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Effect of annealing atmosphere on volatility of Bi in $SrBi_2Ta_2O_9$ thin films

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The changes of structure and chemical composition of $SrBi_2Ta_2O_9$ (SBT) thin films, which were annealed at 500 °C in N_2 and forming gas (5%H_2 + 95%N_2), were investigated. Cross sectional morphology of SBT film was observed by scanning electron microscopy. The chemical composition and state were determined by using X-ray photoelectron microscopy and Auger electron spectrometer, respectively. N_2 played a different role in annealing processes from forming gas. In the case of forming gas annealing, Bi element was reduced and appeared on the surface of SBT film or inside Si substrate. In the case of N_2 annealing, only slight inter-diffusion occurs at SBT/Pt interface and small amounts of Bi are seen at Pt electrode layer. It could be attributed to the high annealing temperature. Compared with films annealed in forming gas, SBT films annealed in N_2 exhibit better microstructure quality.

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Introduction

In recent years, ferroelectric thin films are widely used for many microelectronic applications, such as ferroelectric memory, electro-optic devices, recording devices, and thermoelectric devices [1]. With the development of deposition technology in the past three decades, ferroelectric thin films have the potential for integration into complementary metal oxide semiconductor (CMOS) devices. However, it is necessary to experience through a low temperature annealing for passivation in the production of large-scale integrated microelectronic circuits. A key question is related to annealing atmosphere: Is it preferable to be annealed in passive atmosphere, in inert atmosphere or in reduced atmosphere? The effects of annealing atmosphere and temperature on ferroelectric and dielectric properties of ferroelectric thin films have been investigated by many researchers [2-5]. It has been observed that annealing temperature and time play important roles, but annealing atmosphere has also a major function to improve the properties of the films at the same time [6-8]. Among many ferroelectric materials, low-toxicity $SrBi_2Ta_2O_9$ (SBT) thin film has been the most promising candidates due to superior ferroelectric and dielectric properties [9]. High dielectric constant, excellent fatigue endurance, low coercive field and leakage current are its advantages. On the other hand, small remnant polarization and high annealing temperature are its shortcomings. SBT film is very sensitive to reduced atmosphere. Although annealing temperature is lower, only at 400 °C ~ 500 °C, H_2 can cause severe effects to the properties of SBT films, such as higher leakage current and lower polarization. The most serious degradation behavior occurs at the Curie temperature, which is difficultly recovered [10]. This sensitivity to hydrogen of SBT film is still a major challenge to be overcome for the active large-scale integration. Intensive works on the degradation of SBT film have been done by different groups [11, 12]. They proposed some possible mechanisms for understanding the degradation behavior of SBT film. The primary mechanism is attributed to the large amounts of oxygen and Bi loss and the incorporation of hydrogen into films. However, detailed degradation mechanism needs a further clarification. In particular, effects of different annealing atmospheres on volatility of Bi of SBT film have yet to be fully defined.

In this paper, the effects of forming gas annealing and N_2 annealing on microscopic characteristics and interface properties of SBT thin films are investigated. Several conventional powerful analytical techniques, such as scanning electron microscopy (SEM), X-ray photoelectron microscopy (XPS), Auger electron spectrometer (AES) were used. These analytical techniques will enable better understanding to degradation mechanisms of SBT film.

Experimental Procedures

Many various techniques are used for fabricating SBT thin films. Among these techniques, metalorganic decomposition (MOD) method is simple and low cost. So, SBT thin film was produced on a $Pt/TiO_2/SiO_2/Si$ substrate by MOD method in this study. The size of substrate is 2 cm × 2 cm. Detailed information on

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preparation with films is provided in our early paper [13]. The final film thickness is about 330 nm. Annealing processes include following two stages. Firstly, the deposited sample was annealed at 750 °C for 60 min under pure oxygen atmosphere. The crystallinity of the annealed sample was analyzed by X-ray diffraction (XRD) techniques. XRD results suggested that the sample was fully crystallized and exhibited polycrystalline perovskite structure [13]. Then, film sample was cut into several smaller pieces and annealed at 500 °C for 60 min in an oven equipped with a horizontal-type quartz tube. To differentiate the roles of N_2 and H_2 during annealing, high purity of 99.9% N_2 and typical forming gas (FG, $5\%H_2 + 95\%N_2$) were chosen respectively as annealing atmosphere. The cross sectional morphology and crystallinity of SBT film were observed by SEM. The changes of chemical composition and state for SBT film were analyzed by XPS and AES.

Results and Discussion

The effects of annealing atmosphere on microstructure of SBT films were investigated by using cross section SEM. Figure 1 shows cross-sectional SEM images for SBT thin films annealed at 500 °C for 60 min in N_2 and forming gas, respectively. It can be seen that both samples clearly exhibit polycrystalline structure in nature. In the case of N_2 annealing, a uniform, smooth and crack-free microstructure has been observed for film. The film is composed of continuous dense grains with columnar structures. No significant grain boundaries and inter diffusion are found in cross-sectional SEM images. The presence of sharp boundary at the Si interface and uniform film thickness reveals that N_2 annealing improves the microstructure quality of SBT film. In the case of forming gas annealing, surface morphology and microstructure for film change significantly. As shown in Figure 1(b), the top surface of SBT film becomes rough. Some pores, cracks and spherical structure are presented. An abrupt change occurs at interface with Si substrate. These suggest that more volatile elements (e. g. Bi element) disappear from SBT films. One part of disappeared elements is volatile into air and the other part gathers on the surface of films again. On the other hand, some elements interfuse into Si substrate. The depth of interfusion seems to be the same as the film thickness. According to the SEM results mentioned above, it is clear that the variations on surface of SBT films are related to H_2 but not N_2. The microstructure of SBT films annealed in N_2 gas has better quality than that of films annealed in forming gas.

In order to further analyze the chemical compositions and states of elements presented at the films surface and interface, an Ar^+ ion with 4 kV acceleration voltage was

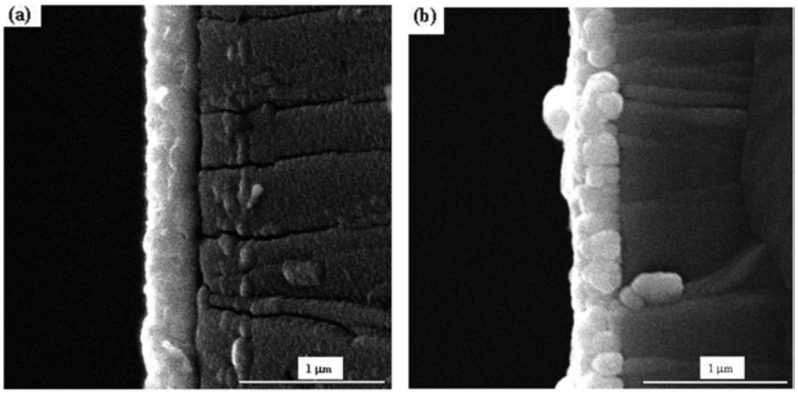

Fig. 1. Cross sectional SEM images of SBT thin films annealed at 500 °C for 60 min in (a) N_2, (b) forming gas.

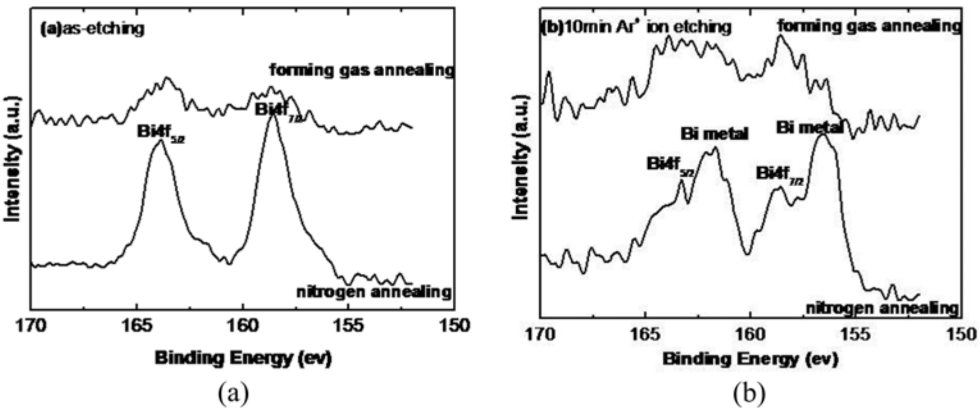

Fig. 2. Bi 4f XPS narrow spectra for SBT films annealed at 500 °C for 60 min in different atmosphere (a) as-etching, (b) 10 min Ar^+ ion etching.

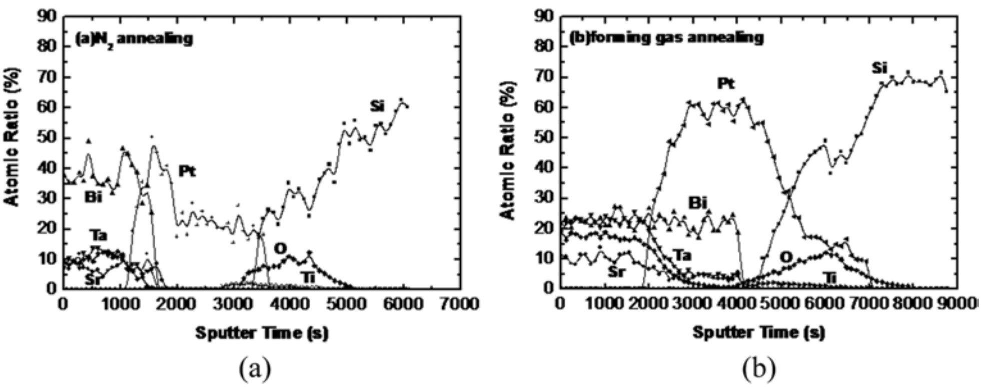

Fig. 3. AES depth profiles of SBT films annealed at 500 ºC for 60 min (a) N_2, (b) forming gas.

used to etch the samples before carrying out XPS narrow scan spectra. C1s standard binding energy (located in 284.6 ev) spectrum was used as a calibration. It is derived from the usual surface contamination. Figure 2 shows Bi 4f spectra of SBT films annealed in different atmosphere before and after Ar^+ ion etching 10 min. As seen in Figure 2, Bi 4f peak is composed of two peaks to correspond the oxidized bismuth. It splits into two peaks because of the spin-orbited coupling. before Ar^+ ion etching, either N_2 annealing or forming gas annealing films exhibit nearly the same Bi 4f peak position. For samples annealed in forming gas, Bi_2O_3 $4f_{5/2}$ and Bi_2O_3 $4f_{7/2}$ peaks are observed at 163.9 eV and 158.6 eV, respectively. The above binding energy values of Bi 4f have some slight changes with published data in literature [8, 14]. The small differences maybe related to different deposition methods and conditions. For N_2 and forming gas annealing samples, Bi $4f_{5/2}$ and Bi $4f_{7/2}$ peaks remain at the same position, respectively. However, an obvious decrease of Bi 4f peak intensities is seen under forming gas annealing compared with N_2 annealing. It is related to Bi deficiency of SBT films. Under a reduced atmosphere such as forming gas, Bi element is easily reduced from SBT films and subsequently evaporates. However, only small amounts of Bi elements can be reduced for SBT films annealed under a non-oxidized atmosphere such as N_2. Neither annealing in N_2 nor annealing in forming gas metallic Bi signals are observed on the surface of films. It indicates that metallic Bi is easily vaporized from the surface of SBT films due to the high temperature annealing at 500 ºC.

As shown in Figure 2(b), no shifts of Bi 4f peaks are observed for samples annealed in forming gas compared with samples annealed in N_2 after 10 min Ar^+ ion etching. The only small difference between them is the different intensities of Bi signals. It indicates that the chemical states of Bi in Bi_2O_2 layer do not change under different annealing atmosphere. However, a new double splitting peak is obviously seen near the major Bi_2O_3 4f peak at the low binding energy side. The presence of new double splitting peaks correspond to the metallic bismuth state (5/2 = 161.7 eV and 7/2 = 156.6 eV). It can be attributed to the etching process and reduced atmosphere. The intensities of metallic Bi peak from inner films are higher than that of oxidized Bi 4f peaks from films surface. Compared with film annealed in N_2, decreased Bi signals for film annealed in forming gas can be attributed to reduction of Bi elements from SBT films and sequential diffusion of Bi from bottom surface to Si substrate. It must be pointed out that the line shape of Bi 4f peak for films annealed in forming gas is just like the continuous waves. So, the signal to noise ratio is bad. It can be related to the rough surface of SBT films. This inference is also supported by above SEM results.

AES depth profiles are useful for understanding the effect of annealing gas on microstructure and interface of SBT film. To obtain direct evident on Bi deficiency in SBT films, we carried out AES depth profiles for SBT/Pt/TiO_2/SiO_2/Si structure films which were annealed at 500 ºC for 60 min. The results are shown in Figure 3. SBT layer, Pt electrode layer, SiO_2 layer and Si substrate are clearly seen in Figure 3 while the TiO_2 layer hardly disappears due to the diffusion into Pt layer. In the case of N_2 annealing, as shown in Figure 3(a), Sr, Bi, Ta and O are mainly seen within SBT films. At the same time, a slight inter-diffusion occurs at SBT/Pt interface. Small amounts of Bi are seen at Pt electrode layer. It could be attributed to volatile Bi from SBT films during annealing at 500 ºC. In the case of forming gas annealing, as shown in Figure 3(b), the intensities of Bi signals in SBT film have a significant decrease. It implies that forming gas atmosphere can cause more Bi element to be reduced. Subsequently, large amounts of reduced Bi diffuse into Pt electrode and react with it to form Bi-Pt compounds. A similar result has been reported by other researchers [6, 12]. One part of compounds accumulates on the SBT surface and form spherical structure. The other part diffuses into Si substrate and form rod-shaped structure. It also is in good agreement with the above

SEM results shown in Figure 1. Overall, we could infer that N_2 and forming gas play different roles in volatilization of Bi during post-annealing treatment.

Conclusions

SBT thin films were grown on Si substrates using MOD method with a spin-coating technique. The effects of forming gas and N_2 gas on the structural properties of SBT thin films were investigated. Good surface morphology of SBT films with uniform, smooth and crack-free microstructure can be obtained under N_2 annealing. However, metallic Bi was easily vaporized from the surface of SBT film due to high temperature annealing at 500 °C under a contained-H_2 atmosphere. Bi-Pt compound was formed at surface and interface regions between SBT film and Si substrate, as found by AES profiles. N_2 and forming gas play different roles in volatilization of Bi for SBT thin film.

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