TFE4575: Chemical methods for thin film deposition

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Abstract

So abstract, wow!

Contents

1. Theory

1.1. Sol-Gel Synthesis Method

This subsection is based on chapter 3 of B. L. Cushing *et al.* review paper *Recent Advances in the Liquid- Phase Synthesis of Inorganic Nanoparticles* [1].

In general, sol-gel processing combines small molecules to form a solid material. This is done using a solution of precursors (the *sol*) that forms a network of bound molecules (the *gel*). Traditionally, sol-gel processing only referred to the hydrolysis and condensation of alkoxide based precoursors such as $Si(OEt)_2$ (tetraethyl orthosilicate), but today it refers to all processes using sol-gel. The sol-gel synthesis method can be divided into the following six distinct steps.

Step (1): The formation of a stable solution of the alkoxide or solvated metal precursor.

Step (2): The gelation that results in the formation an oxide- or alcohol-bridged network by polycondensation or polyesterification reactions. This dramatically increases the the viscosity of the solution.

Step (3): The aging of the cell, also known as syneresis. In this step, the gel network contracts and expulses the solution from the pores, and the reactions continue until the gel forms a solid mass.

Step (4): The drying of the gel where water and other volatile liquids are removed. This step is complicated because it fundamentally changes the gel structure. The drying process comprises of four sub-steps: (i) the constant rate period, (ii) the critical point, (iii), the first falling rate period, and (iv) the second falling rate period. The result is either termed a xerogel, if isolated by thermal evaporation, or an aerogel, if the solvent is extracted under supercritical conditions.

Step (5): Dehydration of the gel using high temperatures. This removes surface-bound M-OH groups, thus stabilizing against rehydration.

Step (6): The densification and decomposition of the gel. This makes the gel pores collapse, and all remaining organic species are volatilized.

1.2. Chemistry of the Sols

Using the sol-gel synthesis method, one can produce several types of materials. One example of such a material is BTO ($BaTiO_3$), which can be made of a mixture of barium sol and titanium sol. The following paragraph explains the components of these sols and what their functions are.

Barium sol can be made of a mixture of water, EDTA (Ethylenediaminetetraacetic acid), ammonia solution, barium nitrate, and citric acid. Titanium sol can be made of a mixture of water, citric acid, Titanium isopropoxide, and ammonia solution. The barium nitrate and the titanium isopropoxide are the sources of the barium and titanium, respectively. Citric acid is a chelating agent, which means that it reacts with the metal ions to form stable, water-soluable metal complexes. In the barium solution, EDTA is works as an additional complexing agent. Finally, since the complex stability depends on the pH, the ammonia solution is used to for adjustments.

1.3. Equipment

1.4. Profilometer

Profilometers are instruments used to extract topographical data from a surface. This can either be from a single

point or a line.

1.5. Scanning Electron Microscope

The section on SEM is based on Goldstein chapter 1, 2, and 3 Scanning electron microscopes (SEM) are used for sample analysis, and the image contrast is due to the sample composition and topography. Composition is given on elemental level with energy dispersive X-ray spectroscopy (EDS), or with Z-contrast imaging with backscattered electrons (BSE). Topography is given primarily with secondary electrons (SE), and partly be achieved with backscattered electrons (BSE). The Everhart Thornley Detector (ETD) combines data from the SE and BSE detectors to give a better image contrast

SEM samples needs to be conductive, if not electrons will accumulate on the surface and the image will become distorted. If the sample is not conductive enough, it can be coated with a thin layer of gold or carbon. If a sample is partly conductive, a lower voltage can be used to get an image without distortion.

The SEM can be used to see ferroelectric domains structures in a sample, as illustrated in The image was taken on the SEM APREO at NTNU NanoLab with 1.5 kV and 50 pA, and gives an overview of the domains in the sample.

2. Methods

2.1. Solution preparation

First, the barium solution was made. In a beaker, 10 mL of DI water was heated to 60°C while being stirred with a magnet. To this, 3.6893 g of EDTA and 7 mL of ammonia solution was added, and the solution was stirred until clear. Then, 3.2676 g of $Ba(NO_3)_2$ and 4.8070 g of citric acid was added, and the solution was again stirred until clear. Finally, about 3.5 mL of ammonia solution was added to achieve a pH of 7. This was verified using pH paper. The final solution was then added to a 50 mL volumetric flask, and the volume adjusted to 50 mL with DI water.

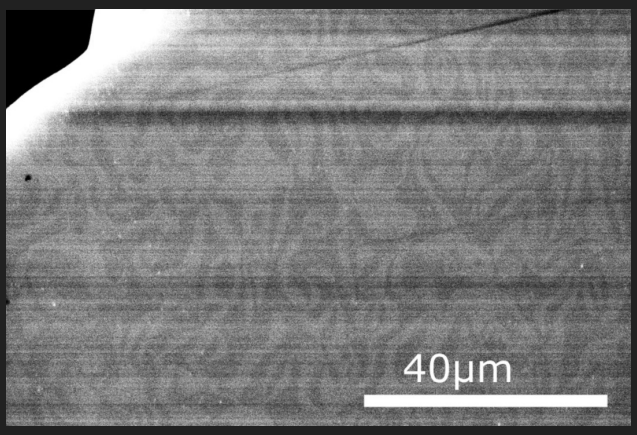

Figure 1: Ferroelectric domains in an $ErMnO_3$ sample. The domains are visible as squiggly lighter and darker gray areas in the image. Image taken by Hunnestad and published in his masterthesis in 2019 Taken on the SEM APREO with EDT, 1.5 kV and 50 pA.

This titanium solution used in this project was premade by NTNU NanoLab. However, the processing steps are included here for completeness and ease of replication. In a beaker, 50 mL of DI water was heated to 60°C while being stirred with a magnet. To this, 14.409 g of citric acid was added. Then, 7.6 mL of titanium isopropoxide was added with a syringe. The solution was then covered with parafilm and stirred overnight, until the solution was clear. Finally, ammonia solution (30 %) was added to adjust the pH to 7. The solution was then added to a bottle, and standardized to 0.501 mmol/gram using DI water.

Finally, to make the barium titanium oxygen (BTO) sol, 3 mL of titanium sol was first added to a beaker. Then, 6.90 mL of barium sol was added, and the solutions were mixed together.

2.2. Substrate coating

The BTO was deposited on a Si-Pt substrate. Before the deposition, the substrate was cleaned with an ISO 5 clean room wipe, submerged in acetone, and rinsed with isopraoanol and water. Then, the wafer was dried with nitrogen gas, and placed in a plasma cleaner for 2 minutes with oxygen flow and 50/50 O_2/generator power. The substrate was then placed in the spin coater and secured using vacuum. Using a syringe with a 0.2 µm filter, the BTO sol was applied to the substrate. The spinning was done at 500 rpm for 10 seconds, then 2500 rpm for 30 seconds, with 5 seconds acceleration time. After the deposition, the substrate backside was cleaned using an ISO 5 clean room wipe and acetone. Then, the substrate was baked on a hot plate at 200°C for about 4 minutes. Finally, sintering was done in a gold furnace at 700°C for 10 minutes, heating and cooling as fast as possible.

2.3. Characterization

First, the thin film was inspected using an optical microscope. This was done at 5X, 10X and 20X magnification. Then, the film was inspected using a Dektak 150 profilometer. This was done at 3 different locations on the sample, and the profiles were made from the edge of the sample to the center. The instrument was set to measure hills and valleys for 4000 microns in 60 seconds, with a resolution of 0.222 µm per sample. Finally, the film was inspected using an APREO SEM. XXXXXXX SEM settings XXXXXXXX

3. Results

4. SEM images

SEM images were acquired on the SEM APREO at NTNU NanoLab, without coating of the sample. One of the engineers at NanoLab suggested that the sample would be conductive enough, and showed examples of SEM

results from other ferroelectric thin films that were not coated, e.g. [2]. The examples used low voltage and low current, which was also used in this work.

Figure **??** shows an overview SEM image of a corner, which is the same area in the optical image in **??**. The image was taken with 3 kV and 50 pA, using the EDT detector to get both topography and z-contrast. The scale bar is 500 μm.

Figure **??** shows a closer SEM image of a part of the sample. The image was taken with 5 kV and 0.1 nA, using the T2 SE detector.

5. Discussion

I think this. No this is much better. Every discussion ever.

6. Conclusion

To conclude, this is boring!

hello bro this is a test

References

[1] B. L. Cushing et al. Recent Advances in the Liquid- Phase Synthesis of Inorganic Nanoparticles. Chem. Rev., 2004, 104 (9), 3893-3946, DOI: 10.1021/cr030027b.

[2] Kasper Hunnestad. *Visualizing Ferroelectric Domain Structures in ErMnO3 and Pb5Ge3O11 by Electron Microscopy*. PhD thesis, 2019.