Preparation of BaTiO$_3$ Films on Si Substrate with MgO Buffer Layer by RF Magnetron Sputtering

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Abstract

Highly (002)- or (200)-oriented BaTiO$_3$ thin films were successfully grown on a Si substrate with a MgO buffer layer by RF magnetron sputtering. The deposition parameters need to be stringently controlled in order to grow BaTiO$_3$ films with good crystallinity. The sputtering parameters such as substrate temperature, RF power, gas flow ratio, and deposition pressure were varied to obtain the optimum deposition conditions for the BaTiO$_3$ films. The as-deposited films were characterized by X-ray diffraction analysis and atomic force microscopy to analyze their crystalline structure and surface morphology. The full width at half maximum intensity of the BaTiO$_3$ (002) or (200) peak of the sample fabricated under the optimum deposition parameters was only 0.28°. The surface roughness of the BaTiO$_3$ films was about 3.2 nm. The results could be useful in the integration of ferroelectric and semiconductor devices on the same Si substrate.

1. Introduction

Barium titanate (BaTiO$_3$) thin films have received much attention for application in thin-film capacitors, nonvolatile memory, and electrooptical and optical storage devices owing to their excellent dielectric, ferroelectric, piezoelectric, and nonlinear optical properties. Often, the grown films are either of the amorphous structure, polycrystalline phase, or nonferroelectric cubic form. Thus, the ferroelectric properties of BaTiO$_3$ thin films markedly deteriorate. The requirements for BaTiO$_3$ films for the above applications are high crystallinity and preferred orientation with a smooth surface. Epitaxial-like BaTiO$_3$ films with a polarization axis, i.e., [001], lying along the substrate normal are apparently required to preserve the large remanent polarization $P_r$ and coercive field $E_c$ of the films. To date, epitaxial BaTiO$_3$ thin films have been successfully deposited on different oxide single-crystal substrates such as LaAlO$_3$, SrTiO$_3$, and MgO using various deposition techniques including RF magnetron sputtering, molecular beam epitaxy, metal-organic chemical vapor deposition, pulsed laser deposition, and reactive evaporation. Among these techniques, sputtering has been known as one of the most promising deposition methods in terms of simplicity, uniformity and reproducibility.

The epitaxial growth of BaTiO$_3$ films on Si is very promising because Si substrates are not only less expensive than oxide single-crystal substrates, but also because it is compatible with current maturing Si-based semiconductor devices. However, the epitaxy of BaTiO$_3$ films directly on Si substrates is very difficult owing to the lattice mismatch between the films and the substrates and the pronounced interdiffusion during deposition, which can prevent the epitaxial growth of BaTiO$_3$ films directly on Si substrates. In order to prevent the interdiffusion and achieve the epitaxial or textured growth of BaTiO$_3$ films, some suitable buffer layers such as MgO, SrTiO$_3$, yttria-stabilized zirconia (YSZ), and TiN are required between the Si substrate and the BaTiO$_3$ film. In this paper, we present the growth of highly (002)- or (200)-oriented BaTiO$_3$ thin films on a Si substrate with a MgO buffer layer by RF magnetron sputtering and study the effect of deposition parameters on the structural properties of the BaTiO$_3$ films. Kim et al. have shown that partially (h00) - or (00l)-textured BaTiO$_3$ thin films could be grown on MgO/Si(100) by rf magnetron sputtering, while randomly oriented BaTiO$_3$ thin films with large cracks on their surface could be grown without a MgO layer. Wei et al. have also demonstrated a completely (001)-textured BTO was obtained on a biaxially textured MgO buffer layer. These results show that the quality of textured MgO buffer is the key factor for the growth of BaTiO$_3$ films on silicon. Moreover, the MgO buffer layer may be a promising
substrate for the high-quality epitaxial growth of BaTiO$_3$ film.

In this paper, we present the growth of highly (002)- or (200)-oriented BaTiO$_3$ thin films on a Si substrate with a MgO buffer layer by RF magnetron sputtering and study the effect of deposition parameters on the structural properties of BaTiO$_3$ films. First, we present the growth behavior of MgO buffer layers on a Si(100) substrate. Then, we discuss the crystallographic orientation of the BaTiO$_3$ thin films grown on Si with a MgO buffer layer under different sputtering conditions. For comparison, we also fabricate BaTiO$_3$ thin films on MgO(100) single-crystal substrates.

2. Experimental Procedure

2.1 Growth of MgO buffer layer and BaTiO$_3$ thin film

In the present study, an RF planar magnetron sputtering system (ANELVA SPF-210HS) was used to prepare the MgO buffer layer and BaTiO$_3$ thin films. MgO (99.95%) and BaTiO$_3$ (99.95%) ceramic discs, 50 mm in diameter and 5 mm in thickness, were used as sputtering targets. A polished wafer of (100) Si was used as the substrate and cleaned by a standard process. The chamber was pumped down to 1×10$^{-6}$ Torr using an oil diffusion pump with a liquid nitrogen cold trap before the sputtering gas (Ar+O$_2$) was introduced into the chamber through the mass flow controllers and controlled by the main valve of the pumping system. In all the experiments, the target was presputtered for 30 min under 50 W of RF power before the actual sputtering to remove any contaminants on the target surface.

The deposition parameters for growing a MgO buffer layer with a thickness of 0.2 µm on a Si substrate were an RF power of 85 W, a substrate temperature of 300 °C, a gas flow rate of Ar (20 sccm) at 1×10$^{-6}$ Torr, a deposition pressure of 18 mTorr, a deposition time of 120 min, and a distance between the target and the substrate of 40 mm. Then, we tried to use a high-temperature furnace tube to improve the quality of the MgO buffer layers. The XRD pattern of the annealed MgO buffer layer grown on a Si substrate is shown in Fig. 1. A strong MgO(200) peak is obtained, which means that the MgO buffer layer grew preferentially with the MgO(100) plane parallel to the Si(100) substrate surface. However, a small forbidden peak, corresponding to MgO(100), was also observed in Fig. 1 because the quality of the as-deposited MgO buffer layer is not good enough. This is because the role of the MgO buffer layer is to promote the preferential growth of the BaTiO$_3$ film by decreasing the lattice mismatch between the BaTiO$_3$ film and the Si substrate. Thus, the quality of the MgO buffer layer significantly affects the orientation of the BaTiO$_3$ film. Thus, we used a high-temperature furnace tube to improve the quality of MgO buffer layers. Figure 2 shows the XRD pattern of the annealed MgO buffer layer grown on a Si substrate. From the XRD pattern (Figs. 1 and 2), we see that the full widths at half maximum (FWHM) intensity of the MgO(200) peaks of the annealed samples are about 0.8 and 0.2°, respectively. The calculated lattice spacings of the MgO(200) peak are about 4.26 and 4.22 Å, respectively. The latter value is very close to that of the MgO(200) peak of the annealed sample, which is about 4.22 Å, respectively. The latter value is very close to that of the MgO(200) peak of the annealed sample, which is about 4.22 Å, respectively.

3. Results and Discussion

3.1 Deposition of MgO buffer layer on Si (100) substrate

The XRD 0-2θ pattern of the as-deposited MgO buffer layer grown on a Si(100) substrate is shown in Fig. 1. A strong MgO(200) peak is obtained, which means that the MgO buffer layer grew preferentially with the MgO(100) plane parallel to the Si(100) substrate surface. However, a small forbidden peak, corresponding to MgO(100), was also observed in Fig. 1 because the quality of the as-deposited MgO buffer layer is not good enough. This is because the role of the MgO buffer layer is to promote the preferential growth of the BaTiO$_3$ film by decreasing the lattice mismatch between the BaTiO$_3$ film and the Si substrate. Thus, the quality of the MgO buffer layer significantly affects the orientation of the BaTiO$_3$ film. Thus, we used a high-temperature furnace tube to improve the quality of MgO buffer layers. Figure 2 shows the XRD pattern of the annealed MgO buffer layer grown on a Si substrate. From the XRD pattern (Figs. 1 and 2), we see that the full widths at half maximum (FWHM) intensity of the MgO(200) peaks of the as-deposited and annealed samples are about 0.8 and 0.2°, respectively. The calculated lattice spacings of the as-deposited and annealed MgO buffers are about 4.26 and 4.22 Å, respectively. The latter value is very close to that of the MgO(200) peak of the annealed sample, which is about 4.22 Å, respectively. The latter value is very close to that of the MgO(200) peak of the annealed sample, which is about 4.22 Å, respectively.
3.2 Deposition of BaTiO₃ thin films on Si substrates with MgO buffer layer

3.2.1 Effect of substrate temperature

Figure 3 shows the XRD patterns of the BaTiO₃ films sputtered at various substrate temperatures, while keeping RF power at 60 W, deposition pressure at 15 mTorr, and gas composition of O₂/(Ar+O₂) at 20 %. The film sputtered at 600 °C showed an amorphous phase, but when the substrate was kept above 650 °C, BaTiO₃ films with a polycrystalline structure were obtained. The strong peaks of the BaTiO₃ film grown on a Si(100) substrate with a [100]-oriented MgO buffer layer is essentially of (002) or (200) orientation with very low levels of other orientations. The MgO buffer layer and BaTiO₃ film are of different crystal structures (NaCl structure for MgO and perovskite structure for BaTiO₃) and have a large discrepancy in lattice parameters. The lattice mismatch $m = \frac{d_{\text{film}} - d_{\text{substrate}}}{d_{\text{substrate}}}$ between cubic MgO ($a = 4.213$ Å, at 300 K) and tetragonal BaTiO₃ ($a = 3.992$ Å, $c = 4.036$ Å, at 300 K) is quite large (BaTiO₃ $a$-axis: $m = 5.3 \%$, BaTiO₃ $c$-axis: $m = 4.2 \%$). The strain experienced by the BaTiO₃ films is, therefore, significant, such that a high substrate temperature is required to overcome this discrepancy for growing highly oriented BaTiO₃ films.

When substrate temperature was increased, the sputtered atoms had a surface mobility large enough for a crystalline structure to form. Substrate temperature affected the crystallinity of the film, as evinced by the sharp peaks in the diffraction pattern. The decrease in FWHM is caused by an increase in grain size. However, Preda et al. have reported that BaTiO₃ layers develop a second chemical phase during their annealing and identified as BaTi₂O₅, when the quantity of titanium present in the layer increases. As such, excess titanium leads to a titanium-rich second phase, BaTi₂O₅. Moreover, the higher the annealing temperature and the longer the duration, the more important the formation of BaTi₂O₅. This explains the appearance of the BaTi₂O₅(020) peak when substrate temperature was increased to 700 °C.

Another important feature of the XRD pattern shown in Fig. 3 is that no tetragonal split is observed, despite bulk BaTiO₃ being tetragonal at room temperature. This is often attributed to the possibility that the small dimension of BaTiO₃ crystallites in the film suppresses the tetragonal structure into a pseudocubic phase. Further study is needed to exactly determine whether a BaTiO₃ film grown on a MgO buffer layer is in a tetragonal or pseudocubic phase. A more conscientious study of crystal quality...
and in-plane orientation upon transition from preferential to epitaxial BaTiO$_3$ films obtained from selected area diffraction patterns (SADP) by transmission electron microscopy (TEM) and pole-figure measurement by high-resolution XRD analysis is also encouraged as promising future work.

### 3.2.2 Effect of RF power

The XRD patterns of the BaTiO$_3$ films prepared under various RF powers are shown in Fig. 4. The other deposition conditions are fixed: a substrate temperature of 650 °C, a deposition pressure of 15 mTorr, and a gas composition of O$_2$/(Ar+O$_2$) of 20 %. The maximum relative intensity was obtained from the BaTiO$_3$ film prepared at an RF power of 75 W. The intensity of the BaTiO$_3$ (002) or (200) peak monotonically increases as RF power increases up to 75 W and then decreases again as RF power increases further. The crystallinity becomes worse as RF power increases up to 80 W, owing to the formation of the titanium-rich second phase BaTi$_2$O$_5$.

Fig. 4. XRD patterns of BaTiO$_3$ films sputtered at various RF powers, (substrate temperature: 650 °C, deposition pressure: 15 mTorr, gas flow ratio of O$_2$/(Ar+O$_2$) of 20 %).

### 3.2.3 Effect of deposition pressure

Figure 5 shows the effects of deposition pressure on the texture characteristics of the BaTiO$_3$ films deposited on a Si substrate with a MgO buffer layer. The other deposition conditions are fixed: a substrate temperature of 650 °C, an RF power of 75 W, and a gas composition of O$_2$/(Ar+O$_2$) of 20 %. The BaTiO$_3$ film deposited at a pressure of 12 mTorr has the strongest XRD intensity. The intensity of the BaTiO$_3$ (002) or (200) peak monotonically increases as deposition pressure increases up to 12 mTorr and then decreases again as deposition pressure increases further. At a lower deposition pressure, the film is bombarded by high-energy particles normal to its surface, resulting in a film with a certain primary orientation. The sputtered particles are expected to arrive at the substrate without significant energy loss. At a higher deposition pressure, particle scattering causes film bombardment by low-energy particles at oblique angles, resulting in a randomly oriented film.

Fig. 5. XRD patterns of BaTiO$_3$ films sputtered at various deposition pressures, (substrate temperature: 650 °C, RF power: 75 W, gas flow ratio of O$_2$/(Ar+O$_2$) of 20 %).

### 3.2.4 Effect of sputtering gas composition

Figure 6 shows the changes in the XRD patterns for various sputtering gas compositions of O$_2$/(Ar+O$_2$), while keeping substrate temperature at 650 °C, RF power at 75 W, and deposition pressure at 12 mTorr. The XRD pattern indicates a (002) or (200) preferential orientation of the BaTiO$_3$ films deposited at 10 % oxygen. A clear streak pattern was obtained at 20 % oxygen partial pressure. This means that BaTiO$_3$ films with better crystalline quality were obtained at a higher oxygen content. However, the phase of BaTiO$_3$ (002) or (200) changed to BaTi$_2$O$_5$(020) when the oxygen partial pressure was kept at 30 %. BaTi$_2$O$_5$ favors a decrease in film porosity with the filling of the voids between columnar BaTiO$_3$ crystals. This could lead to improvements in some electrical properties (such as a decrease in leakage current) of these films although other properties might be affected (dielectric constant). By varying composition, one can optimize BaTiO$_3$/BaTi$_2$O$_5$ phase ratio of crystallized films in order to obtain the desired dielectric properties for the application under consideration. Hence, gas composition plays an important role in determining the preferred orientation of the BaTiO$_3$ film.

From the XRD analysis (Figs. 3-6), the optimum deposition parameters are a substrate temperature of 650 °C, an RF power of 75 W, a deposition pressure 12 mTorr, and a gas flow ratio of O$_2$/(Ar+O$_2$) of 20 %. Figure 7 shows the XRD pattern of the BaTiO$_3$ thin
films deposited under optimum deposition conditions. The FWHM of the BaTiO₃ (002) or (200) peak was only 0.28°. Figure 8 shows the θ-2θXRD pattern of the BaTiO₃ film on a MgO(100) single-crystal substrate, employing the optimum sputtering conditions used for growing a highly (002)- or (200)-oriented BaTiO₃ film, as described in Fig. 7. No diffractions from randomly oriented portions are observed. The FWHM of the BaTiO₃ (002) or (200) peak in Fig. 8 was 0.21°. The narrow FWHM of the film indicates that the crystallinity of the film is good and there is little misalignment of the lattice plane parallel to the substrate surface. The calculated lattice spacings of the BaTiO₃ film on a Si substrate with a MgO buffer and the BaTiO₃ film on a MgO single-crystal substrate are about 4.04 and 4.05 Å, respectively. Both of the above values are close to the lattice spacing of the c-axis of the BaTiO₃ crystal (4.036 Å). Although the FWHM of the BaTiO₃ (002) or (200) peak of the BaTiO₃/MgO/Si layered structure (0.28°) is slightly broader than that of the BaTiO₃/MgO layered structure (0.21°), the experimental results could be useful for integrating the ferroelectric and semiconductor devices on the same Si substrate. The root-mean-square surface roughness of the BaTiO₃ thin film on a MgO/Si substrate with a thickness of 0.2 µm deposited under the optimum deposition conditions with a deposition time of 60 min is about 3.2 nm, as shown in Fig. 9, which is smooth enough for further applications.

Fig. 7. XRD pattern of the BaTiO₃ films deposited under optimum deposition conditions, (substrate temperature: 650 °C, RF power: 75 W, deposition pressure: 12 mTorr, gas flow ratio of O₂/(Ar+O₂) of 20 %).

Fig. 8. XRD pattern of BaTiO₃ thin film grown on MgO(100) substrate, (substrate temperature: 650 °C, RF power: 75 W, deposition pressure: 12 mTorr, gas flow ratio of O₂/(Ar+O₂) of 20 %).

Fig. 9. AFM image of the BaTiO₃ film on MgO/Si substrate deposited at the optimum deposition, (substrate temperature: 650 °C, RF power: 75 W, deposition pressure: 12 mTorr, gas flow ratio of O₂/(Ar+O₂) of 20 %).

Fig. 6. XRD patterns of BaTiO₃ films sputtered at various gas flow ratios, (substrate temperature: 650 °C, RF power: 75 W, deposition pressure: 12 mTorr).
4. Conclusions

Highly (002)- or (200)-oriented BaTiO$_3$ thin films have been grown on a MgO/Si(100) substrate by RF magnetron sputtering. MgO buffer layers were grown on Si(100) with a (200)-preferred orientation. The crystallographic orientation of the BaTiO$_3$ film on a MgO-buffered Si(100) layer was similar to that of the BaTiO$_3$ film on a MgO(100) single crystal used as a reference system, which supports the idea that a MgO film can serve as an effective buffer layer for the preferential growth of BaTiO$_3$ films on a Si(100) substrate. The results could be useful in the integration of ferroelectric and semiconductor devices on the same Si substrate.

5. References