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Influence of layer number and sintering on ferroelectric behaviour of barium titanate films prepared with sol-gel method

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Abstract. We have studied ferroelectric behaviour of barium titanate (BaTiO$_3$) thin films prepared with sol-gel method. BaTiO$_3$ solutions were deposited onto silicon substrates with different numbers of layers via spin coating method. The obtained samples were sintered at 700 °C and 800 °C. Structure and ferroelectric properties of the samples were investigated using X-ray diffraction (XRD) and Sawyer–Tower circuit. As observed from XRD patterns, number of layers affected the films structure. Results also showed that crystallographic system of BaTiO$_3$ thin films was characterized by a tetragonal structure. Maximum polarization increased with an increase in layer number. Spontaneous polarization was also observed increasing with an increase in temperature.

1. Introduction

Barium titanate (BaTiO$_3$), which has a tetragonal structure at room temperature, is considered a good perovskite ferroelectric material. This material has found application as a multilayer ceramic capacitor and as a component of ferroelectric memory devices. The wide usage of BaTiO$_3$ is attributed to its high dielectric constant, ferroelectric characteristics, and piezoelectric properties, in which cations and anions are displaced in opposite directions of the polar axis [1 - 4].

Ferroelectric films have been fabricated through various deposition techniques, such as the hydrothermal method[5], molecular beam epitaxy, chemical vapor deposition[6], electrophoretic deposition[7], laser chemical vapor deposition[8, 9], and sol-gel processing[10, 11]. Among these techniques, sol-gel processing has attracted considerable interest due to its low cost and ease of integration with semiconductor silicon (Si) technology [12]. Through this method, BaTiO$_3$ films can be integrated with ferromagnetic films, thereby enabling the electrical or magnetic tuning of these microwave materials [13 - 15]. The main advantages of sol-gel processing are that it presents good homogeneity, ability for chemical composition control, reducing sintering temperature for crystallization, and good control over the formation of nano-sized particles [12 - 16]. Using sol-gel method and sintering temperature 700-800 °C, BaTiO3 become crystalline with crystallite in the nano-sized range (<100 nm). Sintering time and temperature determine crystallinity, crystallite size, and compactness of BaTiO$_3$ films. It is therefore important to consider various time and temperature of sintering process [2].
Studies on single or multilayer thin film have made significant progress than on the bulk BaTiO$_3$. Single or multilayer BaTiO$_3$ thin films have different properties than bulk materials. Noticeable differences are Pockels effect or linear electro-optic and dielectric properties in BaTiO$_3$ thin films compared to BaTiO$_3$ bulk crystals [5, 6]. By investigating single or multilayer thin film deposition method and its properties, it is possible to synthesize thin films with certain properties.

In this study, sol-gel method was used to prepare BaTiO$_3$ multilayer thin films. Effects of layer number, annealing temperature, and annealing time on structural, morphological, and ferroelectric behaviors of the thin films were investigated.

2. Experimental procedures

Barium acetate and titanium (IV) isopropoxide [Ti((CH$_3$)$_2$CHO)$_4$] were used as precursors for fabrication of BaTiO$_3$ thin films. Glacial acetic acid, 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH), and ethylene glycol were used as solvents. First, barium acetate was dissolved in acetic acid. The solution was continuously stirred at 70 °C for 60 min to obtain a clear and homogeneous solution and then was diluted with CH$_3$OCH$_2$CH$_2$OH. An equimolar amount of Ti((CH$_3$)$_2$CHO)$_4$ was added to the solution at a molar ratio of Ba:Ti = 1:1 under continuous stirring. The solution was continuously stirred at 90 °C for 2 h and was filtered using microfiber glass filter paper.

The obtained precursor solution was transparent and bright yellow. After the precursor solution was aged for 24 h, it was deposited onto a silicon (Si) substrate by spin coating at 3000 rpm for 30 s. Following the deposition, the films were pyrolyzed for 10 min at 200 °C in air. These steps were repeated several times (1, 5, 7) with reference to film thickness. Finally, the films were sintered in an air atmosphere furnace to crystallized and compacted at 700 °C and 800 °C for 3 h.

To investigate structural properties of the films, X-ray diffraction (XRD) was carried out using a Bruker D8 ADVANCE diffractometer with Cu-K$_\alpha$ radiation at $\lambda = 1.547$ Å. From the XRD patterns, crystallite size could be determined using HighScore Plus software. Morphology of the films surfaces was also investigated using scanning electron microscopy (SEM) FEI Inspect F50. Hysteresis loops, which are indicators of ferroelectric properties, were measured using a Sawyer–Tower circuit standard model.

3. Results and discussion

3.1. Crystal structure and crystallite size

Figure 1 shows XRD patterns of BaTiO$_3$ films with various layer numbers (1, 5, and 7 layers). We did not present XRD patterns from the films with 3 layers because the data could not be read. XRD patterns with 1, 5, and 7 layers show quite similar. Multilayer BaTiO$_3$ have different properties to bulk BaTiO$_3$ [3, 6]. All films were heat-treated at 800 °C in air for 3 h. Peaks of XRD patterns were successfully indexed with tetragonal structure of BaTiO$_3$ for all samples. No other phases were observed in the XRD patterns. We observed that with increasing layer number, intensity of major diffraction peaks increases indicating that crystallization of BaTiO$_3$ nanostructure improves at high layer numbers. The most intense peak (110) was found at $2\theta = 31.57^\circ$. Peaks at $2\theta = 22.17^\circ$, $2\theta = 38.89^\circ$, $2\theta = 45.44^\circ$, $2\theta = 51.03^\circ$, and $2\theta = 56.17^\circ$ were (101), (021), (202), (113), and (122), respectively. We observed that XRD peaks corresponding to the (021) and (122) planes split into two peaks due to formation of a tetragonal structure, which is important for ferroelectricity.

Average crystallite sizes of BaTiO$_3$ samples, which were calculated using HighScore Plus, were 47, 33, and 23 nm at layer number 1, 5, and 7, respectively. It is shown that crystallite size of all samples are in the range of nano-sized (less than 100 nm).

Figure 2 shows XRD patterns of BaTiO$_3$ samples sintered at 700 °C and 800 °C for 3 h. We found XRD patterns of the film sintered at 700 °C still shows small peaks corresponding to barium carbonate–titanium dioxide. But, a well-controlled composition, single-phase perovskite structure was formed in the film sintered at 800 °C. Figure 3 shows XRD patterns of the BaTiO$_3$ samples sintered at 800 °C for 3 and 4 h. We suggest that intensity of major diffraction peaks increased with increasing
sintering time. It may indicate that a long sintering time improves crystallization of BaTiO$_3$ nanostructure. From figures 1, 2 and 3, full width at half maximum (FWHM) changes with number of layers, annealed temperature and annealed time. Broadening occurs due to smaller crystallite size in the range of nano scale (<100 nm).

![Figure 1. XRD patterns of BaTiO$_3$ films at various layer numbers.](image1)

![Figure 2. XRD patterns of 5 layers BaTiO$_3$ films sintered at 700 °C and 800 °C.](image2)

![Figure 3. XRD patterns of 5 layers BaTiO$_3$ films sintered at 800°C for 3 and 4 h.](image3)

3.2. Morphology

SEM images for a single phase BaTiO$_3$ with five layers sintered at 800 °C at various sintering times are shown in figure 4. Figure 4a shows that BaTiO$_3$ thin film deposited on Si (100) substrate and sintered at 800°C for 3 h exhibits cracks. BaTiO$_3$ thin film sintered at 800 °C for 4 h exhibits a crack-free and uniform morphology (figure 4b). BaTiO$_3$ thin film sintered at 700 °C is not presented because it is not a single phase. The films sintered for 3 and 4 h have average grain sizes of 33 and 48 nm, respectively. We suggest a significant increase in grain size occurs with rising sintering time, as shown in the SEM cross-section images in figure 4c. Average thickness of BaTiO$_3$ with five layers is 2.9 μm.
3.3. Polarization-electric (P-E) hysteresis loops

Figure 5 shows curves of room-temperature $P$–$E$ loops of BaTiO$_3$ films with various layer numbers. We observed that value of maximum polarization increases increasing layer number. However, the area spanned by a loop decreases. This behavior may be due to the particle size of the samples [17-18]. A previous study reported that spontaneous polarization ($P_s$) and coercive field ($E_c$) in a BaTiO$_3$ single crystal are $P_s = 26$ C/cm$^2$ and $E_c = 1.5$ kV/cm [3]. The low $P_s$ and high $E_c$ values of the films in the current work might be due to small grain size of the films and clamping of the films to the substrates [17]. Room-temperature $P$–$E$ loops of BaTiO$_3$ films sintered at 700 °C and 800 °C are presented in figure 6. We found that these films exhibit almost similar $P_s$ and $E_c$ values because both films have almost similar particle size. Figure 7 shows room-temperature $P$–$E$ loops of BaTiO$_3$ films sintered at 800 °C for 3 and 4 h. We observed that remanent polarization increases when sintering time increases, whereas $E_c$ decreased. Decrease in $E_c$ might be caused by an increase in particle size as sintering time increases [18]. Homogeneity increases with sintering time and this may lead to soften the materials and then decreases $E_c$. In other word, crystallinity degree increases or FWHM decreases. The highest polarization value of 3.32 $\mu$C/cm$^2$ was generated when BaTiO$_3$ film have seven layers and
sintered at 800ºC for 3 h. The curve-hysteresis loops are well-identified as corresponding to ferroelectric behavior.

![Figure 5](image1.png) ![Figure 6](image2.png) ![Figure 7](image3.png)

**Figure 5.** Room-temperature $P-E$ loops of BaTiO$_3$ films at various layer numbers.

**Figure 6.** Room-temperature $P-E$ loops of five layers BaTiO$_3$ films sintered at 700 ºC and 800 ºC.

**Figure 7.** Room-temperature $P-E$ loops of five layers BaTiO$_3$ films sintered at 800 ºC for 3 and 4 h.

4. Conclusion

Effects of layer number, sintering temperature, and sintering time on structural, morphological, and ferroelectric properties of BaTiO$_3$ thin films were investigated. XRD patterns indicate that increasing layer number, sintering temperature, and sintering time may cause an increase in crystallization. SEM images show that increasing sintering time may also increase crystallite size. SEM images also show that sample annealed for 4 h at 800 ºC had a crack-free surface. Results of $P-E$ loop measurements shows that value of maximum polarization increases with increase of layer number. The highest polarization of 3.32 μC/cm$^2$ was achieved with BaTiO$_3$ film has seven layers and sintered at 800 ºC for 3 h.

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