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Preparation of stable sol and free-cracks thin film of Barium Titanate via sol-gel dip coating method

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In this paper the stable Barium Titanate, BaTiO3, (BTO) sol was prepared at the first stage. The obtained results of the mean size of particles showed that the ratio of precursors and their type had a great effect on the stability of the soil and the properties of the thin films. After adjusting the process parameters, the sol with 10 months stability was acquired. The stable sol consisted of acetic acid, barium acetate, TTIP, 2-propanol and deionized water with 7 : 1 : 1 : 1 : 130 molar ratios, respectively. Then, the optimum sol was deposited on the different substrates such as silicon (001), soda-lime glass and alumina and the effect of substrate type was evaluated on the morphology of the thin film. According to AFM and SEM results, it was found that the substrates obviously influenced the microstructure of $BaTiO_3$ thin films and a smooth crack free surface was obtained.

Key words: Sol-gel, Dip coating, Barium titanate, Thin film.

Introduction

Barium Titanate ($BaTiO_3$) has been widely studied in several different forms including bulk, powder, multilayer and thin film, due to outstanding dielectric and ferroelectric properties with different applications such as, Thermistors, multilayer capacitors, piezoelectric and ferroelectric devices [1-3]. $BaTiO_3$ thin films have been prepared by a variety of techniques such as Pulsed laser deposition (PLD) [4], Radio frequency sputtering [5], Laser molecular beam epitaxy (MBE) [6], Flash evaporation technique [7], hydrothermal [8] and sol-gel processing [9, 10].

During recent years, simple and cheap synthesis methods like sol-gel or other precursor-routes have been intensively investigated. Sol-gel method gives pure oxides with stoichiometry control in a low processing temperature, and its ability to produce uniform, chemically homogenous films over large areas and ease of integration with the existing semiconductor technology [10].

It is known that the resultant microstructure of thin films is one of the key factors for the properties of thin films. Therefore, synthesis of uniform and free cracks thin film of $BaTiO_3$ becomes more and more important.

In the present paper, we investigate the preparation of stable BTO sol and optimized precursors and proper ratios selected for the preparation of the sol. In order to produce uniform and free cracks thin film of $BaTiO_3$, the structure and surface morphology of BTO thin films obtained by dip-coating on three different substrates (soda- lime glass, silicon and alumina) were evaluated. The films are studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM); the results are cross-compared and briefly discussed.

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Experimental

Synthesis of stable barium titanate (BTO) precursor sols

To prepare the sol, no modifier was used in the precursors. It is necessary to note that the chemical modifiers such as acetyl acetone are frequently used in the other works to prepare stable sol and free-crack films [11, 12].

Effect of acetic acid

A Acetate derived $BaTiO_3$ sol was prepared by using the glacial acetic acid (Merck, assay 100%), Barium Acetate (Merck, assay > 99%), Titanium Tetraisopropyl alkoxide or TTIP (Merck,assay > 98%), 2-propanol (Merck, assay > 99%) and deionized water as precursors. In all experiments, the molar ratio of Barium Acetate to Titanium Tetraisopropyl alkoxide was constant (Ba : Ti mole ratio = 1 : 1). First, barium acetate was dissolved in acetic acid at 65 °C, and then the solution was cooled down to room temperature. To find the optimal molar ratio of Acetic acid, 4 solutions were investigated with a molar ratio of Acetic acid to Barium acetate 2, 6, 7 and 14. In order to prevent exhaustion of acid, the sol was refluxed.

Effect of water

Then, 2-propanol was added to the solution. In the

next step, partial hydrolysis occurs by introducing of TTIP. To acquire the best amount of deionized water in the mixture, Different H_2O/Ba.Ac molar ratios of 50, 80, 100 and 130 were investigated. During all steps of sol preparation, a magnetic stirrer agitated the mixture. Finally, a transparent and colorless sol was formed.

Formation of Barium Titanate thin film

Three kinds of substrates have been used in this study, Soda-lime glass, alumina and Si (001) wafer. All of the substrates were cleaned ultrasonically in acetone and methanol for 15 min. Nanostructured thin films were deposited on substrates by sol-gel route and withdrawn by the rate of 2 cm/min in ambient atmosphere and at room temperature. Then, the samples were kept in a vapor pressure and dust free atmosphere for 1 hour to form lms after hydrolysis and polymerization process. Dip-coating process was repeated 3-5 times to obtain lms with desired thickness, followed by pyrolysis of each layer at 100 ºC for 10 min. Heat treatment of dried thin lms was carried out in a furnace at the temperature of 700 ºC in air atmosphere for 30 minutes.

Results and Discussion

As before said the molar ratios of acid to Barium Acetate were 2, 6, 7, and 14. All sols kept for two weeks and then the average mean size of particles in sol was evaluated in order to consider the stability of sol. When the size of particles is small after 2 weeks, it can be found that this sol have tended less to gelation so it is more stable.

Fig. 1 shows the effect of the amount of acid acetic on the preparation of the stable sol. As it can be seen, increasing the amount of acetic acid causes the decrease of the mean size of particles in sol. Whatever the average mean size is smaller, sol is more stable. The maximum value of the mean size of nanoparticles in sol formed with a molar ratio of Acetic acid = 2 is 540.8 nm.

Acetate groups in solution increase by enhancement of the Acetic acid and these groups surround alkoxide (see reaction 1), and lead to put hydrolysis off .When the molar ratio of acid to barium acetate is 2 : 1, although the presence of acetate groups reduces the rate of hydrolysis and prevent deposition formation, small amount of protective groups of alkoxide can lead to start the hydrolysis reaction and therefore sol is not stable and this is consistent with Fig. 2. Based on Fig. 2, the best ratio of Acetic acid to Barium acetate is 7 : 1.

$$Ti(OR)_4 + CH_3COOH \longrightarrow Ti(OR)_3CH_3COO + RH \quad (1)$$

Another parameter which affects the stability of sol is the molar ratio of water. When water before TTIP was

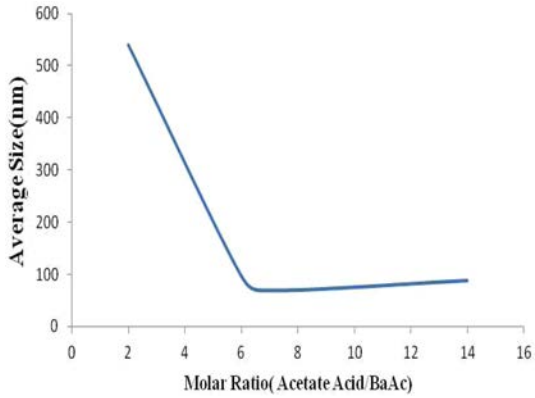

Fig. 1. The effect of the amount of acid acetic to prepare the stable sol.

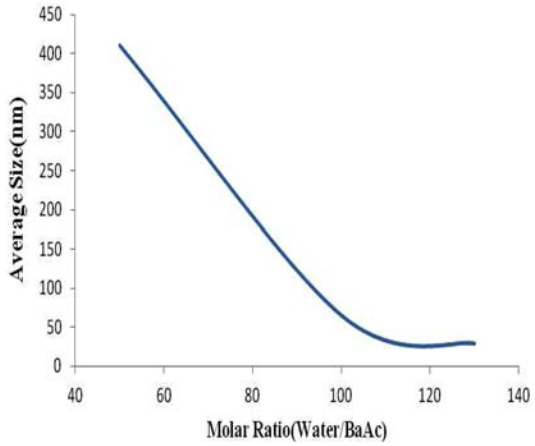

Fig. 2. The effect of the amount of water to prepare the stable sol.

added, it led to the formation of white precipitates and therefore water was introduced in the last step. As it was mentioned, different molar ratios of water to Acetate were selected. The results showed that the hydrolysis was performed by adding excess water (molar ratio of H_2O/ Barium acetate = 130). The effect of water on stability of sol in the present work was depicted in Fig. 3. When the amount of water is low, sol will evaporate rapidly. By adding more amount of water, the mean size of particles reduces so the stability of sol will increase. Therefore the best molar ratio of H_2O to Barium acetate is 130 : 1.

The method of sol preparation, temperature and the best molar ratio of precursors at each step of preparation are shown in the flowchart in Fig. 3.

Fig. 4 shows SEM micrographs of $BaTiO_3$ thin films deposited on soda lime glass, silicon wafer and alumina substrates. It can be observed that the surface morphologies of $BaTiO_3$ thin films are obviously different due to different substrates. Also, the surfaces of thin films deposited on Si wafer and Soda lime glass are dense and compact in nature, while that prepared on Alumina revealed micro-cracking on the surface of the thin film. These cracks can be caused by the different thermal expansion coefficients of $BaTiO_3$ thin film and

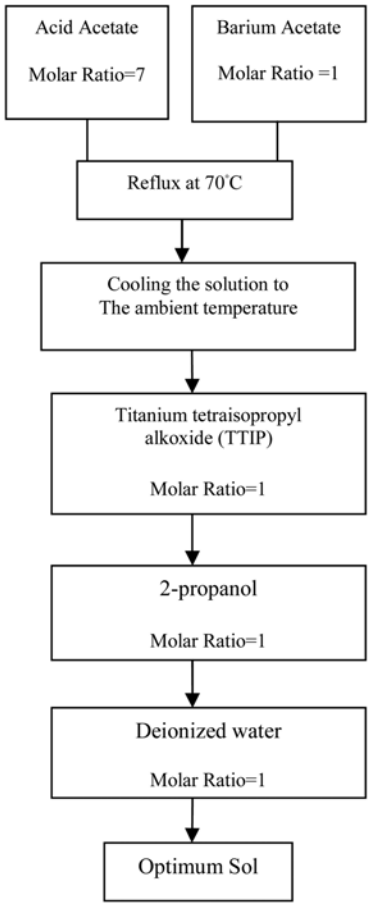

Fig. 3. The appropriate method for sol preparation.

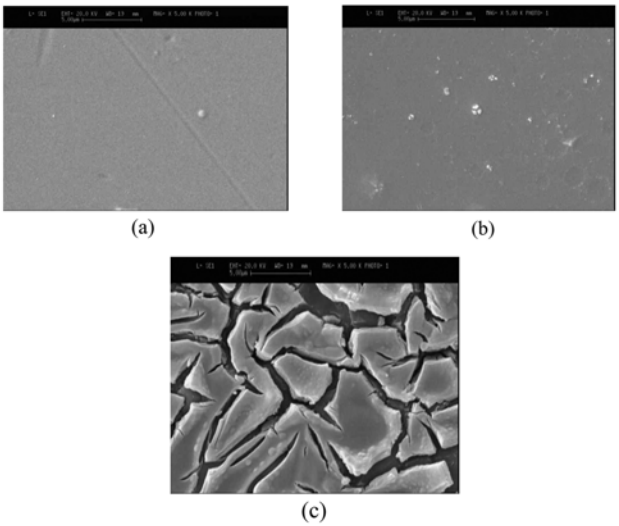

Fig. 4. SEM micrographs of BTO thin films deposited on (a) soda lime glass, (b) silicon wafer, and (c) alumina substrates.

alumina substrate. Also, the alumina substrate had a higher roughness than other substrates. Then silicon wafer and Alumina substrates are heated up to 700 ºC in air atmosphere for 30 minutes, the surface morphology are shown at Fig. 5. During heating or cooling, if the interfacial stresses were larger than the

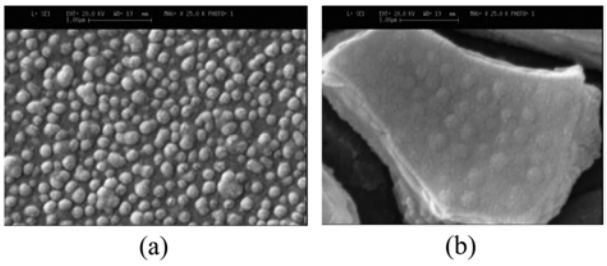

Fig. 5. SEM micrographs of BTO thin films deposited on silicon (a) and alumina (b) substrates after heat treatment.

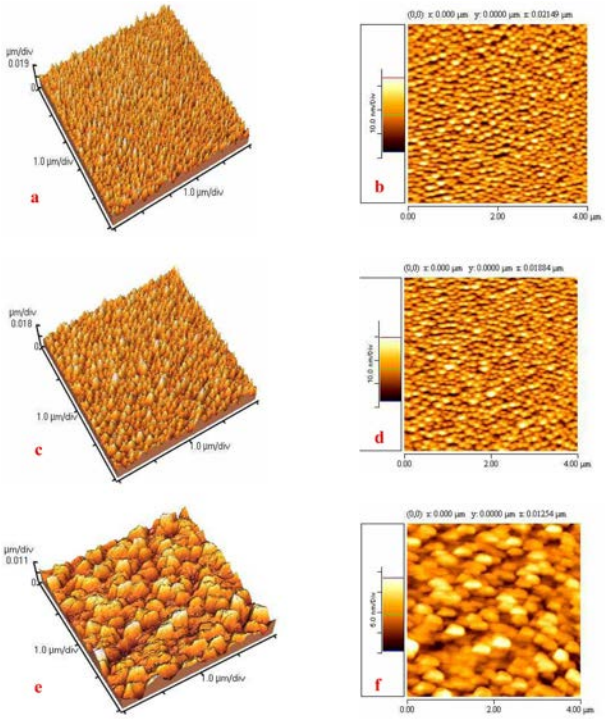

Fig. 6. AFM images of BTO thin films deposited on soda lime glass (a, b), silicon (c, d), and alumina (e, f) substrates.

adhering stresses between the thin film and substrate, the film would drop off from the substrate. In our samples, there were no dropping off of the films from the substrates as it is understood from Fig. 5, the distribution size of grains on silicon substrate is uniform and it is eligible for electrical applications but on the Alumina substrates, some grains were agglomerated and it is due to the fact that Alumina substrate has a porosity and surface roughness and the layers have cracks.

Fig. 6 shows three-dimensional and two-dimensional AFM images of the surface morphology of BTO thin films deposited on the different substrates. Distance scales in x, y and z directions are marked on the 3D images and z scale can be exaggerated as required. The surface features are very small with relationship to x and y dimensions (see Figs. 6b, d, f) however, in 3D image, they look larger (Figs. 6a, c, e) and it reflects that the surface possesses hilly (also valley) regions and it is not absolutely dense and compact surface. The

grains in BTO/Si thin film are much more uniform with an average size of 60-70 nm, while the grains in the BTO/alumina thin film are much smaller with an average size of 30-40 nm and these tiny grains tend to congregate, as indicated. As it is evident, BTO/alumina thin films contain cracks on the surface which is consistent with the previous results. Fig. 6 (a-d) show smooth surface morphologies and all of the crystallites are strongly oriented in the plane perpendicular to the surface substrate, for both soda lime glass and silicon substrates. Overall, the surface morphology and roughness of the BTO thin films on soda lime glass substrates are similar to those that are on the silicon substrates. Topography represents smooth surfaces with root-mean-square (RMS) roughness 4 nm for all thin films, it shows that the surface morphology is different for thin films deposited on alumina in comparison with other two substrates but roughness is similar.

Conclusions

In the present work, a modified sol-gel route was applied to prepare $BaTiO_3$ nanocrystalline thin films. The obtained results showed that the type of precursors and the ratio of precursors had a great effect on the stability of Barium Titanate sol. Nanostructured BTO thin films formed by dip-coating method and SEM and AFM results revealed that dense and uniform BTO thin films could be prepared on the soda lime glass, silicon and alumina substrates. The substrates can influence the morphology of BTO thin films. For $BaTiO_3$ thin film deposited on the alumina, there were some surface cracks in the films .This was caused by the difference between the thermal expansion coefficients of BTO thin film and alumina substrate.

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