

Insulator Oxide Film Formation with Acid Catalyzed Hydrolysis of Alkoxides in Supercritical Fluid Carbon Dioxide

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ABSTRACT

Insulator oxide films can be produced by hydrolysis of metal alkoxide precursors in the presence of an acid catalyst in supercritical fluid carbon dioxide (sc-CO₂). Using tetraethylorthosilicate (TEOS) as a precursor and acetic acid (HAc) as a catalyst, SiO₂ films can be formed on surfaces of different substrates. The chemical equation of the SiO₂ film formation can be expressed as $\text{Si}(\text{OCH}_2\text{CH}_3)_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{CH}_3\text{CH}_2\text{OH}$. The deposition reaction actually starts at room temperature but produces good quality films in sc-CO₂ at temperatures above room temperature (e.g., 50 °C). In the absence of acetic acid, the reaction proceeds very slowly. The acid catalyzed reaction probably involves proton coordination to the oxygen atoms of TEOS molecules that facilitates the hydrolysis. Water involved in the reaction for hydrolysis is generated by the esterification process which can be written as $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$. The ATR-FTIR spectroscopy and EDS data of nanoparticle arrays covered with SiO₂ films are also given.

Keywords: TEOS, sc-CO₂, deposition, SiO₂ film

1 INTRODUCTION

Stability of the optical properties of nanoparticle arrays is important for optical device fabrication and for their durability. For example, without protection, PbS quantum dot (QD) arrays would degrade by oxidation over long periods of time. Techniques for making insulator oxide films in nanostructures are also important in developing new nano-materials and nano-devices. Stouwdam *et al.* [1] grew ~1 nm shell of PbS on the PbSe core to stabilize it with respect to oxidation. However, the observed shifts and reduction in PL signals upon air exposure indicated that the PbSe core was not effectively protected by the PbS shell from oxidation. Ihly *et al.* [2] used room-temperature atomic layer deposition (ALD) to infill the internal pore network of PbS QD films with amorphous alumina and then cap the films with a thin alumina (Al₂O₃) coating to prevent oxidation and ripening/sintering. This infilling method can produce QD films with greatly enhanced photo thermal stability. Recently, our group has explored the formation of silicon oxide films in supercritical fluid carbon dioxide (sc-CO₂) by hydrolysis of a silicon alkoxide precursor in the

presence of an acid catalyst [3,4]. With TEOS as a precursor and HAc as a catalyst, thin silica films on semiconductor substrates were formed in sc-CO₂. The stability and optical properties of nanoparticle arrays coated with SiO₂ films in sc-CO₂ are used as an example to illustrate one of the applications of this technique.

CO₂ is widely used for supercritical fluid studies because of its moderate critical constants, non-flammable nature, low cost, and available in relatively pure form. Recent reports on direct sol-gel processing of SiO₂ in sc-CO₂ show the promise of sc-CO₂ as a green solvent in nanotechnology [3-6], because of its tunable solvating strength, near zero surface tension, high diffusivity and excellent wetting of complex nanostructure surfaces. This report describes conditions of formation of silicon dioxide films with reasonable thickness in sc-CO₂ using TEOS and HAc. Parameters of the SiO₂ film formation that were evaluated included the amount of catalyst, presence of water, molar ratio of HAc/TEOS, reaction time, temperature and pressure of sc-CO₂. The properties of the resulting material that were of interest for the applications were studied, including morphology and components of elements. Formation of SiO₂ protective coating on nanoparticle arrays in sc-CO₂ and related spectroscopic studies are also presented.

2 EXPERIMENTAL

A FEI Sirion scanning electron microscope (SEM) instrument was used to measure the cross section and the image taking. SEM images were collected with a Sirion instrument manufactured by FEI, Inc. Energy dispersive spectroscopy (EDS) instruments FEI Quanta ESEM II was employed to measure for semi-quantitative elemental analysis. Attenuated total reflectance (ATR) in conjunction with Fourier transform infrared (FTIR) spectroscopy was used to identify the Si-O-Si vibrational modes.

Supercritical carbon dioxide precipitation of the nanoparticles was carried out inside a 14 mL chamber of a stainless steel high-pressure apparatus. A detailed procedure can be found in the literature [7].

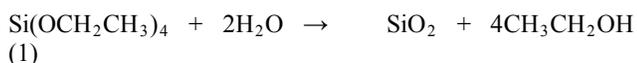
Samples were prepared in a nitrogen glove box which was previously purged by N₂ gas to remove moisture and air. TEOS (50 μL, 2.24 x 10⁻⁴ moles) and HAc (40 μL, 7.04 x 10⁻⁴ moles) were spiked separately into different mini glass beakers. Pieces of substrate were loaded on the top platform and a stainless steel high pressure chamber cap was then immediately sealed. The reaction chamber was installed into

sc-CO₂ system, and then charged with CO₂ from 60 atm to 70 atm, and then heated from room temperature to 50 °C, which took about 1 hour. At this time, the pressure inside the chamber was approximately 160 atm. After that, CO₂ was then charged again from 160 atm to 170 atm. The system was in the static mode for 2 hours, followed by depressurization with a flow rate of 0.1 – 0.3 mL/min.

3 RESULTS AND DISCUSSIONS

3.1. Chemistry of TEOS Hydrolysis Reaction

A traditional method of making SiO₂ film is by hydrolysis of TEOS with water [8,9], according to the following reaction:

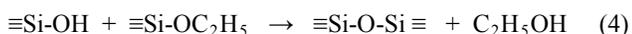


Preliminary benchtop experiments were carried out in our laboratory in a closed system with TEOS and water placed separately next to a carbon coated copper grid with the presence of acetic acid catalyst. The hydrolysis reaction was efficient in the presence of water, even at room temperature, based upon our EDS and SEM information. However, the SiO₂ films generated from TEOS by this method are porous in the entirety of the SiO₂ layer. The more water available, the more efficient and faster the reaction goes from left towards the right side of Reaction 1. Figure 1 shows TEM images of SiO₂ layer from the reaction of the TEOS and a small amount of water in the presence of a catalyst (HAc). An excess amount of water causes the reaction to go too fast, leading to precipitation and agglomeration of aerogel particles, and generates more porosity, thus, resulting in poor quality SiO₂ films. Here, an excess amount of water indicates any addition of a small volume of exterior water even a few microliters.

If no water was added to the system, the water moisture required for TEOS hydrolysis may come from *in situ* water generation [10] from the esterification reaction



and condensation reactions



These procedures could moderate the hydrolysis rate. Uniform SiO₂ films were produced (Figure 1b) on TEM grids when using only TEOS and acetic acid without additional water. In the sc-CO₂ system, water may also be obtained from CO₂ medium, which usually contains 1 x 10⁻² mole fraction of water at 50 °C and 200 atm, a common supercritical fluid experimental condition [11]. Therefore, the water moisture from *in situ* generation and from the CO₂ phase is enough for the TEOS hydrolysis to form good quality SiO₂ films. Ethanol involved in Reaction 2 is

probably generated by hydrolysis of TEOS (Reaction 1) facilitating the interfacial reaction.

Restricting the availability of water and moderating the hydrolysis rate significantly improves the SiO₂ film quality. Water generated *in situ* through the esterification and condensation reactions, thus, provides a better alternative for the formation of high quality insulating oxide films from alkoxide precursors.

In the absence of the acetic acid catalyst at room temperature, the TEOS hydrolysis reactions were extremely slow, as revealed by our EDS measurements. Pope and Mackenzie [12] reported that TEOS gelation time will take 1000 hours at room temperature if there is no catalyst. The authors also pointed out when acetic acid was applied, the TEOS gelation time could shorten to 72 hours [12]. Acetic acid is very soluble in sc-CO₂ [13] and is an *in situ* water producing reactant in the esterification reaction (Reaction 2). Our benchtop experiments showed in the presence of HAc catalyst, the TEOS took more than 72 hours (3 to 4 days) to complete the hydrolysis reaction.

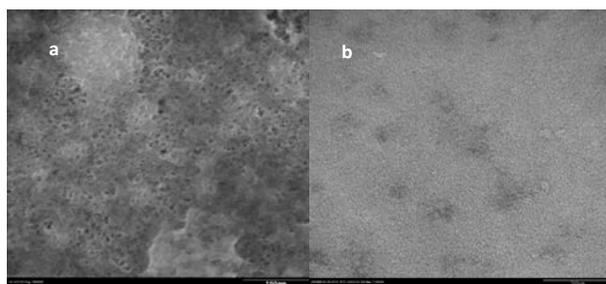


Figure 1: TEM images of the SiO₂ layer from the hydrolysis reaction of TEOS (a) with addition of water and (b) without addition of water.

The higher acid/alkoxide ratio increases the rate of the TEOS hydrolysis reaction [14]. In our experiments, as observed from the cross sections of SEM images, however, if an excess amount of acid was added in the catalytic hydrolysis of alkoxide, the pre-deposited nanoparticle layer, e.g., Au nanoparticle layer, could be damaged showing some porous structures. Moreover, when an excess amount of acid was used in the acid catalyzed hydrolysis, GaAs substrate surfaces started to peel, generating flakes. This was observed at molar ratio of HAc/TEOS > 7.8, for example: HAc = 1.049 x 10⁻⁴ mole and TEOS = 1.34 x 10⁻⁵ mole.

EDS spectral results are also supportive and the atomic ratio of the resulting products of O : Si is around 2 : 1, when the amount of acetic acid changed from 3.5 x 10⁻⁵ mole (2 μL) to 1.75 x 10⁻⁴ mole (10 μL) at a fixed TEOS 1.34 x 10⁻⁵ mole (3 μL), in 25-mL-glass containers, after the hydrolysis reaction. In this reaction, a GaAs substrate was employed. Although the SiO₂ formula is represented with only one silicon atom and two oxygen atoms, it is actually a giant covalent molecular lattice with each silicon atom attached to four oxygen atoms and each oxygen atom attached to two silicon atoms. The simplest formula is SiO₂. When 3.5 x 10⁻⁵ mole (2 μL) of HAc were added, the Si and O peaks in EDS

spectra were barely observed, indicating the hydrolysis reaction was just initiated. The atomic ratios showed a consistent trend of O : Si = 2 : 1 when more HAc were sequentially added, suggesting that SiO₂ film was formed.

3.2 SiO₂ Film Formation in sc-CO₂ with the TEOS Hydrolysis Reaction

Supercritical CO₂ is a good solvent for alkoxides and short chain organic acids (e.g., HCOOH and CH₃COOH) [14]. The reaction temperature in sc-CO₂ phase must be greater than its critical temperature (31 °C). A commonly used temperature in sc-CO₂ is ≥ 40 °C, while organic solvents used in normal sol-gel processes are at room temperature. Thus, the sc-CO₂ process would generally accelerate chemical reaction rates relative to room temperature reactions. Charpentier *et al.* carried out TEOS hydrolysis experiments in a 100 mL autoclave equipped with ATR-FTIR in sc-CO₂ [14]. The volumes of TEOS and HAc added were both 2 mL, calculated from the initial concentrations of TEOS and HAc, and the volume of the high pressure system. The total reaction times undertaken were 6 h, under the temperature of 40-60 °C and pressure of 88.4-204 atm. At 50 °C and 88.4-204 atm, after 200 min (3.3 h), TEOS hydrolysis conversion reached a plateau, suggesting the hydrolysis reaction conversions were complete [14]. Based upon information from the literature, in our experiments, the conditions used were as follows: temperature of 50 °C, pressure of 170 atm, and the hydrolysis reaction time in sc-CO₂ in 2 hours, which should be appropriate to complete the conversions of hydrolysis reactions when the volumes of TEOS and HAc used were at the level of microliters. We chose 50 °C for the hydrolysis reaction, because above this temperature nanoparticles may undergo changes during the SiO₂ coating process.

Figure 2 shows SiO₂ film formation on a GaAs substrate in sc-CO₂. The reason to use the GaAs substrate is due to the fact that it will have less interference with background information related to SiO₂ and it is a commonly used semiconductor material for many applications. Figure 2a and 2b show the EDS spectrum and SEM image of a blank GaAs substrate. After the hydrolysis reaction in sc-CO₂, a SiO₂ film was formed as evidenced by O and Si peaks in the EDS spectrum (Figure 2c) and SEM image (Figure 2d). In this reaction, there is no exterior water added. In the presence of acetic acid as a catalyst, a smooth silicon dioxide film with reasonable thickness can be formed in supercritical fluid CO₂ at 50 °C and 170 atm (Figure 2d).

Attenuated total reflectance (ATR) is a sampling technique used in conjunction with FTIR spectroscopy which enables samples to be examined directly in the solid or liquid state without further preparation. A sample fabricated on a GaAs substrate with 30 μL TEOS and 30 μL of HAc, through the hydrolysis reactions of TEOS in sc-CO₂ at 50 °C, 170 atm and 2 hours, was measured by ATR-FTIR spectra. It revealed a characteristic Si-O-Si peak located clearly at 1066.1 cm⁻¹, and supported the SiO₂ film formation, as shown in Figure 3.

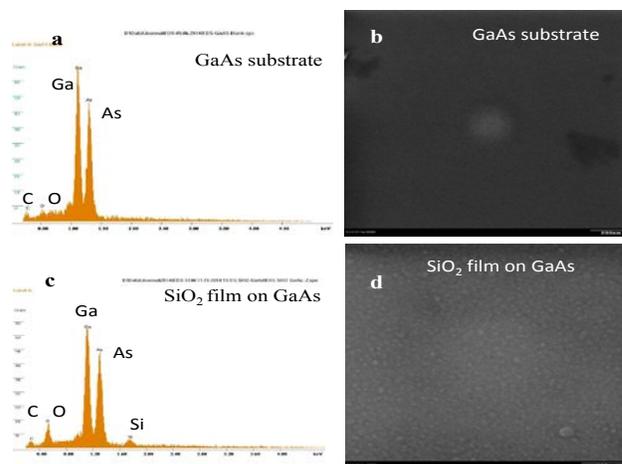


Figure 2: SiO₂ film formation on a GaAs substrate in sc-CO₂. (a) EDS spectrum of GaAs substrate, (b) SEM image of GaAs substrate, (c) EDS spectrum of SiO₂ film on GaAs substrate, and (d) SEM image of SiO₂ film on the surface of GaAs substrate.

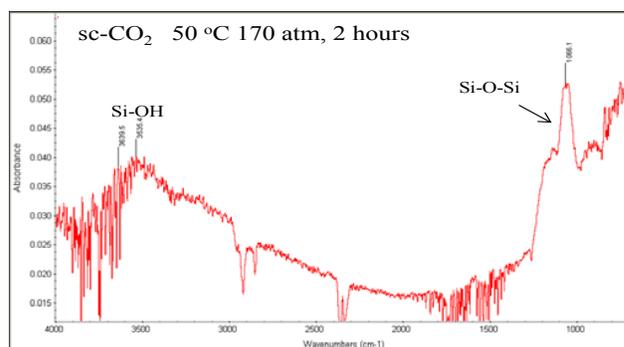


Figure 3: ATR-FTIR spectrum of SiO₂ film fabricated on GaAs substrate with 30 μL TEOS and 30 μL HAc in sc-CO₂ at 50 °C and 170 atm. Si-O-Si vibrational mode is located near 1066 cm⁻¹.

3.3 SiO₂ Film Thickness

Tescan LYRA-3 Model XMH FIB instrument was used for cross section cutting. After cutting, a FEI Sirion SEM instrument was used to measure the cross section and the imaging. The cross sections of the films include Cr coated glass or GaAs substrate, with a nanoparticle layer, silica film layer, and Pt cap protective layer. The reason to use Cr coated glass as a substrate is to meet a requirement for the SEM measurements and to let charges be drained with less imaging interferences. For the purpose of this study of SiO₂ film formation with acid catalyzed hydrolysis of TEOS in sc-CO₂, the SiO₂ film deposited directly on the substrates without the nanoparticle layer will be discussed in this section.

Preliminary experiments of SiO₂ deposition via TEOS hydrolysis were carried out using benchtop experiments at room temperature. Figure 4a shows the cross sections of

SiO₂ films generated from TEOS hydrolysis, on the top of GaAs substrates, with 3 μL of TEOS (1.34×10^{-5} mole) and 6 μL of HAc (1.05×10^{-4} mole) in a closed system. The average thickness of the films was around 81 nm. In addition, Cr coated glass substrates were also used to check the silica layer via TEOS hydrolysis in sc-CO₂ and the average thickness of the cross section of SiO₂ films was approximately 385 nm (Figure 4b), under a condition of 2.24×10^{-4} mole (50 μL) TEOS, 7.04×10^{-4} (40 μL) HAc, and sc-CO₂ at 50 °C, 170 atm.

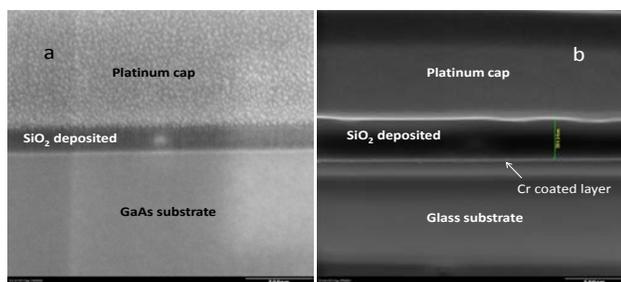


Figure 4: Cross sections of SEM images of SiO₂ film generated from TEOS hydrolysis. (a) on the top of GaAs substrates, in a benchtop experiment. (b) on the top of Cr coated glass substrate, under a condition of 50 μL TEOS, 40 μL HAc, sc-CO₂.

One way to control the SiO₂ film thickness is by controlling the amount of catalyst addition. A set of benchtop experiments was conducted in a nitrogen glove box. 25-mL glass vials were used as sealed systems. The amount of TEOS was fixed at 1.34×10^{-5} mole (3 μL), and the amount of acetic acid was changed from 3.5×10^{-5} mole (2 μL) to 1.75×10^{-4} mole (10 μL). GaAs wafers were used as substrates. The benchtop reactions took approximately 4–5 days to complete at room temperature. When 3.5×10^{-5} mole (2 μL) of acetic acid were used, the thickness of the cross section of the SiO₂ layer was around 29 nm. As the amount of HAc was doubled (4 μL), the thickness of the silica layer was almost doubled, 45 nm, as shown in Figure 5. When the amount of HAc added reached a certain level (6 μL), it was shown that the thickness of the silica film approach a maximum (81 nm), and the plot showed a pseudo-linear relationship at this point. If acetic acid continued to increase to 8 μL or 10 μL, then a slight decline of the thickness from the curve was observed (Figure 5). Figure 5 shows a curve of the average film thickness from cross sections of SEM images. Film thicknesses corresponding to 2, 4, 6, 8 and 10 μL of HAc added were measured. These values were determined to be 29, 45, 81, 73, and 73 nm, respectively.

Formation of SiO₂ films by acetic acid catalyzed hydrolysis of TEOS in sc-CO₂ was studied. In this process, no extra water, organic solvents or other additives were required. Parameters such as the amount of catalyst, water, molar ratio of HAc/TEOS, reaction time, temperature and pressure of sc-CO₂ were evaluated. Uniform SiO₂ films

with variable thicknesses can be formed by adjusting relative amounts of TEOS and HAc. Spectra of

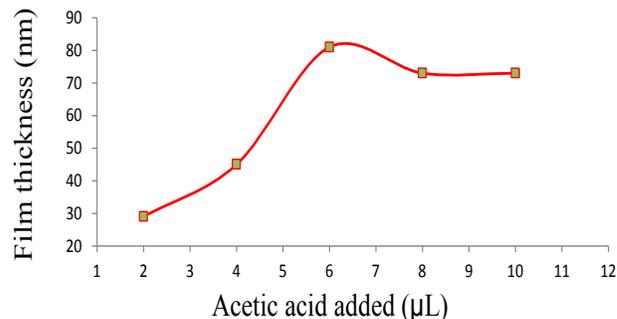


Figure 5: At a fixed TEOS amount (1.34×10^{-5} mole, 3 μL), variation of the amount of HAc from 3.5×10^{-5} mole (2 μL), 7.0×10^{-5} mole (4 μL), 1.05×10^{-4} mole (6 μL), 1.4×10^{-4} mole (8 μL), to 1.75×10^{-4} mole (10 μL). The curve shows SiO₂ film thickness changes with the amount of HAc added.

the nanoparticle layer with a SiO₂ protective coating can be measured by UV-Vis spectroscopy without any interference. EDS measurements provided quantitative information regarding the atomic ratio of O to Si in the protective coating. Further exploration for the research of the formation of SiO₂ protective coating on nanoparticle layers in sc-CO₂ and related spectroscopic studies are currently underway.

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