties allow supercritical fluids to wet high aspect ratio structures, dissolve metal organics, remove impurities from depositing surfaces, and enable conformal deposition of thin film coatings. In particular, supercritical carbon dioxide (scCO₂) has a reasonably accessible critical point ($P_C = 7.4$ MPa, $T_C = 31$ °C) and is non-toxic and environmentally benign. To date, a number of metal thin films including Pt, Cu, Co, Ni and others have been deposited from scCO₂-based process using suitable precursors on different substrates [10–12]. However, the deposition of metal oxides in scCO₂ is much less studied [1,4,13,14]. Recently, Uchida et al. [1] observed that the deposition of TiO₂ onto native oxide Si by pyrolysis of Ti(Oi-Pr)₂(dpm)₂ could be carried out at much lower deposition temperature (50–120 °C) in scCO₂-based process than in a

* Corresponding author.

E-mail address: parsons@ncsu.edu (G.N. Parsons).

conventional CVD process ($>210\text{ }^{\circ}\text{C}$). However, no characterization or analysis of the enhanced TiO_2 deposition kinetics in scCO_2 -based process was presented.

Previous work has shown that supercritical fluids (including scCO_2) can uniquely affect critical chemical reaction rates in homogeneous systems, as well as in heterogeneous catalysis [15–18]. For example, the work of Johnston and Haynes [19] helped clarify the extreme solvent effects in homogeneous reactions by analyzing in detail the homogeneous pyrolysis of α -chlorobenzyl methyl ether. That report showed a dramatic decrease in the homogeneous decomposition activation energy when the reaction was carried out in supercritical 1,1-difluoroethane as comparison to other liquid solvents such as carbon tetrachloride. The pronounced effect of pressure of supercritical fluids on the reaction rate constant was interpreted in terms of a large negative activation volume within the solvent clustering theory [19].

While several studies have characterized solvent-enhancement effects in homogeneous reactions [15–18], there are few previous results demonstrating details of supercritical solvent effects in heterogeneous film deposition reaction kinetics. In this article, the kinetics of low temperature pyrolysis of metal organics is characterized in scCO_2 , producing uniform coatings of metal oxide thin films. Specifically, Al_2O_3 and Ga_2O_3 deposition in scCO_2 from the pyrolysis of metal diketonates is analyzed as a model system to study the kinetics of heterogeneous scCO_2 -based thin film deposition, and to understand the unique effects of scCO_2 solvent on the deposition process. We found that the scCO_2 solvent can help lower the energy barrier of the pyrolysis reaction and thus decrease the pyrolysis temperature of metal organics, when compared with the corresponding vacuum-based pyrolysis reaction [3,5]. Moreover the observed effect of scCO_2 on the enhanced rate of pyrolysis of metal diketonates is consistent with theoretical understanding of solvent effects on homogeneous reaction kinetics [18–20], including Onsager's reaction field theory [18,19]. The results and analysis presented here lead to an improved comprehension of heterogeneous thin film deposition reaction systems.

2. Experiment

Native oxide Si(100) wafers were used as substrates for deposition, and were prepared by wet cleaning in BakerClean[®] JTB-100 solution (Mallinckrodt Baker Inc), followed by rinsing in deionized water, then drying in a N_2 flow. Metal containing precursors utilized in this study including aluminum acetylacetonate (99%) ($\text{Al}(\text{acac})_3$) [$\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$], $\text{Ga}(\text{acac})_3$, $\text{Fe}(\text{acac})_3$, $\text{Zn}(\text{acac})_2$, $\text{Zr}(\text{acac})_4$, $\text{Co}(\text{acac})_3$, $\text{Cr}(\text{acac})_3$, $\text{Hf}(\text{acac})_4$, aluminum hexafluoroacetylacetonate ($\text{Al}(\text{hfac})_3$) [$\text{Al}(\text{C}_5\text{HO}_2\text{F}_6)_3$] and $\text{Zr}(\text{hfac})_4$, were used as received (Strem Chemicals). Coleman grade CO_2 (99.99%) (National Welders) was used in experiments. Deposition reactions were carried out in a homemade stainless steel batch type reactor with a total volume of 110 mL as illustrated schematically in Fig. 1.

In a typical experiment, a piece of pretreated native oxide Si substrate ($\sim 1\text{ cm} \times 1.5\text{ cm}$) was fixed onto the heating block,

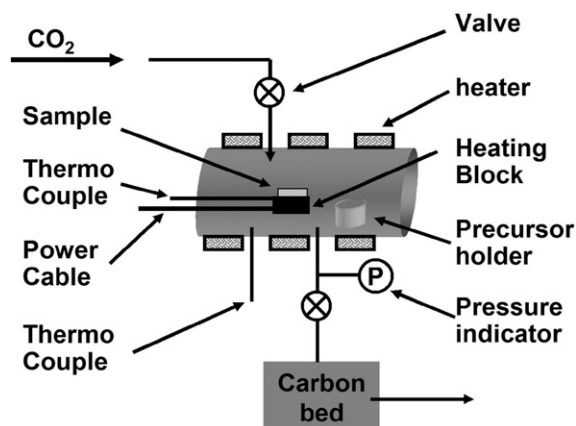


Fig. 1. Schematic diagram of the experimental apparatus. The inner volume of the reactor is $\sim 110\text{ mL}$. The reactor wall temperature is typically held at $100\text{ }^{\circ}\text{C}$. The sample is located on a block that is heated independently from the reactor chamber wall.

which was attached to a gland fitting (Conax Buffalo Corp.), as shown in Fig. 1. Three cartridge heaters (Tempco) were fit into the heating block, enabling substrate surface temperature to be controlled by using a feedback thermocouple fit through the gland fitting. A predetermined amount of precursor was weighed and placed in the reactor with the substrate holder before sealing. Air was purged from the reactor by flowing low pressure CO_2 through a vent valve for 5 min at a temperature of $\sim 70\text{--}100\text{ }^{\circ}\text{C}$. The reactor was then pressurized with CO_2 and heated to the predetermined set point ($P=21\text{ MPa}$, $T=100\text{ }^{\circ}\text{C}$). Subsequently, the system was kept stable for 2 h to allow the precursor to dissolve. The typical precursor concentration was approximately $170\text{ }\mu\text{mol/L}$ for $\text{Al}(\text{acac})_3$ and $230\text{ }\mu\text{mol/L}$ for $\text{Ga}(\text{acac})_3$. For some experiments, to examine the effect of oxidizing species, oxygen or water was intentionally added to the reaction. For these experiments, after the precursor was loaded into the clean vessel, the vessel was purged with low pressure CO_2 for $\sim 10\text{ min}$ to remove ambient air. The vessel was then filled with high purity dry air or a small known volume of deionized water and subsequently sealed and filled with high pressure CO_2 . The concentration of oxidant was then estimated using the known volume of the system.

After the precursor dissolution time, the temperature of the substrate was increased to the growth temperature set point. This transition occurred relatively rapidly, typically within 1 min. After a predetermined reaction time, the cartridge heaters were turned off and the temperature of the substrate quickly decreased to $<150\text{ }^{\circ}\text{C}$, typically within 1 min. For higher substrate temperatures, the reactor temperature was observed to increase above the set wall temperature of $100\text{ }^{\circ}\text{C}$ during the first 20 min, but temperature generally stayed below $\sim 190\text{ }^{\circ}\text{C}$. After the set deposition time, the effluent from the reactor was vented through an activated carbon bed, and fresh scCO_2 was used to purge the reactor to remove byproducts and remaining precursor in the system. The reactor was allowed to cool, and the samples were then removed from the reactor and characterized.

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