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Leakage-current characteristics of sol–gel-derived $Ba_{1-x}Sr_xTiO_3$ (BST) thin films

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Abstract

Thin films of $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) were fabricated on $RuO_2/Ru/SiO_2/Si$ substrates by spin coating multicomponent sol prepared using metal alkoxides. To analyze the surface effect of the dielectric film on the leakage current characteristics required for DRAM applications, post-annealing was carried out under O_2 or Ar atmosphere. Based on AES and RBS data, we have concluded that doubly ionized oxygen vacancies are readily generated on the outermost surface of the BST thin film post-annealed under Ar atmosphere. The leakage current densities of the BST thin film post-annealed with O_2 and with Ar gases are approximately 1×10^{-6} A/cm^2 and 4.6×10^{-6} A/cm^2 at 1V, respectively. This observation was interpreted in terms of (i) the increase in the tunneling current caused by the decrease in the depletion width at the surface region under Ar atmosphere and (ii) the effect from the bottom electrode under oxidative environment.

Keywords: Leakage current; Sol–gel derived; $Ba_{1-x}Sr_xTiO_3$; Thin films

1. Introduction

Dielectric capacitors with high relative permittivities have been extensively investigated for memory cells of dynamic random access memories (DRAM's). Among them, $(Ba,Sr)TiO_3$ (abbreviated as BST) is a promising candidate material for the capacitor dielectric of future DRAM applications because of its paraelectric phase at room temperature and low leakage current compared with other ferroelectric materials. It is well established that the dielectric and electrical properties of BST thin films are dependent on the compositional ratio [1], the film thickness [2] the electrode materials [3], and many processing conditions. However, there appear to be a few reports on the post-annealing under oxygen and reducing atmosphere (N_2 or Ar). Various parameters including the surface chemical state and the microstructure such as the grain size and the surface roughness can be estimated to be dependent on the atmospheric condition. The major characteristics of post-annealed BST thin films, however, are not clearly understood yet.

Recently, it was reported that the leakage current of BST films could be reduced by post-annealing under oxygen atmosphere [4–5]. It is generally believed that oxygen vacancies in the BST films are mostly responsible for a high leakage current. Therefore, oxygen treatment seems to be a useful method for repressing oxygen vacancies. On the other hand, according to the work done by Hwang and co-workers [6], the annealing of the thin film under N_2 atmosphere is very important to obtain low leakage current characteristics because n-type BST film is required to establish a high interfacial potential energy barrier. They stated that a potential energy barrier at the interface, a Schottky-type barrier, was formed by the electrons generated during the post-annealing with N_2.

Current research activities on the electrical properties of BST thin film are mainly focused on the bottom-electrode materials and on the interfacial region between the bottom electrode and the BST thin film. It is found that the leakage current of BST thin films, irrespective of the deposition technique, is usually dependent on the above factors. Therefore, the characteristics of the surface chemical state of BST thin film, that can also be controlled by the post-annealing, may explain why the electrical properties are closely related to the nature of the interface.

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In view of these facts, the main purposes that we try to address are (i) to profile the surface chemical state of the BST thin film prepared using a sol-coating route, and (ii) to investigate the effect of post-annealing on electrical properties. For these purposes, a sol–gel route using metal alkoxide precursors was attempted and characterized.

2. Experimental

Ba-, Sr-isopropoxides (99.5% in isopropanol, Chemat Technology, Inc.) and Ti-isopropoxide (99.999%, Aldrich Chemical Co.) were used as starting precursors for synthesizing homogeneous multicomponent BST sols. In the present study, acetylacetone ($CH_3COCH_2COCH_3$), an appropriate chelation agent, was also introduced to regulate the mutually different hydrolysis/condensation rates of the starting metal alkoxides. The concentration of the multicomponent BST sol was controlled to 0.13 M under flowing nitrogen atmosphere.

BST films having thickness of 250 nm were prepared by spin coating on "RuO_2(150 nm)/Ru(100 nm)/SiO_2 (100 nm)/Si(100)" substrates. Finally, the spin-coated BST thin films were fired at 700°C for 2 h. On the other hand, to understand the surface effect on the electrical properties of BST films, post-annealing was carried out at 600°C for 1 h under O_2 or Ar atmosphere. More detailed experimental procedure and results on the fabrication of BST thin films and electrical measurement were described previously [7].

3. Results and discussion

3.1. *Phase formation and chemical characteristics*

The XRD pattern of the sol–gel-derived BST thin film indicates that the formation of the perovskite phase completes at 700°C (Fig. 1). There is no tendency of preferential orientation in the sol–gel-derived BST thin films fabricated on RuO_2/Ru/SiO_2/Si substrates. The average grain size of the thin film, as estimated by the Scherrer formula [8], is approximately 30 nm.

The AES depth profile of a flat BST/RuO_2/Ru/SiO_2/Si thin film is shown in Fig. 2. The Zalar rotating method for the depth profile was attempted to improve the accuracy of compositional analysis of BST thin films. Since the concentration of the Sr-component is not correctly normalized, it is actually underestimated. This is due to a background level change around the energy corresponding to Sr MNN peak caused by Ru NVV or Si LVV peaks. The metal components of BST-thin films are assumed to diffuse out through the substrate. Therefore, metal vacancies remaining at the interfacial region (called "Diffuse Region") may have an effect on controlling the leakage current.

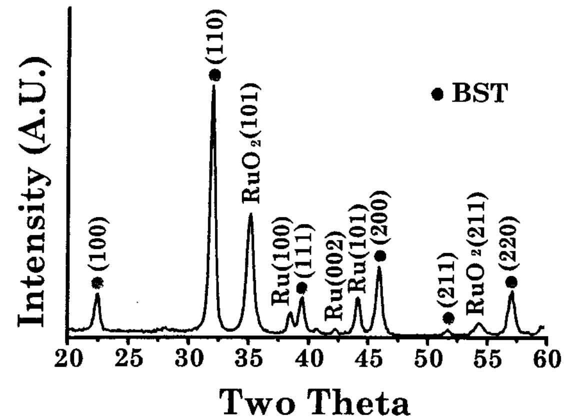

Fig. 1. The XRD pattern of spin-coated BST thin film heat-treated at 700°C for 2 h. BST film was fabricated on RuO_2/Ru/SiO_2/Si substrates.

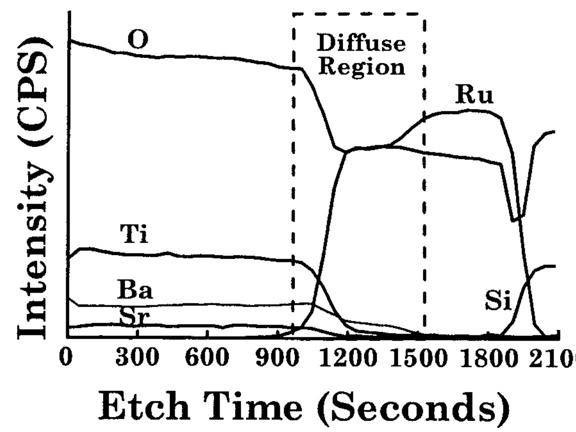

Fig. 2. The AES depth profile of BST thin film post-annealed at 600°C for 1 h with Ar gas.

RBS spectroscopy was also conducted on the post-annealed BST thin films. The depth analysis of the Ar-annealed BST thin film in accordance with channels is presented in Fig. 3. As indicated in the figure, the Ti-component is tailed out into the bottom electrode. This observation is consistent with our previous conclusion deduced from AES spectroscopy. The Ti-component of the BST-thin film may be assumed to infiltrate into the bottom electrode with a penetration depth of about 50 mn. Because the Ru channel is similar to those of Ba and Sr elements, it is difficult to discriminate a particular channel from the others in BST thin films. Based on the RBS data, the compositional variation of the perovskite BST film was simulated in accordance with the film thickness, and the result is depicted in Fig. 4. Thus, in terms of the chemical composition, the BST thin film can be viewed as consisting spatially, of two different regions: a homogeneous region and a metal-deficient region. No compositional fluctuation was detected in the homogeneous region.

As deduced from the AES data (Fig. 2), the oxygen concentration of the BST thin film post-annealed with

Ar gas decreases in accordance with the film-thickness. This observation suggests that charged oxygen vacancies can be readily generated on the BST surface post-annealed under Ar atmosphere. Moreover, metal components in the interfacial region defined as the "metal-deficient region" are evidently diffused-out into the bottom electrode (Fig. 2). Therefore, metal vacancies such as V''_{Ba}, V''_{Sr}, and V''''_{Ti} may play a major role in modifying the potential barrer in the interfacial region of BST/RuO_2 thin film and, thus, in controlling the leakage current characteristics. Dietz and co-workers [9] suggested that oxygen vacancies might be created at the BST/Pt interface. Until now, however, the formation of metal vacancies in BST thin films due to the diffusion into the substrate or the bottom electrode has not been noticed, despite its importance in the leakage current characteristics. Little has been known on the formation of metal vacancies or the diffusion-out of metal into the substrate. According to the thermionic conduction mechanism, the leakage current will be dependent on the Schottky barrier height, which is usually controlled by the amount of defects at an interfacial region.

To identify the metal inter-diffusion through the bottom electrode, EDS (energy dispersive X-ray spectroscopy) analysis on the cross-sectional specimen was conducted. BaL_α (4.465 eV), SrL_α (1.806 eV), SrK_α (14.14 eV), and TiK_α (4.508 eV) peaks were detected in the cross-sectioned BST thin film only. No evidence was found on the characteristic Ru X-ray energy used for the bottom electrode. On the other hand, in addition to the characteristic X-ray energy for Ru peak [RuL_α (4.508 eV) or RuK_α (19.233 eV)], the characteristic X-ray energies for Ba, Sr, and Ti elements were also detected in the RuO_2 bottom electrode. Consequently, the metal vacancies formed at the metal-deficient region are expected to make a significant contribution to the electrical properties required for DRAM applications.

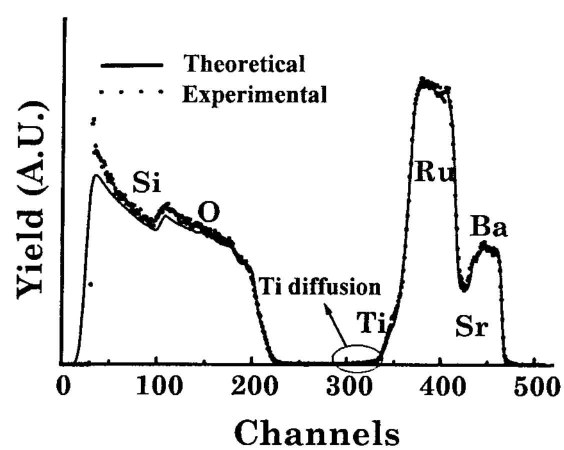

Fig. 3. The RBS depth profile of BST thin film as a function of channel. The thin film was post-annealed at 600°C for 1 h under Ar atmosphere.

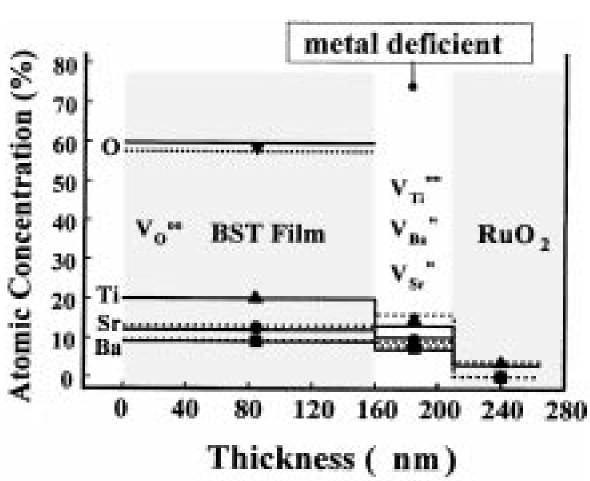

Fig. 4. Atomic concentration profile of BST thin film post-annealed at 600°C for 1 h under O_2 or Ar atmosphere (solid line: O_2, dashed line: Ar).

3.2. Electrical characteristics

The leakage current densities of BST thin films post-annealed under O_2 or Ar atmosphere were plotted as a function of the applied voltage, as shown in Fig. 5. The leakage current density at room temperature shows a linear dependence of log J with $E^{1/2}$. As suggested previously [7], Schottky emission is the dominant conduction process for the sol–gel-derived BST thin film.

The leakage current densities of the BST thin films post-annealed with O_2 and with Ar gases are approximately 1×10^{-6} A/cm^2 and 4.6×10^{-6} A/cm^2 at 1V, respectively. The leakage current of the post-annealed BST thin film with O_2 is lower than for the post-annealed film with Ar at a given applied voltage. This observation indicates that the leakage current depends on the post-annealing treatment. As discussed previously in the Ar-annealed BST thin films, the doubly

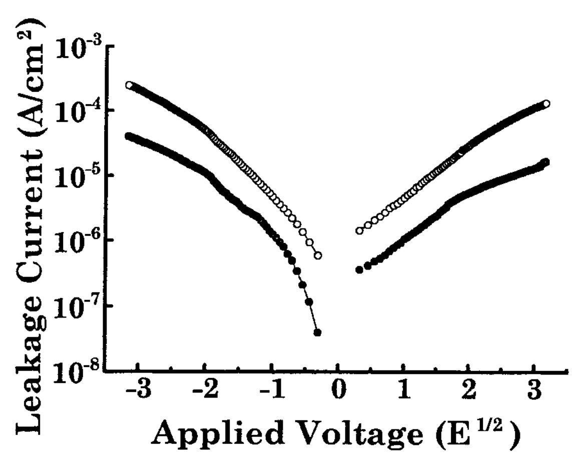

Fig. 5. Leakage current density (J-E) of BST thin films post-annealed at 600°C for thin film 1 h under O_2 or Ar gas (filled circle: O_2, open circle: Ar).

ionized oxygen vacancies can be readily generated on the BST outermost surface [10, 11]. Therefore, the highly charged layer on the BST thin film surface, similar to highly doped surface layers in semiconductors, can either reduce a potential barrier or result in an ohmic contact [12]. When the external electric field is zero, the width of the depletion region (W) can be expressed as [13]

$$W = \left[\frac{2\varepsilon_0\varepsilon_i V_{bi}}{qN_D}\right]^{1/2} \text{with } qV_{bi} = \phi_M - \chi - (E_C - E_F) \quad (1)$$

where V_{bi} is the built-in potential, χ is the electron affinity of BST thin film, and ϕ_M refers to the metal work function. The depletion region width (W) is inversely proportional to the square root of the charge concentration, N_D. The width of the depletion region decreases as the doping concentration increases. Thus, with increasing concentration of electrons at the interfacial region the tunneling current through the barrier increases. An energy-band diagram of a metal/BST contact in thermal equilibrium can be represented by a schematic plot shown in Fig. 6. Therefore, post-annealing using oxygen gas is expected to be useful in reducing the leakage current of BST thin films.

The bottom electrode, RuO_2, seems to have an influence on the leakage current density of BST thin film. It has been reported that Ru oxides other than RuO_2 (e.g. RuO_3, RuO_4) are generally unstable and volatile [14]. It is known that there is an increase in the etching rate with O_2 addition to the etch gas, possibly due to the formation of volatile RuO_3/RuO_4 compounds [15–16]. Thus, it is likely that the excess oxygen in the film enhances the formation of the volatile oxides at a high temperature [17]. A plausible chemical reaction occurring on the bottom electrode can be written as

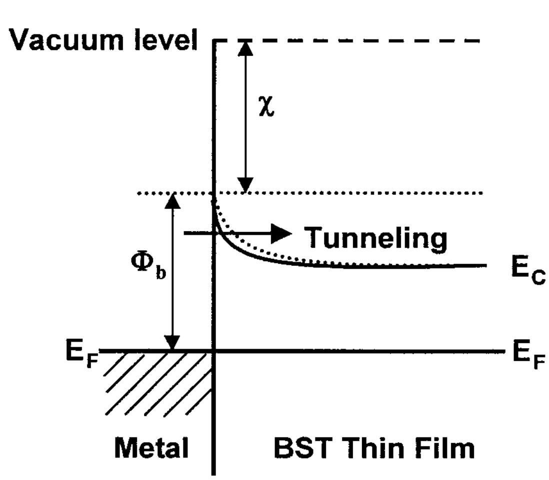

Fig. 6. Energy-band diagram of metal/BST thin film post-annealed at 600°C under Ar gas.

$$\begin{aligned} 1/2O_2 + Ru(IV)O_2 &\Rightarrow Ru(VI)O_3 + 2e' \\ 2e' + 2h\cdot &\Rightarrow \text{null} \end{aligned} \quad (2)$$

The above equation suggests that electrons produced by the oxidation at the bottom electrode are annihilated with holes generated by the metal inter-diffusion in the metal-deficient region. This model further suggests that the relative resistivity of the O_2-annealed BST thin film increases because of the decrease in the concentration of charged carriers. Therefore, a significant reduction in the leakage current is expected in the BST thin film post-annealed under O_2 atmosphere, and this agrees with the result shown in Fig. 5.

Until now, a quantitative correlation between the electrical properties and the surface-binding-energy induced by a post-annealing has not been established. To establish a quantitative leakage current mechanism of the BST thin film aimed for DRAM applications, more systematic investigations on the band structure of the surface region are strongly recommended.

4. Conclusions

$Ba_{0.5}Sr_{0.5}TiO_3$ thin films were prepared on $RuO_2/Ru/SiO_2/Si$ substrates using the spin-coating method. For the preparation of chemically homogeneous multi-component sols, Ba-, Sr-, and Ti-isopropoxides were chosen as starting materials. A post-annealing procedure was employed to identify the chemical state of the surface of BST thin film under 0_2 or Ar atmosphere. The leakage current densities of the BST thin films post-annealed with O_2 and with Ar gases are approximately 1×10^{-6} A/cm^2 and 4.6×10^{-6}A/cm^2 at 1V, respectively. Because of the decrease in the depletion width at the interfacial region of the thin film post-annealed with Ar gas, the contribution of the tunneling current to the leakage current was significantly increased. Contrary to this, the excess electrons produced by the oxidation of the bottom electrode (RuO_2) are expected to be annihilated with the holes remained at the metal-deficient region. Therefore, a lower leakage current is expected in the BST/RuO_2 thin film post-annealed under O_2 atmosphere, and this is consistent with the present experimental results.

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