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Low Temperature Fabrication of Barium Titanate Crystalline Film by Bombardment onto Growth Interface

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Barium titanate thin films were prepared on Si (100) wafers by rf sputtering method with an additional rf power supply to apply rf bias to the substrate. Using rf bias to the substrates, the crystallinity and the electronic properties of the deposited films were improved even deposited at low substrate temperature as 250 °C. The crystallization could be achieved by the surface migration assisted by the ion bombardment rather than the resputtering of non-crystalline parts of the deposits.

Key words: rf bias sputtering, barium titanate crystalline film, low temperature crystallization

1. INTRODUCTION

Many studies for obtaining crystalline films of ferroelectric perovskite oxides such as $BaTiO_3$ have been performed. Generally, the films must be heated over 500 °C during or after deposition to crystallize the films. Component atoms of films, however, are diffused between the substrate and the film when the heat treatment is performed at such a high temperature. It is known that the electronic properties of the films are degraded by the diffusion. Many researches to avoid the diffusion have carried out. For example, the materials that can suppress such diffusions have been used as electrode materials or barrier layers [1]. Also the rapid annealing technique has been applied to shorten the time of heating, which means that the diffusion time is decreased [2].

For fabrication of crystalline $BaTiO_3$ thin films, the bias sputtering system have been used in our recent studies. By applying rf bias to the substrate during deposition by rf sputtering, bombardments of Ar ions onto growth surface of films would be enhanced and the film crystallization is promoted by the ion energy as we have expected. In this paper, the effect of the substrate bias on the crystallization of was discussed with the crystallization mechanism.

2. EXPERIMENTAL

Barium titanate films were fabricated by the rf sputtering system shown in Fig. 1. This apparatus was based on conventional rf sputtering system. The substrate holder was electrically isolated from the vacuum chamber and connected to another 13.56 MHz rf power supply to apply rf bias to the substrate. The substrates could be heated up to 500 °C by an infrared radiation heater set above substrate holder. Sintered $Ba_xTi_yO_z$ (x/y = 1/1.3), which were commercially prepared (DOWA MINING Co., Ltd.), were used as sputtering target to regulate chemical composition of deposited films. P-type Si (100) wafers of 20×20 mm^2 that was degreased in an ultrasonic acetone bath were used for substrates.

Experimental conditions were listed in Table I. Ar was fed through a mass flow controller to 0.2 Pa to the deposition chamber that had been pre-evacuated to 2×10^{-4} Pa. The target surface was pre-sputtered for 30 minutes before deposition. The deposited films were cooled down to a room temperature in vacuum.

Film thickness of deposited films was determined by surface profiler (DEKTAK). Thin film crystallinity was performed by X-ray diffraction (XRD) with CuKα

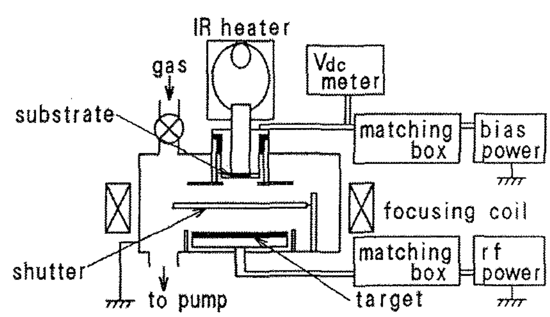


Fig. 1 Schematic drawing of experimental apparatus

Table I. Experimental conditions

Target	Sintered $BaTiO_3$ disk
Substrate	Si (100) wafer
Target-substrate distance (d)	40 mm, 60 mm
Substrate Temperature (T_s)	250 °C
Rf frequency	13.56 MHz
Rf power (P_{rf})	2.1 W/cm^2, 4.3 W/cm^2
Substrate dc bias (V_s)	0 V ~ -300 V
Sputtering gas	Ar
Sputtering gas pressure	0.2 Pa

radiation. Chemical composition of films was determined by X-ray florescence analysis (XRF) and X-ray photoelectron spectroscopy (XPS). Surface morphology of films was observed by atomic force microscope (AFM).

For electronic properties measurement, N-type (100) Si substrates, of which resistivity was 7×10^{-3} Ω cm, were used as bottom electrode. After barium titanate films of 0.5 μm thickness were deposited, platinum dots (1 mm in diameter and 0.2 μm in thickness) were deposited as top electrodes by another rf sputtering system in Ar atmosphere. Relative dielectric constant and hysteresis character of these metal-insulator-semiconductor (MIS) capacitors were measured by LCR meter and ferroelectric characterization system (RADIANT RTA6000HVS), respectively.

3. RESULTS AND DISCUSSION

The thickness of the deposited barium titanate films were uniform, which was confirmed by the surface

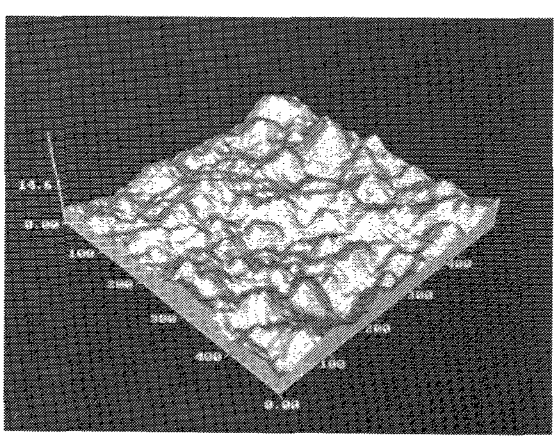
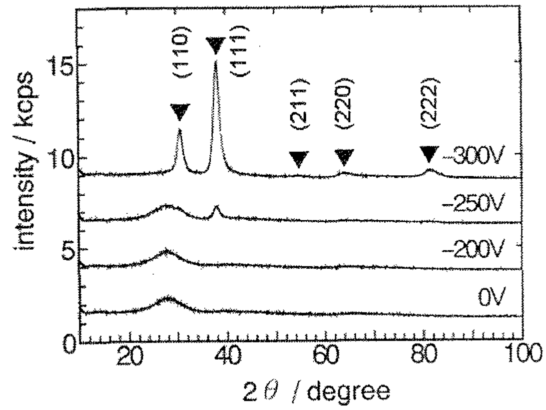
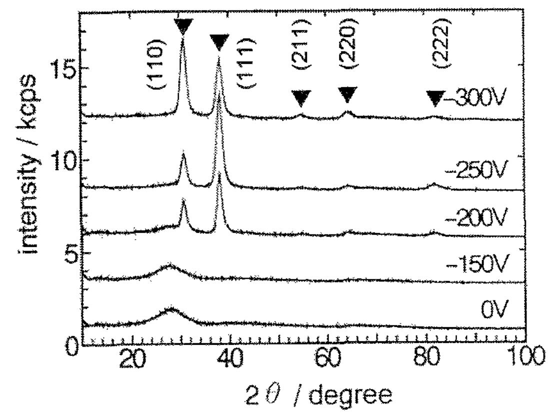


Fig. 2 The AFM image of films deposited at P_{rf} = 4.3 W/cm^2, T_s = 250 °C and V_s = -200 V.



(a) P_{rf} = 2.1 W/cm^2



(b) P_{rf} = 4.3 W/cm^2

Fig. 3 The XRD patterns of the films deposited at various substrate biases, T_s = 250 °C and (a) P_{rf} = 2.1 W/cm^2, (b) P_{rf} = 4.3 W/cm^2

profile measurements. Ba/Ti ratio of the deposited films was within the range of 0.9 - 1.1 for all films, although Ba ratio in the deposited films was enriched in case of using the stoichometric $BaTiO_3$ targets in our experimental system.

Fig. 2 shows AFM image of the film deposited at T_s = 250 °C, V_s = -300 V and P_{rf} = 4.3 W/cm^2. It shows that the deposited films were consisted of grains of several tens nm in size, and that the surface roughness was within a few nm. The grain size tended to increase according to the rf power for sputtering.

The XRD patterns of the films deposited at various conditions shown in Fig. 3. In both case of P_{rf} = 2.1 W/cm^2 (Fig. 3(a)) and 4.3 W/cm^2 (Fig. 3(b)), two peaks of (110) and (111) of $BaTiO_3$ became stronger as the substrate bias voltage was increased. Weak peaks of

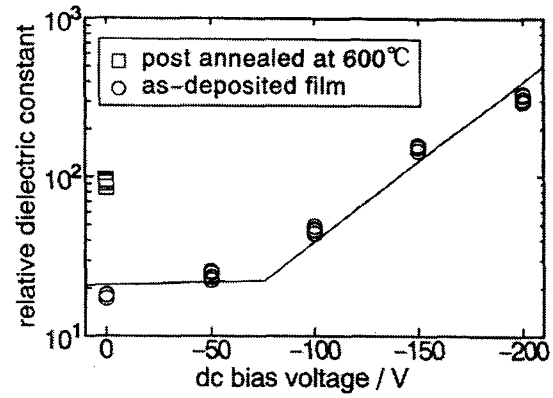


Fig 4 The relative dielectric constants of the films as the function of the substrate bias, T_s = 250 °C and P_{rf} = 4.3 W/cm^2 (circle marks) and those of the films deposited without the substrate bias and post-annealed at 600 °C (square marks).

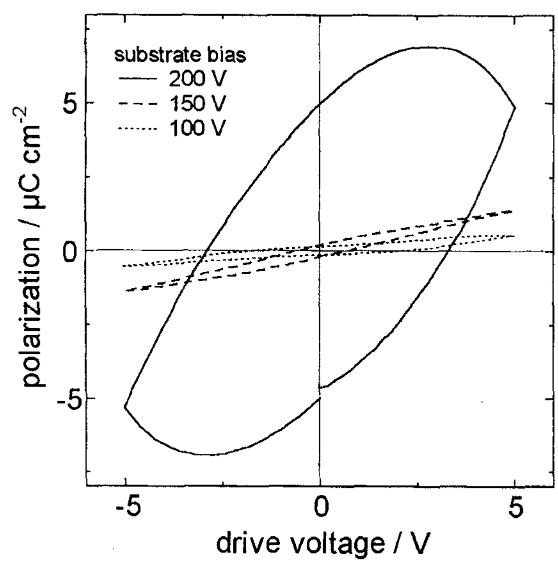


Fig. 5 The hysteresis loops of the films deposited at various substrate bias, T_s = 250 °C and P_{rf} = 4.3 W/cm^2

(220) and (222) were also seen at high substrate bias conditions. These show that substrate bias caused crystallization of films. It is discussed below that the films deposited at rf power 4.3 W/cm^2 showed the diffraction peaks over -200 V of the substrate voltage while the films at 2.1 W/cm^2 showed over -250 V.

Relative dielectric constants of the MIS capacitors as the function of the substrate bias were shown as circle marks in Fig. 4. As the substrate bias was increased, the relative dielectric constant was dramatically increased. As reference, the square marks in Fig. 4 were the

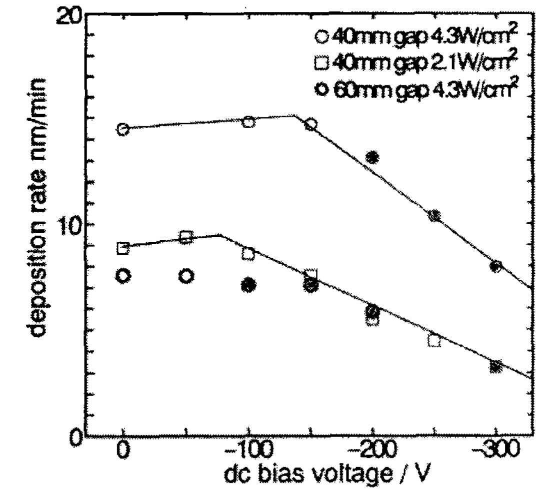


Fig.6 The effect of the substrate bias on the deposition rate. The solid marks mean the films with crystalline phase.

relative dielectric constants of the film that were deposited without the substrate bias and post-annealed at 600 °C in air, which were smaller than the case of V_s > -150 V. Hysteresis loops were shown in Fig. 5. The ferroelectric characters also improved by the substrate bias. It is clear that the substrate bias is very effective to obtain as-deposited crystalline films.

Fig. 6 shows the effect of the substrate bias on deposition rate. Two mechanisms how the ion bombardments acted on the crystallization are conceivable. One is that the ion bombardments promoted the surface migration of depositing atoms. The other is that the non-crystalline part of films was selectively removed by the bombardment ions due to the difference of sputtering yield. Increasing rf power means the large fluxes of both the ion and the deposition species onto the growing surface, which could influence the ion flux, the substrate-target distance was spread from 40 mm to 60 mm so that the deposition rates under the different rf power conditions become almost the same. In Fig. 6, solid marks mean the films with crystalline phase, which demonstrated the diffraction peaks by XRD. The plateau regions indicate that the resputtering did not occur due to low ion energy compared with the sputtering threshold. The crystallization occurred even in the plateau region in case of P_{rf} = 4.3 W/cm^2 and d = 60 mm, while the crystalline films deposited only in the leans region in case of P_{rf} = 2.1 W/cm^2 and d = 40 mm. This indicates that the crystallization was promoted even if the resputtering did not occur. That is, the film crystallization by the substrate bias is led mainly by the surface migration rather than by removal of non-crystalline deposits.

4. CONCLUSION

By using of rf bias sputtering technique, barium titanate films were fabricated. The films consisted of the grains of several nm in size. The film thickness was uniform and the roughness was within a few nm. Applying rf bias to the substrates, the crystallinity and electronic properties of the films were dramatically improved at low substrate temperature of 250 °C. The substrate bias enhanced the bombardment of Ar ions onto film surface and the ions provided energy to the growing film surface to crystallize films. It was confirmed that this effect was mainly from the surface migration of atoms rather than the re-sputtering of non-crystalline part of films.

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