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REVIEW

Highly-transparent Perovskite Thin Films Obtained by a Wet Chemical Processing Method

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ABSTRACT

Barium titanate thin films are widely used for making the multilayer capacitors. High transmittance barium titanate thin films are rarely reported in the literature. This work reports a new sol-gel routine for obtaining high transmittance $BaTiO_3$ (BTO) thin films, then the optical responses of the products are evaluated. Experimental results show that the topography and morphology of BTO coating are improved using our established method and thus the better optical responses have BTO obtained. It is seen that the optical losses of BTO thin coating are lower in contrast to similar works. Results also indicate that increment of the calcination temperature reduces the thin films transparency and thickness. Other results show that an increase in the withdrawal rate of the substrate from the sol results in an increase in the BTO coating thickness and a decrease in transparency of the BTO coating. The prepared highly transparent nanothin films are amorphous due to the maximum temperature experienced and are as thin as 30 nm. We think that obtained BTO thin coatings are desired for optical and electro-optical applications.

1. Introduction

Barium titanate ($BaTiO_3$; BTO) exhibits high dielectric and ferroelectric responses. It was used for making multilayer ceramic capacitors and for electro-optic applications[1,2]. Thin films made by BTO recently have found some applications in industry[3,4]. Due to outstanding properties and capabilities of BTO recently there have been many attempts to prepare various shapes and products of BTO[5-8]. In optics, To meet the miniaturization, high transmittance nanothin films are required. In the literature, diffent approaches including electrodeposition[9], sputtering[10], plasma-enhanced PVD[11], hydro and solvothermal[12,13] and sol-gel processing methods[14-19] were utilized to obtain BTO coatings. Dip-coating approach and sol-gel processing method are desirable options for obtaining BTO thin uniform coating[20- 22].

High transparency quality is one of the most importance requirements in many optical applications. In this way, preparing high transmittance films can lead to improvement in the optical devices based on BTO. In this research, BTO thin coatings are applied on the soda-lime glass substrate using dip-coating approach. Optical responses of the BTO thin coating and effect of preparing parameters on BTO thin coating transparency are characterized. Results indicate the outstanding transparency as a key property of prepared BTO thin coatings.

2. Materials and Methods

The precursors used in this research for obtaining the BTO

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colloidal sol are mentioned elsewhere[7]. The BTO colloidal sol was prepared using acetic acid, barium acetate, TTIP, 2 propanol and deionized water with 6:1:1:1:150 molar ratios (Figure 1). BTO thin coatings were obtained by dipping the glass substrate in the BTO colloidal sol. The coated glass were then dried at 100 °C and afterward were calcined at 500 °C. The prepared BTO thin coating are characterized by optical spectroscopy, fourier transform infrared (FT-IR) spectroscopy. The structural characterizations were carried out by TGA, XRD, DEKTAK,SEM, TEM and AFM.

Figure 1. Sol preparatiom method and coating stages

3. Results and Discussion

In this research, BTO thin coatings were synthesized at low temperature in a relatively short period of time through a newly developed sol-gel processing method. For this purpose, the hydrolysis conditions were modified according to the procedure that is shown in Figure 1. In contrast to many previous researches[1,20,23-26], we used a two-step, hydrolysis at low temperature, least possible amounts of acetic acid and 2-propanol. In these conditions, much deionized water was added to the precusor mixture. Unlike other reports, acetyl acetone was not used as the modifier in the precursors[20,26]. These conditions have great effects on lowering the synthesis temperature and time. On the other hand, the cost of preparation is significantly reduced in contrast to the literature[1,27]. Meanwhile the sol is prepared quickly in 90 minutes. Other researchers spent very long time on sol preparation (e.g. more than 8 h)[1,2]. Hence, the process developed here is cost-effective and therefore can be serving, as is a good candidate for mass production. The prepared sol has enough stability and is stable for at least three months. Figure 2 shows the sol appearance with the time of the as-prepared colloidal sol during its lifetime and clearly shows sol to gel transformation.

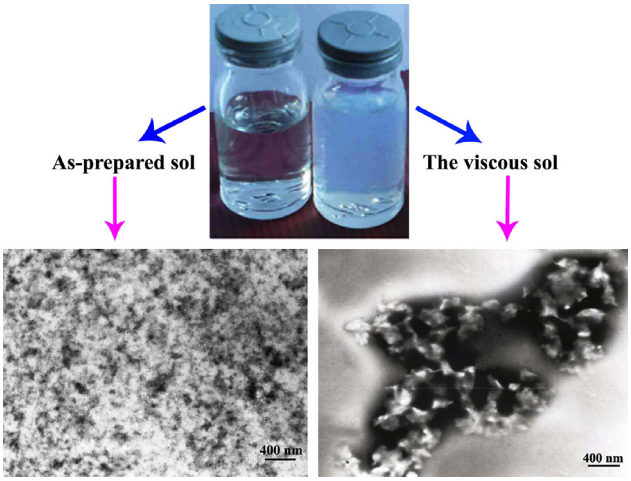

Figure 2. The change in the sol appearence with time

FT-IR spectrum of the sol is presented in Figure 3. The peak at 3467 cm^{-1} is attributed water in the sol. Reflection at 3176 cm^{-1} is assigned to C-H functional group. The reflection at wavenumber of 1640 cm^{-1} is related to BTO[28]. The doublet bands at 1560 cm^{-1} and 1410 cm^{-1} are assigned to carboxylate functional groups induced by acetic acid[20]. The reflection at 1040 cm^{-1} is attributed to alcoholic C-O functional groups, and the reflections at 950, 840, 770, 670, 550 and 480 cm^{-1} are due to M-O bonds[20,29]. The broadening of the FT-IR reflection at wavenumber range of 770-840 cm^{-1} is assigned to complexes of Ba and Ti. The functional groups at 550 and 670 cm^{-1} are attributed to Ti-O band. The peak at 480 cm^{-1} is assigned to Ti-O-Ti band[30,31].

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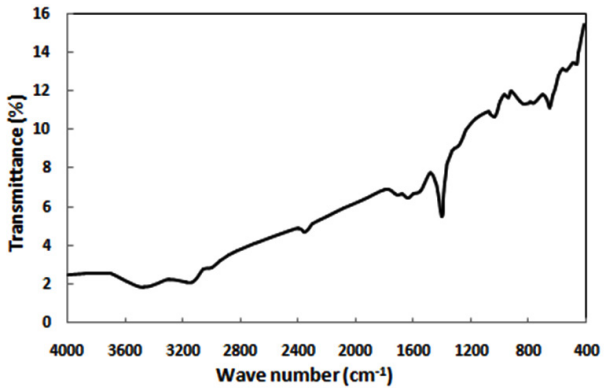

Figure 3. FT-IR spectrum of prepared $BaTiO_3$ sol

Thermogravimetric (TGA) analysis of the colloidal sol after its drying is presented in Figure 4. This figure indicates that the dried gel experinces 40 pct weight loss totally. The successive steps of weight loss include a weight loss step at themperature range of 50-240 °C mainly attributed to evaporation of volatile materials, a weight loss at the temperature range of 240-570 °C is due to the pyrolysis of the Ba-Ti complexes and the final weight loss step at the temperature range of 570-770 °C is mainly due to BTO formation from the reaction of barium carbonate and TiO_2. X-ray diffractometry results of the BTO coating after 1 hour firing at 500 °C is presented in Figure 5 indicating the amorphous nature of obtained BTO thin coating.

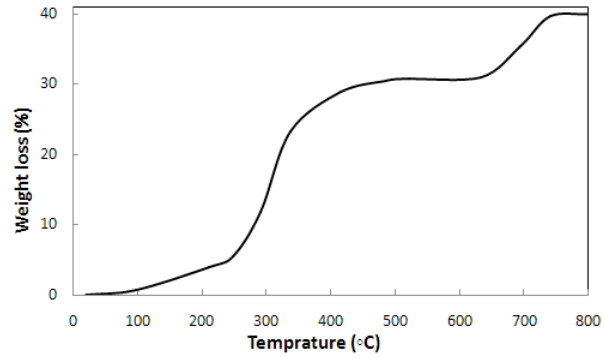

Figure 4. TGA curve for dried gel

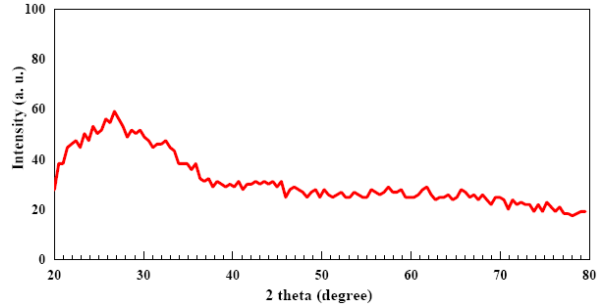

Figure 5. XRD spectra of prapared thin film calcined at 500 °C for 1h

The optical properties of the uncoated substrate and the coated one are shown in Figure 6 indicating the better optical response of the obtained thin BTO coating in contrast to the literature[4,19,32]. It is seen that the deposited BTO thin coating presents the high transmittance quality in the wavelengths of 400 to 1200 nm. With a mean transmission of 86.5 pct in the mentioned range which is much more than the similar works[4,19,32] with a mean transmittance of 70-75 pct. As shown in Figure 7a the incident light to the BTO coating is divided to three portions including absorbtion, reflection and transmittance[33,34]. This figure clearly shows the high transparency of the deposited coating. Following the method published in the literature[4,19,32] and optical response of the film the bandgap of the film was calculated to be 3.9 eV (see Figure 7b).

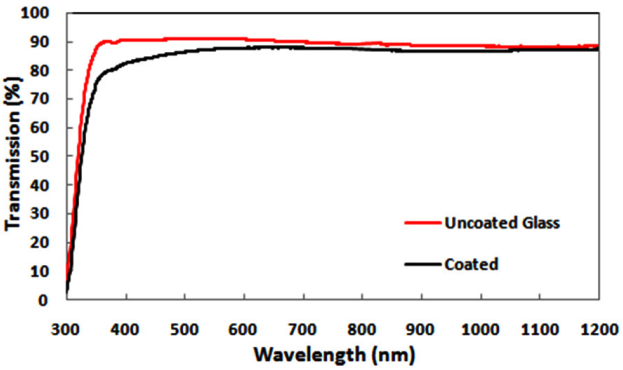

Figure 6. UV-Vis-NIR transmission spectra of sol-gel derived $BaTiO_3$ nanothin film and glass substrate

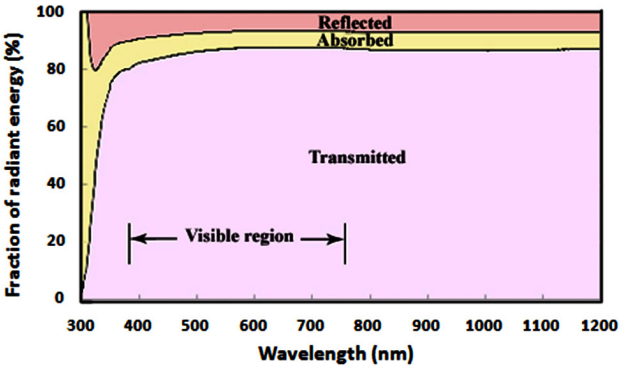

Figure 7a. The variation in fraction of incident light transmitted, absorbed, and reflected through $BaTiO_3$ nanothin film with wavelength

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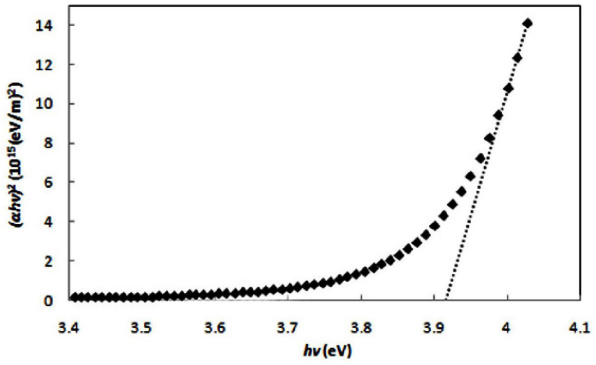

Figure 7b. The variation of $(ahv)^2$ versus photon energy hv for $BaTiO_3$ nanothin film

Figure 8a presents atomic force microscopy micrograph of the thin BTO coating. It is seen from this micrograph that the surface of the coating has a dense amorphous texture without presenting the crack and voids. On the other hand, RMS roughness of the thin BTO coating is about 0.743 nm which approves the smoothness of the coating. The smoothness of the thin BTO coating can result in a decrease in the optical losses and thus high transparncy quality in the BTO thin coatings in contrast to the crystalline and thick films[4,19,32]. Figure 8b shows SEM micrograph of a coated sample. It is seen that no grain has been formed on the surface of the film indicating the amorphous nature of the BTO film.

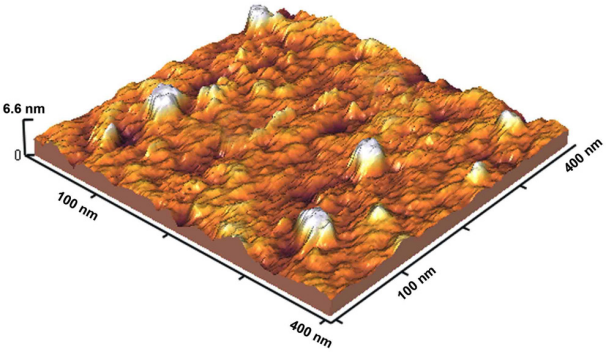

Figure 8a. 3D view AFM image

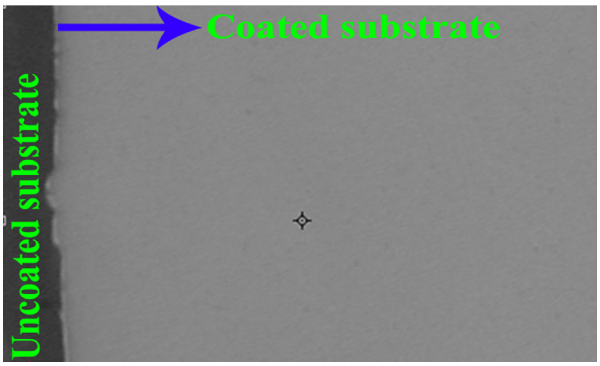

Figure 8b. SEM micrograph of $BaTiO_3$ nanothin film

In Figure 9 and Figure 10, effect of calcination temperature on transmission spectrum and film thickness was characterized. Results show that the transparency and film thickness decreases with increment of calcination temperature. The thin film transparency is affected by its density. Increment in calcinations temperature cause decomposition of organic compounds and release of volatile compounds and consequently increase in thin film density. This fact decreases the film thickness and transparency.

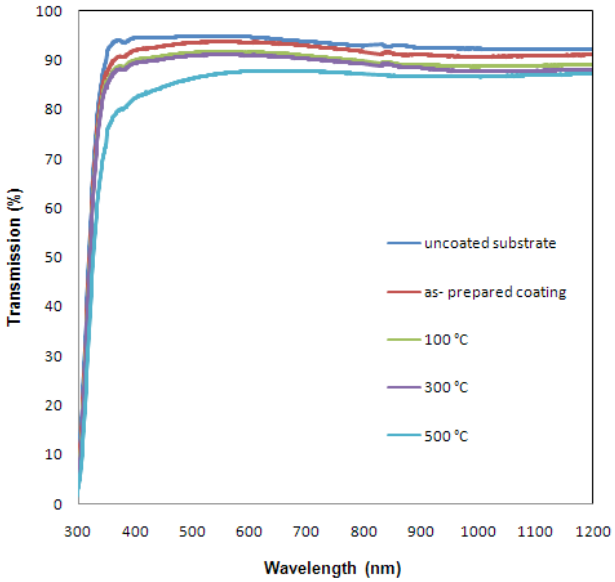

Figure 9. Effect of calcination temperature on thin film transparency

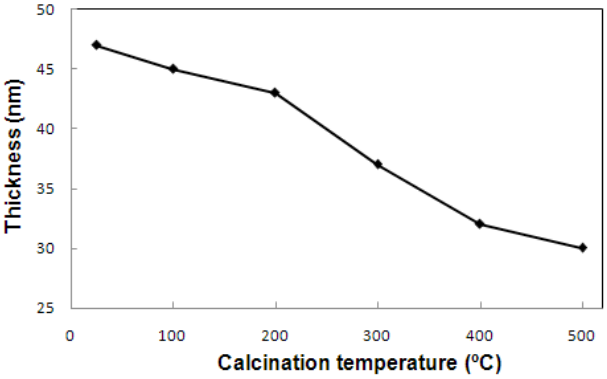

Figure 10. Effect of calcination temperature on thin film thickness

In the dip-coating technique the thin films are formed after dipping and withdrawal the substrate in sol and after drying and firing the thin films is prepared. In Figure 11 and Figure 12, effect of withdrawal rate on transmission spectrum and film thickness has been evaluated. Results show that thin film thickness increases and the transparency decreases with increment of withdrawal rate. At lower withdrawal rate, draining of the sol, leads to a decrease

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in the film thickness. This fact leads to an increase in thin film transparency as well.

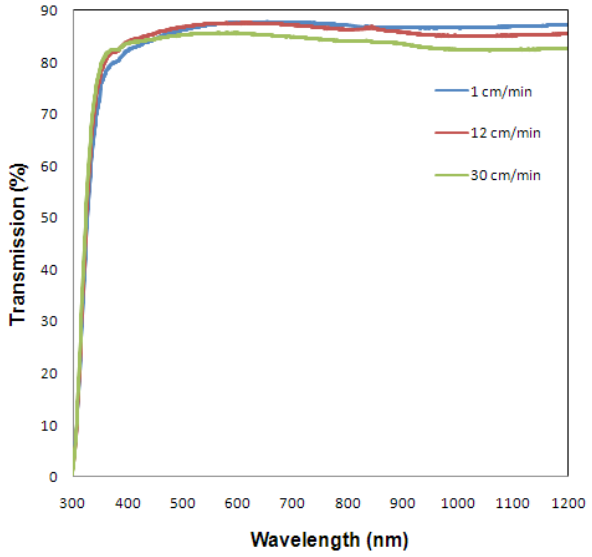

Figure 11. Effect of withdrawal rate on thin film transparency

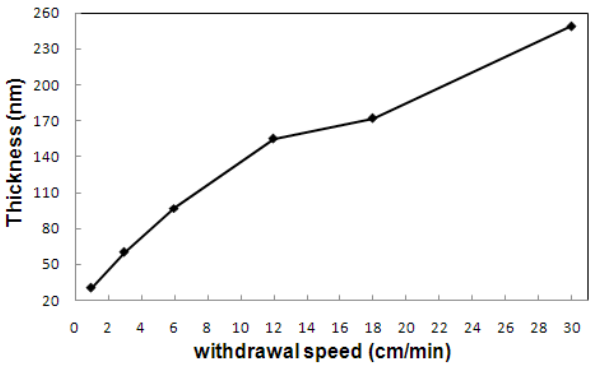

Figure 12. Effect of withdrawal rate on thin film thickness

4. Conclusion

This work reports a sol-gel routine to obtain high transmittance BTO thin coatings. The prepared BTO thin coating exhibits less optical losses in contrast to the polycrystalline BTO coating explored in the literature. AFM results indicate the nanoscale smoothness of the coating leading to high transparency quality of the deposited BTO thin coating. Results also indicate that increment of the calcination temperature and withdrawal rate reduces the thin films transparency. Finally, the results advocate the outstanding transparency as a key property of the prepared BTO thin coating.

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