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Nitrogen-incorporated (Ba, Sr)TiO_3 thin films fabricated by r.f.- magnetron sputtering

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Abstract – In this study, two kinds of barium strontium titanate (BST) samples were prepared. One is a conventional BST film that is sputtered in a mixture of argon and oxygen. The other is a nitrogen-incorporated BST film that is sputtered in a mixture of oxygen and intentionally added nitrogen instead of argon gas. The structural properties of both of the BST films had not changed significantly with the species of sputtering gas. However, the leakage current of BST films sputtered at ($N_2 + O_2$) atmosphere was lower than those sputtered at ($Ar + O_2$) atmosphere: 1.9×10^{-8} A/cm^2 at 2V for the films prepared at ($Ar + O_2$) atmosphere and 8.6×10^{-9} A/cm^2 for the films at ($N_2 + O_2$) atmosphere. From an XPS analysis, it has been found that nitrogen atoms are incorporated in BST films with a concentration of 1.92 at% and form a certain oxynitride phase. It is proposed that nitrogen atoms are able to fill the oxygen vacancies of BST films during sputtering process, and then the leakage current reduces due to a decrease in the vacancies. The BST films sputtered at ($N_2 + O_2$) atmosphere have superior electrical properties to the films sputtered at ($Ar + O_2$), without any significant structural changes.

Keywords: Barium strontium titanate, Sputtering, Nitrogen incorporation, Oxynitride, XPS, XRD, SEM

I. Introduction

Ferroelectric materials with high permittivity make them potential candidates for capacitor dielectrics in future generations of high-density dynamic random access memories (DRAMs). In recent years, many kinds of ferroelectric thin films with a high dielectric constant, such as Pb (Zr, Ti) O_3 [1-3], $SrTiO_3$ [4, 5], and (Ba, Sr) TiO_3 (BST) [6-11] have been studied for this application. BST thin films are one of the most promising materials for the DRAM capacitor, because the films have not only high dielectric constant, but also no fatigue feature caused by ferroelectric domain switching in the device operating temperature range. However, BST thin film capacitors for realistic applications should have a low leakage current in addition to the high dielectric constant. The low leakage current is a very important factor for the capacitors since the level of leakage current determines the reliability of data storage in a DRAM cell and refresh-time.

It has been reported that the high leakage current of perovskite-type oxide material, including BST, is closely correlated with the existence of oxygen vacancies which act as donors in the oxides and these vacancies can be suppressed by doping of metallic atoms such as Nb, Ta [12-14].

In this study, we introduce a new method to reduce the leakage current of BST films, which is incorporating nitrogen atoms as a dopant into the BST films. The nitrogen-incorporated BST films were prepared by a rf sputtering method in a mixture of oxygen and intentionally added nitrogen. A nitrogen-doping method has also been used in the case of ZnO thin films [15, 16]. Sato [16] reported that nitrogen-contained ZnO films had higher resistivity than un-doped ZnO films, as a result of substituting nitrogen for oxygen.

This is a very convenient way compared with the method of doping metallic atoms, because it does not require an extra process to add dopants into an original ceramic target (a sputtering source).

In this work, BST capacitors with the structure of RuO_2/BST/RuO_2 were fabricated and the characteristics of nitrogen-incorporated BST films were investigated.

II. Experiment

RuO_2 bottom electrodes of 125 nm were prepared on Si wafer by sputtering. A mixture of Ar and O_2 was used as sputtering gas. The sputtering target used was a

Table 1. Sputtering conditions of BST films

rf input power	60 W
Substrate temperature	600°C
Working gas	$Ar/O_2 = 1/1$ and $N_2/O_2 = 1/1$
Working pressure	13.3 Pa
Substrate	RuO_2/(100) p-Si wafer
Target-to-substrate distance	35 mm

2-inch disk of Ru metal. The sputtering conditions have been described previously in detail [17].

BST thin films were prepared on the RuO_2 bottom electrode by rf magnetron sputtering. The sputtering target was fabricated from the mixture of $BaTiO_3$ and $SrTiO_3$ by conventional ceramic powder process. The mixture was calcined at 1100°C and sintered at 1200°C for 12 hrs in air. BST films were deposited at the substrate temperature of 600°C, the working pressure of 13.3 Pa, and the rf power of 60 W. We prepared two kinds of samples in the present work. One is a conventional BST film that is sputtered in a mixture of argon and oxygen. The other is a nitrogen-incorporated BST film that is sputtered in a mixture of oxygen and intentionally added nitrogen instead of Ar gas. Typical sputtering conditions of the BST films are illustrated in Table 1.

In order to make metal-insulator-metal capacitors, RuO_2 top electrodes of 100 nm were deposited on BST films using a metal shadow mask with the area of 6.15×10^{-4} cm^2 by sputtering without substrate heating.

The crystallographic characteristics of the films were analyzed by x-ray diffraction (XRD) methods using CuK_α radiation (RIGAKU Co., Model D/MAXI-A). The surface morphology and cross section of films were observed by field-emission scanning electron microscope (FE-SEM). The film thickness was measured with a surface profilometer (DEKTAK III) and a cross-sectional view of SEM. The leakage current-voltage measurements (I-V) were carried out using an HP4140B pA meter/DC voltage source system interfaced with a computer. The voltage step and delay time were 0.2V and 2s, respectively. The capacitance-voltage (C-V) measurements were carried out using an HP4275A LCR meter at 100KHz. X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS) were used to identify the chemical state of the elements and atomic concentration that is present in the films.

III. Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of BST thin films deposited on RuO_2 substrate with a different preparation condition. Fig. 1(a) and (b) represent the BST films sputtered at the atmosphere of $(Ar + O_2)$ and $(N_2 + O_2)$, respectively. It is seen that both of the films have similar XRD patterns. The diffraction peaks of BST (100), (110), and (111) were observed, together with the RuO_2 peaks. This result shows that there is no dependence of the crystallographic properties of BST films on the sputtering gas species.

Fig. 2 shows the planar and cross-sectional images of the BST films. Fig. 2(a) and (b) indicate the images of BST films sputtered at the atmosphere of $(Ar + O_2)$ and also, 2(c) and 2(d) indicate the images at the atmosphere of $(N_2 + O_2)$. From the planar images, it is observed that both films have quite smooth surface morphology so, it is difficult to find

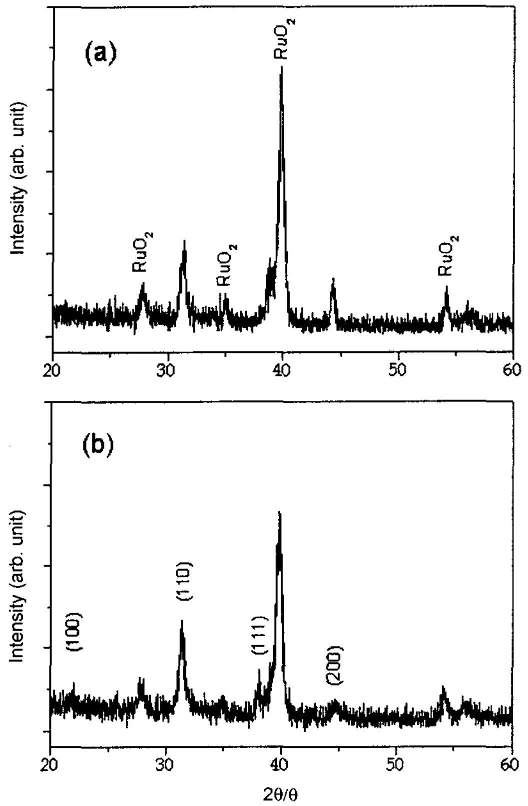

Fig. 1. XRD patterns of BST films prepared at different sputtering atmosphere. (a) The films deposited at $(Ar + O_2)$ atmosphere and (b) at $(N_2 + O_2)$ atmosphere.

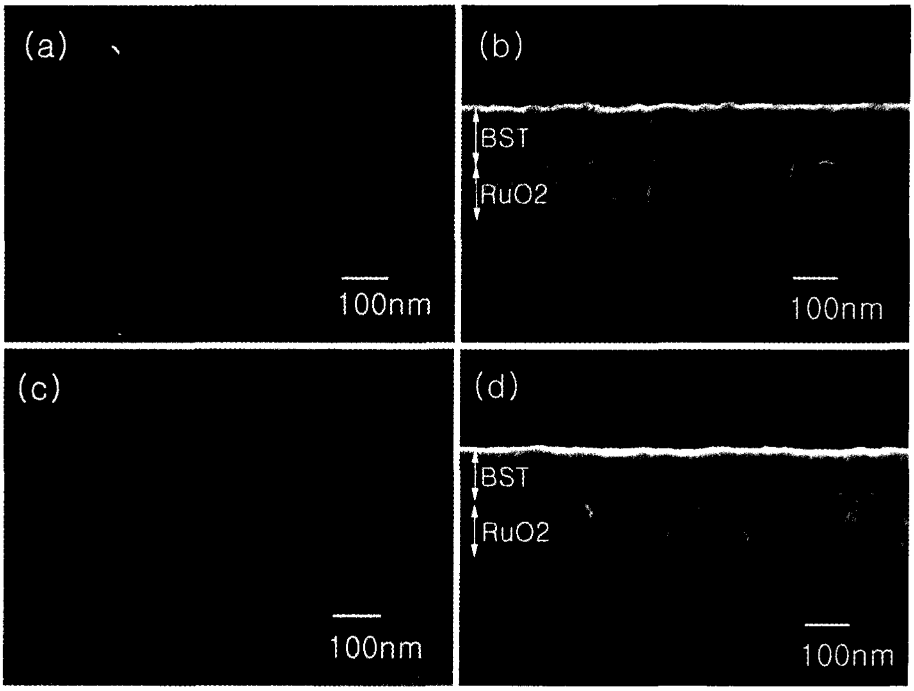

Fig. 2. SEM images of BST films: (a) planar view and (b) cross-sectional view of the films deposited at $(Ar + O_2)$ atmosphere, and (c) planar view and (d) cross-sectional view of the films deposited at $(Ar + O_2)$ atmosphere.

any shape of grain structure. Cross-sectional views show that the thickness of the films prepared at $(Ar + O_2)$ and at $(N_2 + O_2)$ atmosphere are 129 nm and 114nm, respectively and both of the films have very dense structure without any voids and cracks.

From the XRD patterns and SEM images, it was found that the structural properties of BST thin films were not changed largely with the species of sputtering gas.

Fig. 3 shows the leakage current characteristics of the both films with applied voltage. At the low voltage side, the leakage currents for both samples are almost fixed and then they rise sharply at a certain voltage. Thus, it is supposed that the films have different parallel conduction mechanisms and show preferential conduction behavior on each of the low and high voltage sides. Films deposited at $(N_2 + O_2)$ atmosphere have lower leakage current than those deposited at $(Ar + O_2)$ atmosphere, even though the films deposited at $(N_2 + O_2)$ atmosphere are slightly thinner. The leakage currents of the two samples at 2.0 V are 1.9×10^{-8} A/cm^2 for the films prepared at $(Ar + O_2)$ atmosphere and 8.6×10^{-9} A/

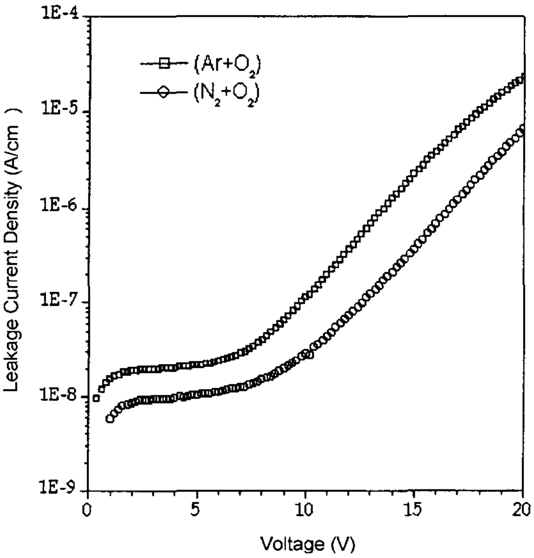

Fig. 3. Leakage current characteristics of BST films prepared at different sputtering atmosphere. Square symbol indicates a sample deposited at $(Ar + O_2)$ atmosphere and circle indicates a sample deposited at $(N_2 + O_2)$ atmosphere.

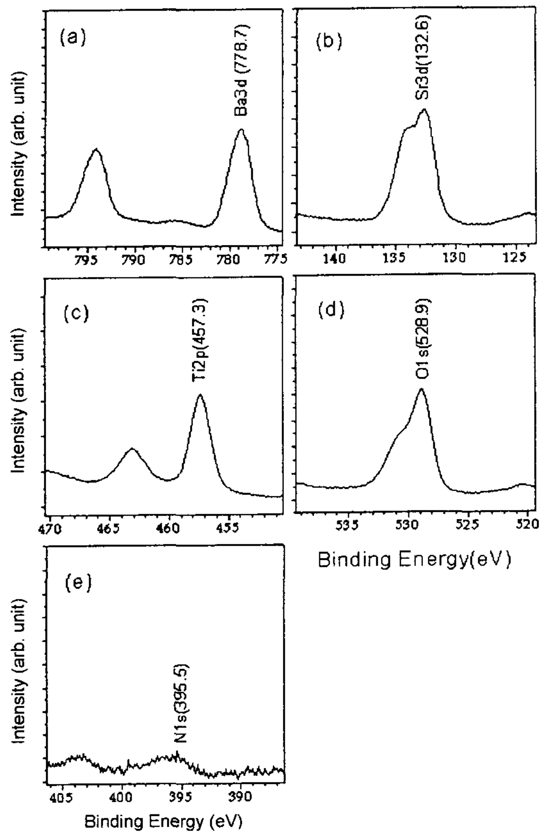

Fig. 4. XPS spectra for BST films deposited at ($N_2 + O_2$) atmosphere: (a) Ba 3d, (b) Sr 3d, (c) Ti 2p, (d) O 1s, and (e) N 1s.

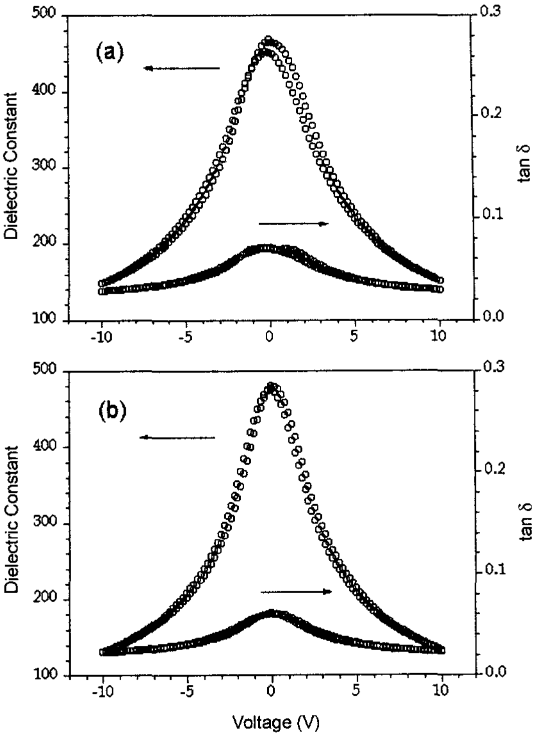

Fig. 5. Dielectric constant and dissipation factor (a) for the BST films deposited at (Ar + O_2) atmosphere and (b) for the films deposited at (N_2+O_2) atmosphere.

cm^2 for the films at ($N_2 + O_2$) atmosphere. From this result, it is thought that the lower leakage current of the films deposited at ($N_2 + O_2$) atmosphere is closely related to the sputtering gas N_2. It is supposed that the nitrogen atoms are incorporated into BST films during sputtering and fill the oxygen vacancies giving rise to leakage current. As a result, the leakage current of the BST films is reduced by a decrease in the oxygen vacancies. This will be ascertained by XPS analysis.

Fig. 4 shows the XPS spectra of the BST films deposited at ($N_2 + O_2$) atmosphere. Fig. 4(a)-(e) are the signals of Ba 3d, Sr 3d, Ti 2p, O 1s, and N 1s, respectively. The central peak positions of the atomic species are as follows: 778.7 eV for Ba, 132.6 eV for Sr, 457.3 eV for Ti, 528.9 eV for O, and 395.5eV for N. It was found that Ba/Sr atomic ratio was 0.75 and (Ba+Sr)/Ti was 1.1, which are very similar to the result of EDS analysis. Especially, an N 1s peak with the binding energy of 395.5 eV and the atomic concentration of 1.92% was observed. This is an obvious evidence of nitrogen incorporation into the BST films. Owing to the similarity of the ionic radii of oxygen and nitrogen, some limited concentration of nitrogen can be reasonably assumed. Although the chemical state of N 1s is not found exactly, it is proposed that the N 1s peak of our film comes from a titanium oxynitride (TiNO), as compared with a few other reports [18, 19]. According to their reports, the N 1s peak, in most of plasma-nitrided samples, could be separated into two components: a main component of 396.6 eV (N-1) and a second component of 395.8 eV (N-2). In addition, the intensity of this N-2 component increased significantly when the samples were subjected to N_2^+ or ($N_2^+ + O_2^+$) bombardment. Ernsberg [19] found the component of N-2 correlated with the Ti 2p component for heavily oxidized TiNO. It is shown that the N 1s peak at 395.5 eV of our BST films is deeply related to the N-2 peak of

TiNO, and also the nitrogen incorporated into BST films produces a certain oxynitride phase in the films. We believe that the incorporated nitrogen atoms can fill some parts of the oxygen vacancies successfully. Therefore, the leakage current of the BST films decreases, as shown in Fig. 3, as a result of this phenomenon reducing oxygen vacancies.

Fig. 5 shows the dependence of dielectric constant and dissipation factor (tan d) on the applied voltage. The bias voltages were applied from 0V to +10 V, then from +10 V to −10 V and back to 0V at 0.2 step. The capacitance (or dielectric constant) and tan d measured at 100 kHz and 0.1 V oscillation level. As shown in Fig. 5(a) and (b), there are no large differences in dielectric constant and tan d between the two samples. This is, we think, because there is no significant difference in the crystallinity of films, as shown in Fig. 1. For the case of BST films deposited at $(Ar+O_2)$, the dielectric constant is 464 and tan d is 0.07 at zero bias. For the films deposited at (N_2+O_2), the dielectric constant is 478 and tan d is 0.06.

IV. Conclusions

The structural properties of BST films had not changed significantly with the species of sputtering gas. However, the leakage current of BST films sputtered at (N_2+O_2) atmosphere was lower than those sputtered at $(Ar+O_2)$ atmosphere: 1.9×10^{-8} A/cm^2 at 2 V for the films prepared at $(Ar+O_2)$ atmosphere and 8.6×10^{-9} A/cm^2 for the films at (N_2+O_2) atmosphere. This suggests that nitrogen atoms are able to fill the oxygen vacancies of BST films during the sputtering process. Therefore, the leakage current is reduced by a decrease in the vacancies. From an XPS analysis, it has been found that nitrogen atoms are incorporated in BST films with a concentration of 1.92 at% and form a certain oxynitride phase. However, further study is needed to understand this phenomenon completely. The dielectric constant is 464 for the films deposited at (N_2+O_2) atmosphere, and 478 for those deposited at (N_2+O_2) atmosphere.

In the present work, it has been shown that the BST films sputtered at (N_2+O_2) atmosphere have superior electrical properties to the films sputtered at $(Ar+O_2)$, without any significant structural changes.

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