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Characteristics of $SrTiO_3$ thin films deposited under various oxygen partial pressures

S. H. PAEK, J. H. WON, J. E. JANG, Y. S. HWANG
Department of Materials Engineering, Hanyang University, Seoul, Korea

J. P. MAH
Department of Electronic Engineering, Honam University, Kwang-ju, Korea

J. S. CHOI, S. T. AHN, J. G. LEE
Semiconductor R&D Centre, Samsung Electronics, Kihung-eup, Kyungki-do, Korea

C. S. PARK
Department of Electronic Engineering, HanSeo University, Hae-mi, Korea

$SrTiO_3$ thin films were deposited by rf-magnetron sputtering under various sputtering conditions followed by conventional furnace annealing at 600 and 700 °C. The amorphous $SrTiO_3$ thin films crystallized into polycrystals at 600 °C. The leakage current of the $SrTiO_3$ thin films decreased with increasing oxygen partial pressure in the sputtering gas. On the contrary, the dielectric constant increased with increasing the oxygen content in the sputtering gas. The leakage current and dielectric constant increased with increasing substrate temperature and post-annealing temperature. The ratio of Sr:Ti approached 1:1 with increasing oxygen content in the sputtering gas and substrate temperature during deposition. The oxygen content in the film decreased with increasing the substrate temperature. The capacitance–voltage (C–V) curves showed that the capacitance was nearly independent of the applied voltage. Scanning electron microscopy (SEM) micrographs showed that interdiffusion between the bottom electrode (Pt) and the buffer layer (Ti) occurred during post-annealing, but that the interface between $SrTiO_3$ and Pt was stable.

1. Introduction

To meet the increasing demand for oxide ferroelectrics for use in micro-sized dielectric capacitors in large-scale integrated circuits, perovskite structured lead zirconium titanate and lead lanthanum zirconium titanate (PZT), (PLZT) and also $BaTiO_3$, have been extensively studied. However, common problems in all these systems are fatigue and ageing [1, 2], which degrade the reliability and durability of these oxide ferroelectrics. Much attention has been focused on $SrTiO_3$ and $Ba_{1-x}Sr_xTiO_3$ in attempts to overcome these problems. These compounds are paraelectric at room temperature and have high dielectric constants. $SrTiO_3$ has a low Curie temperature (108 K), a low temperature coefficient of capacitance and is a thermally stable compound [3]. Takashi *et al.* [4] have reported that nonstoichiometry in $SrTiO_3$ thin films influenced their dielectric properties. However, there are few reports regarding the effect of processing conditions on the electrical properties of $SrTiO_3$ thin films.

In the present work, a systematic examination was carried out of the processing conditions for $SrTiO_3$ thin films. Reasons are given as to why the processing conditions influence the characteristics of the $SrTiO_3$ thin films.

2. Experimental procedure

$SrTiO_3$ thin films of thickness 300 nm were deposited by rf-magnetron sputtering of a ceramic powder target onto $Pt/Ti/SiO_2/Si$ substrates held at either room temperature or at 300 °C. The sputtering conditions are listed in Table I. The target was compacted at a pressure of 300 MPa. $SrTiO_3$ thin films were deposited under various oxygen partial pressures in argon. The thin films were treated by conventional furnace annealing at 600 and 700 °C for 1.5 h in an air atmosphere. The crystal structures of the films were examined by X-ray diffraction. A Tencor α-step was used to measure the film thickness. The deposition rates were related to the oxygen fractions in the sputtering gas and to the substrate temperatures. SEM cross-sectional and surface images were used to observe the thermal stability of the interface between the $SrTiO_3$ films and the substrate during the heat treatment. The chemical composition of the films was analysed by Rutherford backscattering spectrometry (RBS). Aluminium dots (dia 0.2 mm) were evaporated onto the $SrTiO_3$ thin films as upper electrodes. The current–voltage (I–V) characteristics of the $SrTiO_3$ thin films were measured by a d.c. parameter analyser (HP4145B). The dielectric constants were estimated from a C–V curve measurement using an impedance

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TABLE I Sputtering conditions for the $SrTiO_3$ thin films

Target	$SrTiO_3$ powder
Target size	3-inch
Sputtering gas	Ar/O_2 = 10/0–5/5
Working pressure	1×10^{-2} torr
RF power	120 w
Substrate temperature	R.T., 300 °C
Target–substrate distance	40 mm

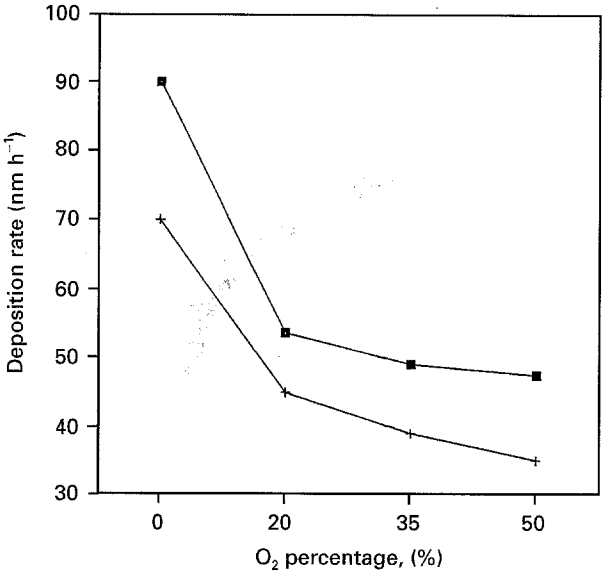


Figure 1 Deposition rate dependence on the oxygen partial pressure in the sputtering gas with (■) data collected for growth on the substrate at room temperature and (+) data collected for a substrate temperature of 300 °C.

analyser (HP4280A) at 1 MHz for $Al/SrTiO_3/Pt$ metal–insulator–metal (MIM) structures with a $\pi \times 10^{-4}$ cm^2 electrode area. The dissipation factors were measured with an LCR meter (Phillips PM9541) at 10 kHz.

3. Results

3.1. Formation of the $SrTiO_3$ thin films with varying processing conditions

Fig. 1 shows the dependence of the deposition rate on the processing conditions. On increasing the ratio of oxygen to argon in the sputtering gas, the deposition rate of the $SrTiO_3$ thin films decreased. The reason for this result is not yet clear. Increasing the substrate temperature during the deposition, also decreased the deposition rate of the $SrTiO_3$. The re-evaporation of adatoms increased with increasing substrate temperature and the density of the films was enhanced. Hence the deposition rate of the $SrTiO_3$ thin films was decreased,

The XRD patterns of the $SrTiO_3$ thin films grown at various processing conditions are shown in Fig. 2a and b. The $SrTiO_3$ thin films were crystallized by conventional furnace annealing in air. The $SrTiO_3$ thin films crystallized at 600 °C (Fig. 2a). To enhance the crystallization, the post-annealing was performed at the higher temperature of 700 °C, however the intensities of the XRD peaks remained almost constant.

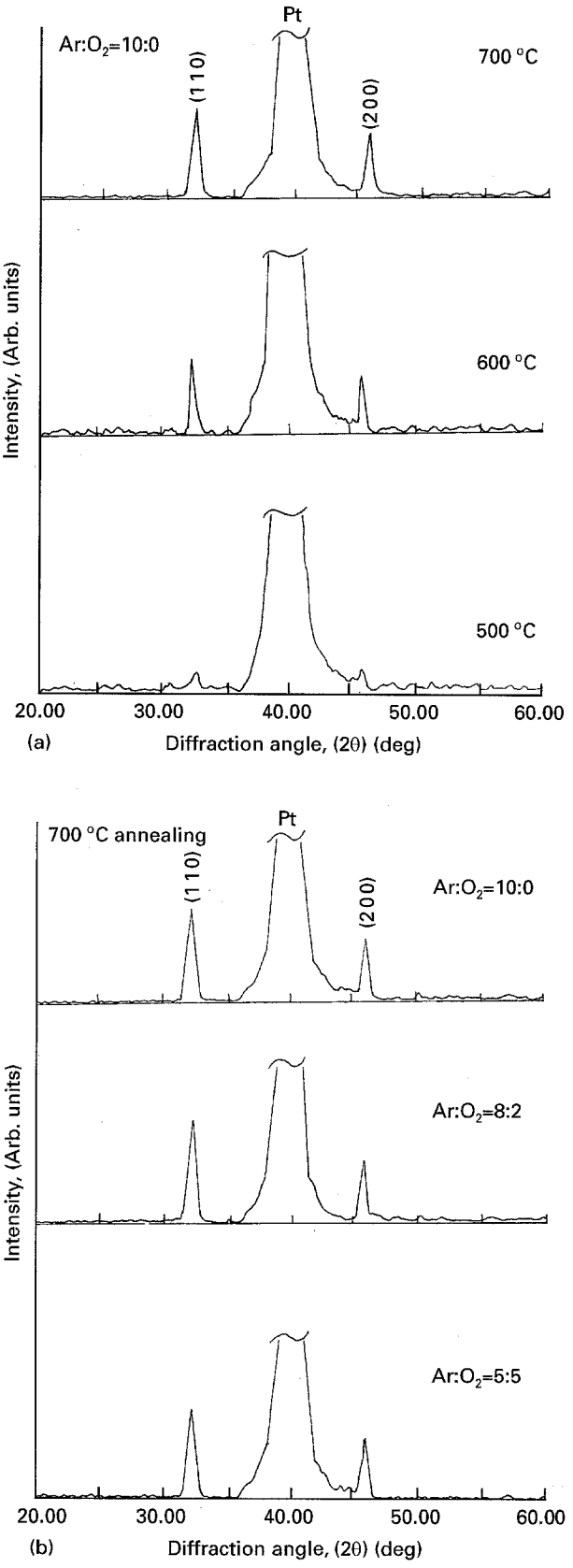


Figure 2 X-ray diffraction patterns of $SrTiO_3$ films (deposited at R.T.) (a) XRD patterns of $SrTiO_3$ film with post-annealing temperature. (b) XRD patterns of $SrTiO_3$ film with oxygen partial pressure in the sputtering gas.

The effect of the oxygen partial pressures on the crystal structure of the $SrTiO_3$ thin films was investigated (Fig. 2b). There was no observable difference in the XRD patterns of the $SrTiO_3$ thin films deposited under the various oxygen partial pressures. From the

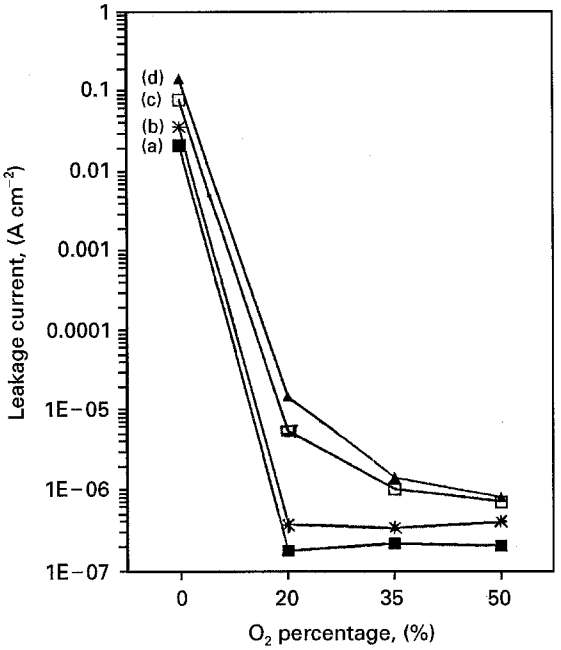


Figure 3 Leakage current density of $SrTiO_3$ film (300 nm thickness) deposited under various oxygen partial pressures in the sputtering gas with the following heating conditions. (■) Room temperature substrate, furnace anneal at 600 °C, (*) room temperature substrate, furnace anneal at 700 °C, (□) substrate at 300 °C, furnace anneal at 600 °C, and (▲) substrate at 300 °C, furnace anneal at 700 °C.

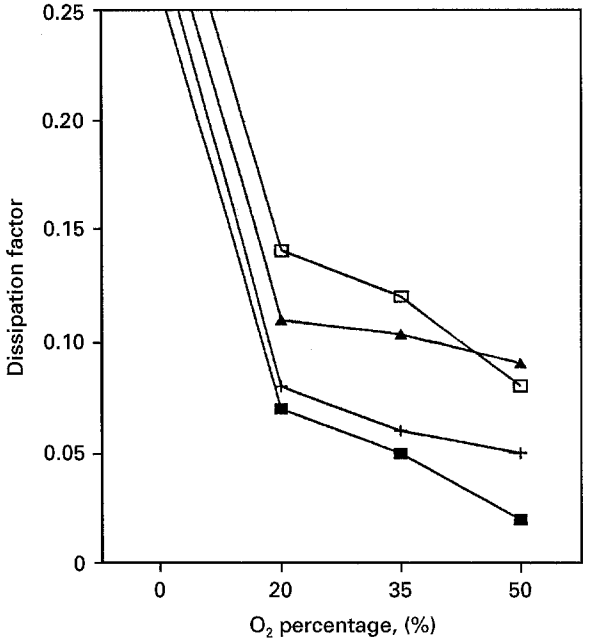


Figure 4 Dissipation factor of $SrTiO_3$ films (300 nm thickness) deposited under various oxygen partial pressures in the sputtering gas with the following heating conditions. (■) Room temperature substrate, furnace anneal at 600 °C, (+) room temperature substrate, furnace anneal at 700 °C, (▲) substrate at 300 °C, furnace anneal at 600 °C, and (□) substrate at 300 °C, furnace anneal at 700 °C.

XRD results it is assumed that the interface between the $SrTiO_3$ and the bottom layers was thermally stable up to a temperature of 700 °C.

3.2. Variation of the electrical properties of the $SrTiO_3$ thin films with processing conditions

Fig. 3 shows the leakage current densities of the films deposited for various oxygen partial pressures in the sputtering gas. With increasing oxygen partial pressure, the leakage current densities of the $SrTiO_3$ thin films decreased steeply. In Fig. 3 lines (a) and (b) show the leakage current density of films deposited at room temperature as a function of the oxygen partial pressure and lines (c) and (d) in Fig. 3 show the data for films deposited at 300 °C. The (a and c) curves of Fig. 3 were taken on films annealed at 600 °C and curves (b) and (d) on films annealed at 700 °C. The higher the post-annealing temperature, and the higher the substrate temperature during the deposition, the higher the leakage current density. From a thermodynamic analysis, the possible point defects in polycrystalline $SrTiO_3$ thin films are oxygen vacancies and strontium vacancies. Garblinger and Meixner [5] have reported that the density of strontium vacancies is three orders of magnitude lower than that of oxygen vacancies. It is therefore probable that the concentration of oxygen vacancies is the dominant factor in the electrical conduction created in an insulator ($SrTiO_3$). It is reported that a higher oxygen partial pressure during the deposition promotes the fabrication of highly oxidized films, and consequently reduces the concentration of oxygen vacancies in the films [6].

The dependence of the dissipation factor on processing conditions is shown in Fig. 4. This is similar to that observed for the leakage current densities. As increase in the oxygen partial pressure in the sputtering gas, decreases the dissipation factors. This means that the insulating behaviour of the films was enhanced with the oxygen partial pressure.

Fig. 5 shows the variation in the dielectric constant with the processing conditions. Because the films deposited in pure Ar were conductive, the dielectric constants of these films were not measured. The dielectric constants of the $SrTiO_3$ thin films increased with increasing oxygen partial pressures, substrate temperature and post-annealing temperature.

3.3. Chemical composition analysis of the $SrTiO_3$ thin films

In order to understand the effect of the processing conditions on the electrical properties, the chemical composition of the films was analysed by RBS [Figs 6, 7].

Fig. 6 shows the surface density of $SrTiO_3$ thin films with processing conditions. (a) is the variation in surface density with oxygen partial pressure (deposited at 300 °C) and (b) is the variation in surface density with the substrate temperatures during deposition at (Ar: O_2 = 5:5). Increasing the oxygen partial pressure in the sputtering gas, increases by a small amount the surface densities of the $SrTiO_3$ thin films (Fig. 6a). An increase in oxygen partial pressure resulted in a decrease in the deposition rate. The probability for surface diffusion of adatoms increases with decreasing deposition rate. Thus, the surface densities increased

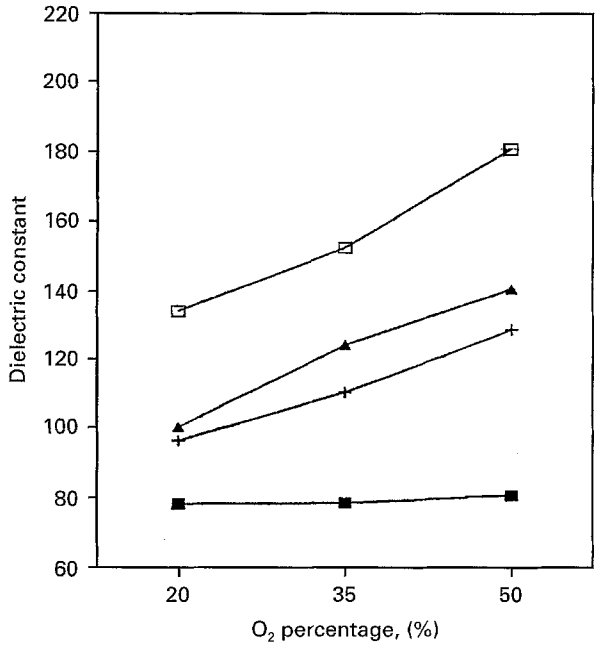


Figure 5 Dielectric constants of $SrTiO_3$ films (300 nm thickness) deposited under various oxygen partial pressures in the sputtering gas with the following heating conditions. (■) Room temperature substrate, furnace anneal at 600 °C, (+) room temperature substrate, furnace anneal at 700 °C, (▲) substrate at 300 °C, furnace anneal at 600 °C, and (□) substrate at 300 °C, furnace anneal at 700 °C.

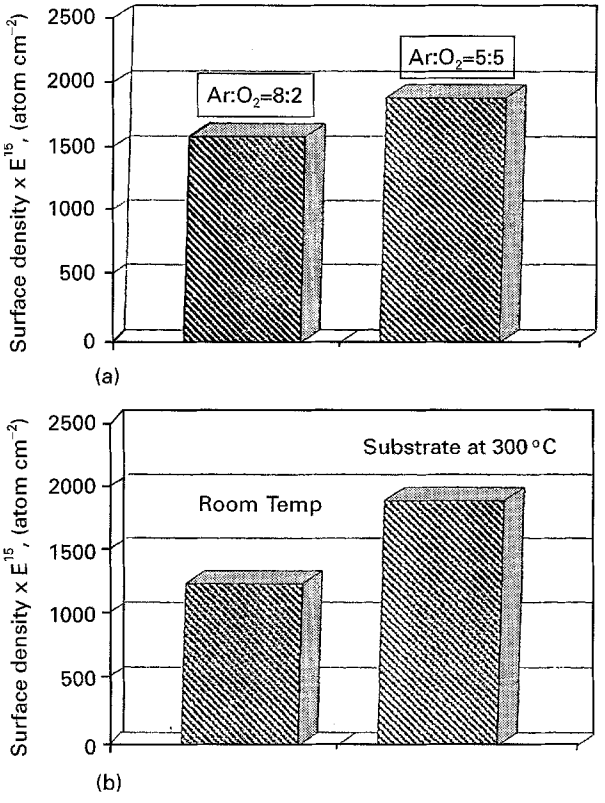


Figure 6 Surface density analysis of $SrTiO_3$ film by RBS. (a) Surface density with oxygen partial pressures in sputtering gas (substrate temperature 300 °C). (b) Surface density with substrate temperature ($Ar:O_2 = 5:5$).

with increasing oxygen partial pressure. In the case of Fig. 6b, increasing the substrate temperature during deposition enhanced the diffusivity of adatoms. Therefore, the surface densities of $SrTiO_3$ thin films increased with increasing the substrate temperature.

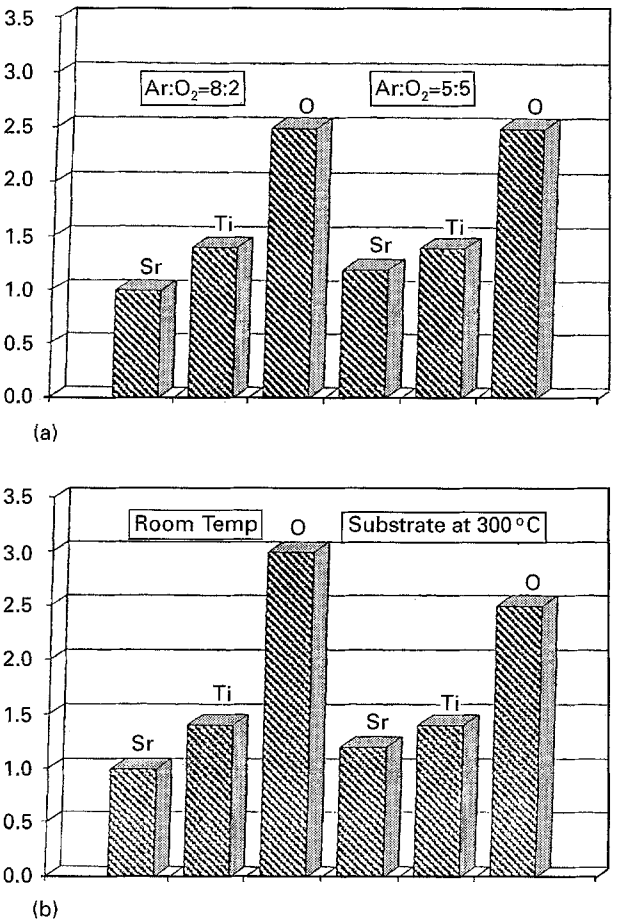


Figure 7 Chemical composition analysis of $SrTiO_3$ film by RBS. (a) Chemical composition analysis with oxygen partial pressure in sputtering gas (substrate temperature 300 °C). (b) Chemical composition analysis with substrate temperature ($Ar:O_2 = 5:5$).

Fig. 7 illustrates the variation in the chemical composition of the $SrTiO_3$ thin films with the processing conditions. (a) is the chemical composition versus oxygen partial pressure (deposited at 300 °C) and (b) is the chemical composition versus substrate temperature for deposition at ($Ar:O_2 = 5:5$).

The effect of the oxygen partial pressures on the dielectric constant can be interpreted. As the oxygen partial pressure in the sputtering gas increased the Sr:Ti ratio increased to 1:1 [Fig. 7a]. Takashi *et al.* [4] reported that the Sr: Ti ratio in $SrTiO_3$ thin films influenced the dielectric constant of the films and that films showed their highest dielectric constant values at a ratio of 1:1. It is assumed that the sputtering yields of Ti and Sr in pure Ar are different from those of Ti and Sr in pure O_2. Therefore, the variation of oxygen partial pressures in the sputtering gas results in a variation in the Sr:Ti ratios in the thin films. On increasing the oxygen partial pressures in the sputtering gas, the Sr:Ti ratio in the films approached 1:1 and the measured dielectric constant increased. Fig. 7b shows that the Sr:Ti ratio also varied with substrate temperature. It is also assumed that the dependence of the re-evaporation rates of Ti and Sr on substrate temperature are different from each other. Therefore on increasing the substrate temperature during deposition, the Sr:Ti ratio in the films varied and hence the dielectric constants increased.

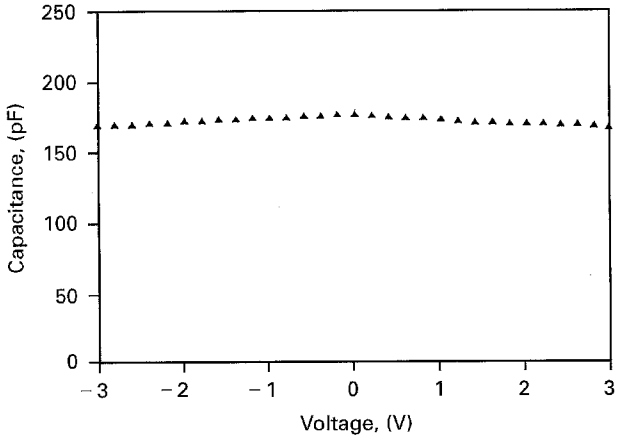


Figure 8 C–V characteristic of a $SrTiO_3$ thin film grown at a substrate temperature 300 °C, furnace anneal at 700 °C with Ar: O_2 = 5:5.

The effect of oxygen partial pressure on the leakage currents can also be explained. On increasing the substrate temperature during deposition, the oxygen content in the thin films decreased [Fig. 7b]. A deficiency of oxygen in the thin films means that oxygen vacancies exist in the thin films. Takeharu [6] explained the conduction in $SrTiO_3$ thin films in terms of Poole–Frenkel emission caused by oxygen vacancies. Oxygen vacancies in the thin films act as donor levels. When an external electric field is applied, electrons trapped in oxygen vacancies are injected into the conduction band. Therefore the leakage current densities increased, on increasing the substrate temperatures during deposition. However, the oxygen content in the films were almost constant for the oxygen partial pressure range of 20–50% in the sputtering gas [Fig. 7a]. This result revealed that the oxygen vacancies were effectively constant above an oxygen partial pressure of 20% in the sputtering gas. The decrease in the leakage current density at oxygen partial pressures above 20% of the sputtering gas could mainly be due to other charged defects (metal vacancy, void, etc) as the density of the film changes.

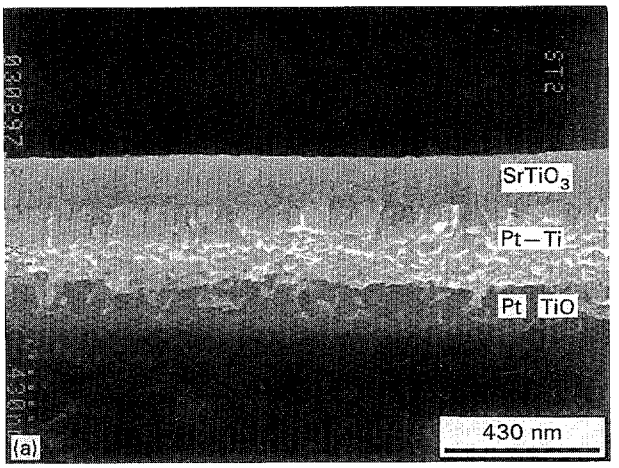
3.4. C–V curve and the thermal stability of $SrTiO_3$ thin film

Fig. 8 shows the C–V curve of a $SrTiO_3$ thin film that showed the highest dielectric constant. The shape of the C–V curve was flat and the capacitances were nearly independent of applied voltage. The dielectric constants were calculated from;

$$C = (\varepsilon_0 \varepsilon_r A)/d \quad (1)$$

and showed the highest value (ε_r = 190) at 0 V and the lowest value (ε_r = 180) at 3 V.

SEM cross-sectional and surface micrographs of a $SrTiO_3$ thin film annealed at 700 °C are shown in Fig. 9. Interdiffusion between the Pt (bottom electrode) and Ti (buffer layer) occurred and oxygen in the $SrTiO_3$ thin film diffused into the Pt/Ti layers, but the interface between $SrTiO_3$ and Pt was stable at the annealing temperature of 700 °C [Fig. 9a]. The surface morphology of the $SrTiO_3$ thin films was also



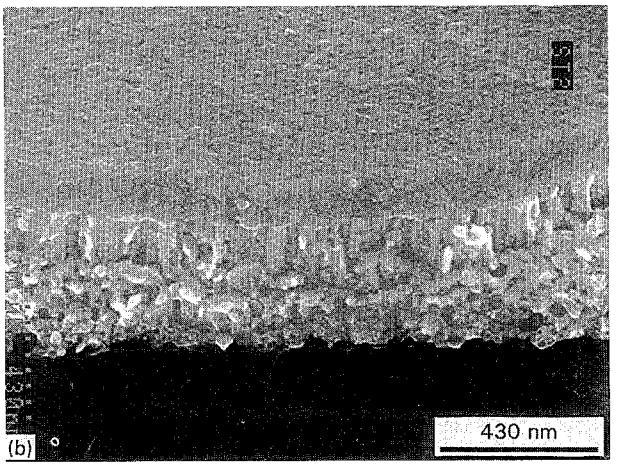


Figure 9 SEM micrographs of $SrTiO_3$ film grown at a substrate temperature of 300 °C at a gas ratio of Ar:O_2 = 5:5 followed by a furnace anneal at 700 °C. (a) SEM micrograph of cross-sectional view of $SrTiO_3$ film. (b) SEM micrograph of surface morphology of $SrTiO_3$ film.

investigated [Fig. 9b]. The surface of the $SrTiO_3$ thin films was continuous and no microcracks due to thermal expansion coefficient difference during annealing were found. The $SrTiO_3$ thin film surface was rough.

4. Conclusions

$SrTiO_3$ thin films were deposited by rf-magnetron sputtering under various sputtering conditions and heat-treated by conventional furnace annealing at various temperatures. The amorphous $SrTiO_3$ thin films crystallized into polycrystals at 600 °C.

The effect of the processing conditions on the crystal structure and electrical characteristics of $SrTiO_3$ thin films were investigated. On increasing the oxygen partial pressure in the sputtering gas, the leakage current of the $SrTiO_3$ thin films decreased. On the contrary, the dielectric constant increased with increasing the oxygen partial pressure. The leakage current and dielectric constant increased with increasing substrate temperature and post-annealing temperature.

These effects were explained by chemical composition analysis. The Sr:Ti ratio approached 1:1 with increasing oxygen partial pressure in the sputtering

gas and substrate temperature during deposition. The oxygen content in the film decreased with increased substrate temperature.

The C–V curve showed that the capacitances were nearly independent of the applied voltage. SEM micrographs show that interdiffusion between the bottom electrode (Pt) and buffer layer (Ti) occurred during post-annealing, but that the interface between $SrTiO_3$ and Pt was stable.

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