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Synthesis of $BaTiO_3$ Thin Film by PED Method

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Abstract: $BaTiO_3$ thin films were successfully synthesized by Pulsed Electron Deposition method from target prepared by ceramic method. The structure and morphology of the as-prepared powder as well as thin film were investigated. The results indicated that the prepared films have fine surface, which can be used to investigate the heterostructures between film layers. The technique conditions were tested many times to find out the optimal synthesis procedure. This technique is a hopeful way to produce fine surface films.

Keywords: Barium Titanate; thin films, ceramic; pulse laser deposition.

1. Introduction

Perovskite materials have attracted much attention for several decades because they exhibited interesting properties and potential applications in many science and technology fields. Research on perovskite materials was focused mostly on studying electrical and magnetic properties of bulk material such as: giant magnetoresistance, superconducting properties at high-temperature, spin valve effect... in order to fabricate various devices: thermistors, capacitors, memory, and sensors, etc [1-3]. $BaTiO_3$ (BTO), which belongs to a ferroelectric perovskite family of structure ABO_3, is one of the most well studied perovskie materials due to its high-dielectric constant and large piezoelectric coefficient [4, 5]. Bulk material of BTO has been very famous for various applications such as piezoelectric detectors, thin film capacitors, and magnetoelectric devices. Recently, the discovery of 2D gas effect at the interface of layers of perovskite materials has renewed the interest in perovskite thin films [6-8] and hence raise a demand on preparation of perovskite thin films of fine surface at low cost. In this regard, pulse electron deposition is a good choice with many advantages.

In this report, we present the some of our first results on preparation of $BaTiO_3$ thin films on PED system which has been set up on Faculty of Physics recently. By optimizing the synthesizing process, we were able to get $BaTiO_3$ thin film of high quality and fine surface, which could be used to fabricate layers to study 2D electron gas effect on hetero interface of perovskies.

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2. Experiment

$BaTiO_3$ perovskite target was produced by conventional ceramic method. Equi-molar amount of $BaCO_3$ (99%) and TiO_2 (99%) were grinded together thoroughly for 4 hours. After grinning process, suitable amount of polyvinyl alcohol solution was added to the powder mixture and mixed together for one more hour. Then the mixture was pressed into pellet by using 15 tons molding machine. The pellet was preliminary calcined at 850 °C for 8h. The soft agglomeration was broken, grinded, and pressed again into pellet of 1 inch in diameter and 0.5 mm in thickness. The second annealing process was conducted at 1100 °C in 6h. All the experiments were done in air. The as prepared material was used as a target to fabricate thin films of $BaTiO_3$ by PED method. There are several parameters that could affect the quality of $BaTiO_3$ thin films but we focus only on studying the effect of voltage and substrate temperature, which are the most important parameters in the deposition of $BaTiO_3$ thin films by PED methods.

Table 1. Sample information

Sample	Voltage (keV)	Substrate temperature (°C)	Substrate
M1-1	15	100	Glass
M1-2	15	200	Glass
M1-3	15	300	Glass
M1-4	15	400	Glass
M1-5	15	500	Glass
M2-1	12	100	Si
M2-2	12	200	Si

Other technical parameters were kept constant as follow: frequency f = 10Hz, pulse numbers 20 000, pressure $p = 5.7 \times 10^{-3}$ Torr. A scanning electron microscope (JEOL- J8M5410 LV) and an atomic force microscopy (XE-100 AFM Park systems-Korea) were used for the characterization of morphology analysis, phase analysis was performed on X-ray diffractometer, Bruker-AXSD5005.

3. Results and discussion

After preliminary calcination process, XRD pattern showed that the precursor had not been converted into $BaTiO_3$. $BaTiO_3$ was crystalined only after the second annealing process. Figure 1 shows the X-ray diffraction pattern of the $BaTiO_3$ target fabricated by ceramic method with annealing time of 6h and annealing temperature of 1100°C. All of the diffraction peaks matched well with the standard pattern of $BaTiO_3$ of tetragonal structure from database. Peaks appear at 22.15; 31.54; 38.92; 44.89; 45.37; 50.68; 50.98; 56.29; 65.77, 66.32 corresponding to reflection from (100); (110); (111); (002); (200); (102); (210); (211); (202); (220) lattice planes of $BaTiO_3$ as shown in the pattern. Lattice constants of $BaTiO_3$ materials were estimated: a= b = 3.99 Å, c = 4.02 Å. These numbers are in good agreement with the reported values for bulk material of $BaTiO_3$ a = b = 3.99 Å, c = 4.03 Å [1].

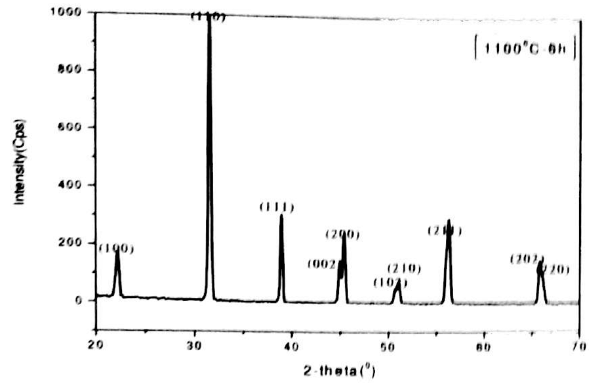

Fig. 1. XRD pattern of $BaTiO_3$ target used for fabrication of thin film by PED method.

SEM image of the target showed that particle size was quite large and uniform. EDS spectra showed that target contains of only Ba, Ti, O, element without any impurities. These results implied that the target was pure of phase and fulfilled the qualifications to fabricate thin film by PED method.

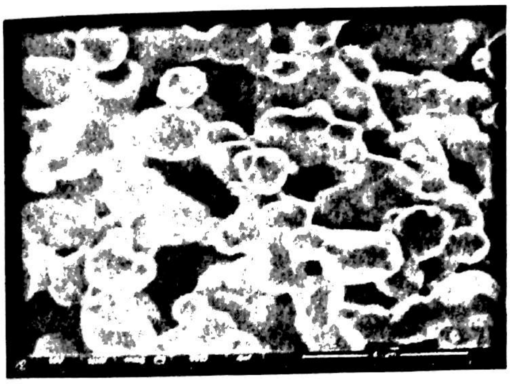

Fig. 2. SEM image of $BaTiO_3$ target.

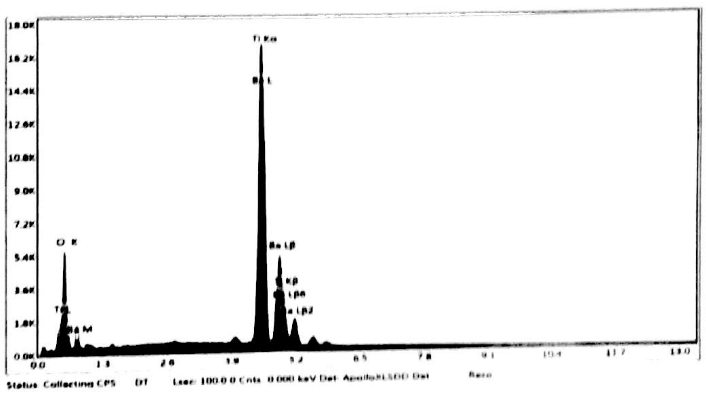

Fig. 3. EDS spectra of $BaTiO_3$ target.

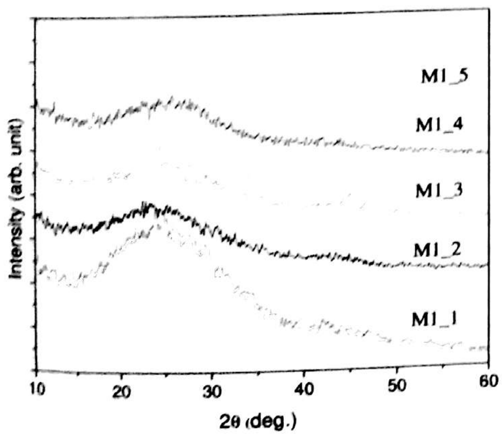

Fig. 4. XRD patterns of thin films prepared on glass substrate with substrate temperature from 100^0C to 500^0C.

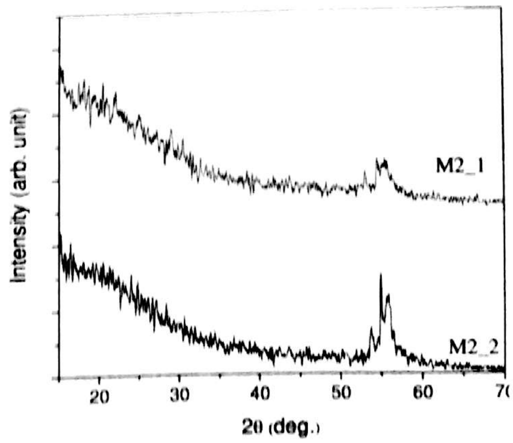

Fig. 5. XRD patterns of thin films prepared on Silicon substrate with substrate temperature of 100^0C and 200^0C

Figure 4 shows XRD patterns of samples M1_1 to M1_5. All of the patterns show a broad band which is characteristic of amorphous materials. XRD patterns of films prepared at 300^{0}C show some peaks but these peaks do not belongs to $BaTiO_3$. These samples were subsequently post-annealed at 500°C to check if the crystalinity could be improved. The results showed that annealing at this temperature did not make any notable change in the crystalline nature of the films prepared on glass substrates (data not shown).

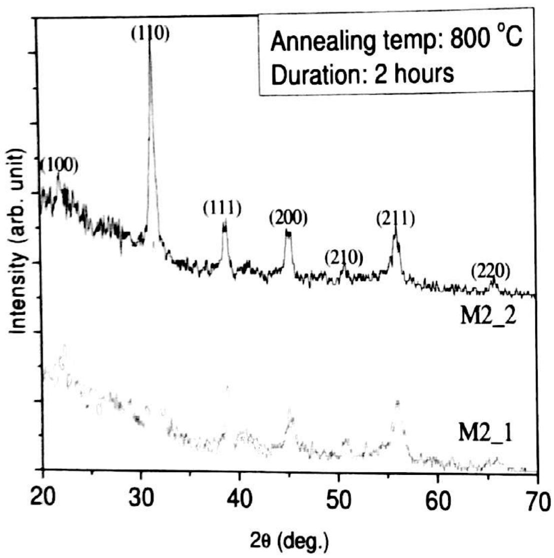

Fig. 6. XRD patterns of $BaTiO_3$ thin films annealed at 800^{0}C for 2h.

Cover glass is used as substrate at first because it is cheap and quite easy to process. However, the major disadvantage of glass is its amorphous nature, which can have some effect on the crystalinity of the film grown on top. A much better choice is silicon substrate, which has crystalline structure and can help to grow expitaxy thin film better. Furthermore, low melting point of glass (~600 °C) limit us to do the post annealing at higher temperature, which is expected to be able to improve the crystalinity of the as produced films. Another important point is that the very first thin films were prepared at voltage of 15 kV. Such high voltage may create beam of atoms of kinetic energy higher than necessary, which resulted in thin films of amorphous phases as observed. Hence, we reduced the voltage to 12 kV for the following process.

Figure 5 shows the Xray diffraction patterns of the as produced $BaTiO_3$ thin films. Some peaks of low intensity was observed at 2 theta angle of around 56$^\bullet$. These peaks have higher intensity for sample prepared at 200 °C. These peaks belongs to $BaTiO_3$ phase as compared with standard pattern. Figure 6 shows the X-ray diffraction pattern of $BaTiO_3$ thin films post-annealed at 800^{0}C for 2h. After post annealing process, strong reflection peaks in the XRD pattern of the sample, which match very well with the standard pattern of BaTiO3, imply that the crystalline quality of the films were much improved. Films prepared with substrate temperature of 200 °C show slightly higher intensity in the XRD pattern; this result suggested that substrate temperature is also a parameter could be used to control the quality of the product thin films.

SEM and AFM images of $BaTiO_3$ thin films prepared at 200^0C are shown in figure 7 and 8, respectively. Both SEM and AFM images show that the film has fine surface and small roughness which is very important to make hetero interface between layers of perovskies. Thickness of sample M2_1 and M2_2 were 106 and 98 nm as determined by anpha step measurement.

Fig. 7. SEM images of $BaTiO_3$ thin films at 200^0C

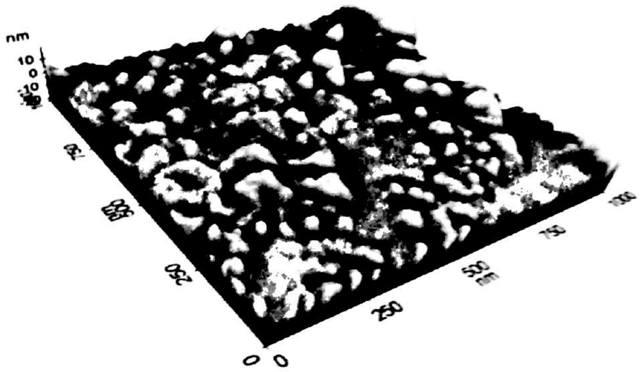

Fig. 8. AFM imagines of $BaTiO_3$ thin film at 200^0C

4. Conclusion

We successfully prepared $BaTiO_3$ thin film by PED method. The results show that voltage of electron beam, substrate type and substrate temperature are important parameters, which can affect the morphology and quality of the films. Voltage and substrate type had more clear effect on the crystalinity of the films than substrate temperature. Post annealing the films prepared on Silicon substrate further improves the crystalinity of the films. The films has fine surface with small roughness when prepared at frequency f = 10Hz, pulse numbers 20 000, pressure p = 5.7×10^{-2} Torr, voltage 12 kV, substrate temperature 200 °C . These first results of preparation $BaTiO_3$ thin film by PED method imply that this method is hopeful to prepare hetero interface of layers of perovskie. Further optimization of electron beam voltage and substrate temperature will be conducted in the near future to enhance the crystalline of $BaTiO_3$ thin films prepared by PED method and pave the way to investigate the heterostructure between layers of perovskies.

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References

[1] S.F. Wang, G.O. Dayton, Dielectric Properties of Fine-grained Barium Titanate Based X7R Materials, Journal of the American Ceramic Society, 82, (1999) 2677.

[2] C. Pithan, D. Hennings, R. Waser, Progress in the Synthesis of Nanocrystalline $BaTiO_3$ Powders for MLCC, International Journal of Applied Ceramic Technology, 2 (2005) 1.

[3] P. Kumar, S. Singh, J.K. Juneja, C. Prakash, K.K. Raina, Influence of Calcium on Structural and Electric Properties of Substituted Barium Titanate, Ceramics International, 37 (2011) 1697.

[4] Z.C. Li, B. Bergman, Electrical Properties and Ageing Characteristics of $BaTiO_3$ Ceramics Doped by Sing Dopants, Journal of the European Ceramic Society, 25 (2005) 441.

[5] V. Mitić, V. Paunović, D. Mančić, Lj. Kocić, Lj. Živković, V.B. Pavlović: Dielectric Properties of $BaTiO_3$ Doped with Er_2O_3, Yb_2O_3 based on Intergranular Contacts Model, Advances in Electroceramic Materials: Ceram Transactions, 204 (2009) 137.

[6] Ohtomo, A. Hwang, A high-mobility electron gas at the $LaAlO_3/SrTiO_3$ heterointerface. Nature 427 (2004), 378

[7] S.Thiel, G. Hammerl, A. Schmehl, A. Schneider, C. W. Mannhart, Tunable quasi-two-dimensional electron gas in oxide heterostructures. Science 313 (2006) 1942.

[8] J. Mannhart, D. G. Schlom, Oxide interfaces-an opportunity for electronics. Science 327, (2010) 1607.