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Control of the leakage current in $SrTiO_3$ films by acceptor doping

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Stoichiometric $SrTiO_3$ (STO) films doped with Fe or Cr were prepared by r.f. magnetron sputtering technique. The effects of Fe or Cr doping in the $SrTiO_3$ films were studied on the leakage current property which was discussed by defect chemistry. The experimental results can be explained by a model in which oxygen vacancies are the key defects responsible for the leakage current. Acceptor doping, with a small concentration of Fe or Cr, has led to a substantial improvement to 10^{-9} order in the leakage current density. Above the concentration of $0.01 \sim 0.02$ mol % Fe_2O_3, Cr_2O_3, however, as the concentration increased, the leakage current increased. These acceptors in Ti^{4+} site are expected to electrically compensate for donor species such as oxygen vacancies, thereby reducing the concentration of mobile carriers that contribute to electrical conduction. Consequently, acceptor doped STO films have been shown to be superior to undoped films for applications requiring high leakage resistance, such as dynamic random access memory capacitors.
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1. Introduction

STO ($SrTiO_3$) is one of the perovskite oxides that have recently become the subject of intensive research for the dynamic random access memory (DRAM) capacitor because of their excellent dielectric properties. STO is a more attractive dielectric than other oxides because it is in paraelectric phase at the range of operating temperatures and therefore is independent of fatigue and ageing. In the DRAM capacitor, a low dielectric loss, a low leakage current, and a high breakdown strength as well as a high dielectric constant are needed [1–3]. Among them, a low leakage current is particularly important because a leakage current is often used to monitor the electrical "health" of integrated circuit systems [4]. So, it is necessary to minimize (and hence to understand the mechanism for) the high leakage current in thin perovskite titanate films in order to acquire the reliability of them in spite of their excellent dielectric properties.

It must be noted that the electrical properties depend strongly on the microstructure and the imperfection of the film that are determined by the deposition technique and ambient atmosphere during deposition [5]. STO films have been reported to exhibit n-type conductivity which results from the oxygen vacancies in high temperature deposition process. The thermodynamic analysis of possible point defects in STO has suggested that, besides the oxygen vacancies, strontium vacancies which act as intrinsic acceptor also have a dominant effect on the electrical properties. So the stoichiometric film of Sr/Ti ratio was used as optimum reference in this extrinsic doping study.

Through the present work STO films were prepared with the substrate temperature of 550 °C (leading to "in-situ" crystallization) on $Pt/Ti/SiO_2/Si$ substrate using a r.f.-magnetron sputtering technique which is a relatively simple technique and permits excellent control of film composition. The dependence of the leakage current on O_2 partial pressure in the atmosphere was studied and then the acceptor effects on the leakage current property in stoichiometric STO films were investigated by doping of Cr^{3+} or Fe^{3+} ions in films at the concentration range of $0.02 \sim 1.0$ mol %. The leakage current mechanism of the STO films is discussed in relation to oxygen vacancies in the films.

2. Experimental procedure

The sputtering conditions of STO films are shown in Table I. The substrate was $Pt/Ti/SiO_2/Si$. The Ti adhesion layer with a thickness of 25 nm and the Pt bottom electrode for the capacitor with a thickness of

TABLE I Sputtering conditions of STO films

Sputtering parameter	Conditions
Starting target	$SrTiO_3$ + 5 mol % excess SrO
Doping concentration (mol % Fe_2O_3 or Cr_2O_3)	0.01, 0.02, 0.05, 0.10, 0.50
Substrate	Pt (270 nm)/Ti (25 nm)/SiO_2 (100 nm)/Si
Substrate temperature	550 °C
r.f. power density	2.63 W cm^{-2}
Base pressure	$< 1.333 \times 10^{-4}$ Pa
Sputtering gas	Ar and O_2 (various O_2/Ar ratios)
Sputter working pressure	1.333 Pa
Substrate–target distance	4 cm
Film thickness	230 nm

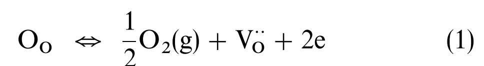
270 nm were d.c. sputter deposited at 200 °C and at room temperature on the (1 0 0) p-silicon wafers with a thermally oxidized layer, 100 nm in thickness, respectively. Base pressure for sputtering was prepared below 1.333×10^{-4} Pa using the diffusion pump and the working pressure of (Ar + O_2) gases was kept at the pressure of 1.333 Pa. The presputtering prior to the deposition of the STO films was performed in the atmosphere of Ar only for about 1 h, shuttering the substrate. Ar and O_2 gas were used for sputtering gases and O_2 percentage ratio in sputtering gases varied from 0 to 50% to investigate the dependence of the leakage current on O_2 partial pressure. Targets with various compositions were prepared by conventional ceramic powder processing with $SrTiO_3$, SrO, Fe_2O_3 and Cr_2O_3 powders. Care was taken so that the target composition was uniform. A 5 mol % excess SrO content was typically required for the starting target chemistry to obtain the stoichiometric films (which was confirmed by Rutherford backscattering spectroscopy (RBS)) because a common problem associated with preparing STO films by sputtering technique is the deficiency of Sr in the film from the differences of sputtering yield among the individual atoms. Stoichiometry of Sr/Ti ratio in the film could ensure that doping effect on the leakage current would be identical. In order to evaluate the effects of the acceptor (Cr^{3+}, Fe^{3+}) concentration on the leakage current property in stoichiometric STO films, the doping concentration varied from 0.01 mol % to 0.50 mol % for Fe_2O_3 or Cr_2O_3, respectively.

For the electrical measurement, the top electrodes of Al (300 nm thick, 200 μm in diameter) were thermally evaporated at the pressure of below 1.333×10^{-4} Pa to establish a parallel-plate capacitor geometry with the Pt bottom electrode. I–V characteristic was analysed with a HP4145B d.c. parameter analyser and leakage current density was defined as a current density when (+) 1.5 V biased to the Al top electrode. Leakage measurements were conducted on several test capacitors of each samples to verify that the observed behaviours were representative for each sample. To determine the film thickness, a step was chemically etched and the step height was measured with Tencor α-step 200 (mechanical stylus) and then it was confirmed with cross-sectional scanning electron microscopy (SEM) images, the thickness of STO film was fixed at 230 nm throughout the present work. The chemical composition of the films and the distribution of the dopant was analysed by RBS and SIMS (secondary ion mass spectroscopy), respectively.

3. Results and discussion

Correlation between the leakage current density and the O_2 percentage ratios in (Ar + O_2) sputtering gases are shown in Fig. 1. The leakage current density decreased with the inclusion of O_2 gas and with the increasing O_2 gas percentage ratio. It is obvious that oxygen vacancies play quite an important role in the leakage current mechanism in STO films, indicating n-type conductivity [3, 6–8].

Many researchers have studied the defect chemistry of the titanate ceramics over many years [3, 6–10]. According to defect chemistry, an oxygen atom is removed from the lattice and goes into the gas phase leaving the oxygen vacancy during the crystallization or post-annealing. Assuming that the oxygen vacancy is almost always doubly ionized, an oxygen vacancy with two compensation electrons ($V_O^{\cdot\cdot}$) is left behind Equation 1. As a result of this, the n-type conductivity has been observed in STO films. Its mass-action relation is expressed in terms of the thermodynamic parameter, P_{O_2}, T and ΔH. The term n is the concentration of conducting electrons to which the conductivity of the film is proportional. ΔH is the enthalpy of reduction and the square brackets [ ] indicate the concentration of the species that they enclose. Therefore, in n-type conducting region, the conductivity of the film at constant temperature decrease with increase in P_{O_2}.



$$O_O \Leftrightarrow \frac{1}{2}O_2(g) + V_O^{\cdot\cdot} + 2e \quad (1)$$

$$[V_O^{\cdot\cdot}]\,n^2 = K e^{-\Delta H/kT} P_{O_2}^{-1/2} = K'(T) P_{O_2}^{-1/2} \quad (2)$$

As shown in Fig. 1, with the inclusion of oxygen in sputtering gases, oxygen partial pressure changed from 1.333×10^{-4} Pa to the order of 1.333 Pa which is the working pressure, and therefore the leakage current could decrease markedly.

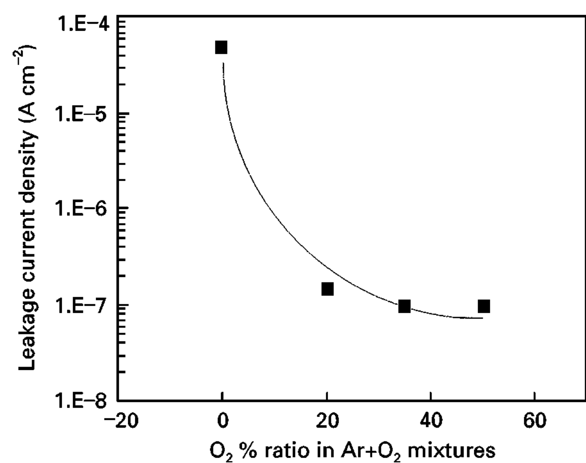
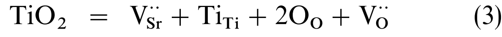


Figure 1 Dependence of leakage current density on the O_2 percentage ratio in (Ar + O_2) plasma gases. Leakage current decreased markedly by the inclusion of oxygen in sputtering gases. Substrate temperature 550 °C.

As a result, this experimental result could be explained by a model in which oxygen vacancies are the key defects responsible for the leakage current and the leakage current was expected to be controlled by controlling the concentration of the mobile carrier resulted from donor species such as oxygen vacancies.

On the other hand, there are two other possible mechanisms for $V_O^{\cdot\cdot}$ creation independent of P_{O_2}. One would relate to the Sr/Ti ratio. For Sr/Ti < 1, i.e. excess Ti, in the form of TiO_2 due to Sr deficiency, could be incorporated as follows



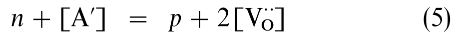
$$TiO_2 \; = \; V_{Sr}^{\cdot\cdot} + Ti_{Ti} + 2O_O + V_O^{\cdot\cdot} \qquad (3)$$

and for Sr/Ti > 1, similar corporation in relation to $V_O^{\cdot\cdot}$ could be also expressed.

However, it is reported that the solubility of excess TiO_2 or SrO are extremely small in STO films and the presence of excess TiO_2 or SrO in the solubility limit has almost no effect on the conductivity of the films, while the excess Sr or Ti out of the solubility limit, in the forms of Sr-O or Ti-O_2 planes, deform the crystal structure, resulting in the electrical degradation [11].

The other mechanism for $V_O^{\cdot\cdot}$ creation would result from acceptor impurities [12]. An acceptor impurity is an ion which has a lower-valent positive charge than the ion for which it substitutes, such as Na^+, K^+ for A site (Sr^{2+}) and Fe^{3+}, Cr^{3+}, Al^{3+}, Mg^{2+} etc. for B site (Ti^{4+}). For example, if the trivalent acceptor ion substitute for negative charged site (Ti^{4+}), a hole is left behind (Equation 4). Combined with Equation 1, for charge neutrality (Equation 5), the incorporation of acceptor ion lead to the creation of oxygen vacancies (Equation 6) during the crystallization: p is the concentration of conducting holes; A′ is a trivalent cation whose oxide A_2O_3 replaces $2TiO_2$ leaving the oxygen vacancy. If [A′] could not be neglected, the $[V_O^{\cdot\cdot}]$ could be controlled by the acceptor impurities content in the near stoichiometric region. This is essential for a detailed interpretation of the effects of impurities' addition.

$$A \; \Leftrightarrow \; A' + h \qquad (4)$$



$$n + [A'] \; = \; p + 2[V_O^{\cdot\cdot}] \qquad (5)$$

$$A_2O_3 \; \Leftrightarrow \; 2A'_{Ti} + 3O_O + V_O^{\cdot\cdot} \qquad (6)$$

As expressed in Equation 6, if Fe^{3+} or Cr^{3+} ion substitutes for Ti^{4+} site during crystallization, oxygen vacancies are created. As a result, an approximate condition of charge neutrality could be expressed (Equation 7)

$$2[V_O^{\cdot\cdot}] \; \approx \; n + [A'] \qquad (7)$$

In this study, the Fe^{3+} or Cr^{3+} ion was selected for dopant in Ti^{4+} site because of similar size in which it was likely to substitute for Ti^{4+} site [13]. Fig. 2 shows the SIMS depth profiles of the sputter-Cr^{3+}-doped STO films. The distribution of dopant in films was very uniform and identification of the concentration of Cr ion was qualitatively clear, which has led to much difference of the leakage current property. The Fe^{3+} or Cr^{3+} dopant effects on the leakage current were shown in Figs 3 and 4, respectively. The leakage current decreased to the order of 10^{-9} near $0.01 \sim 0.02$ mol % doping concentration of Fe_2O_3 or Cr_2O_3 independent of dopant species, and as the concentration of dopant increases above that, the leakage current density increases.

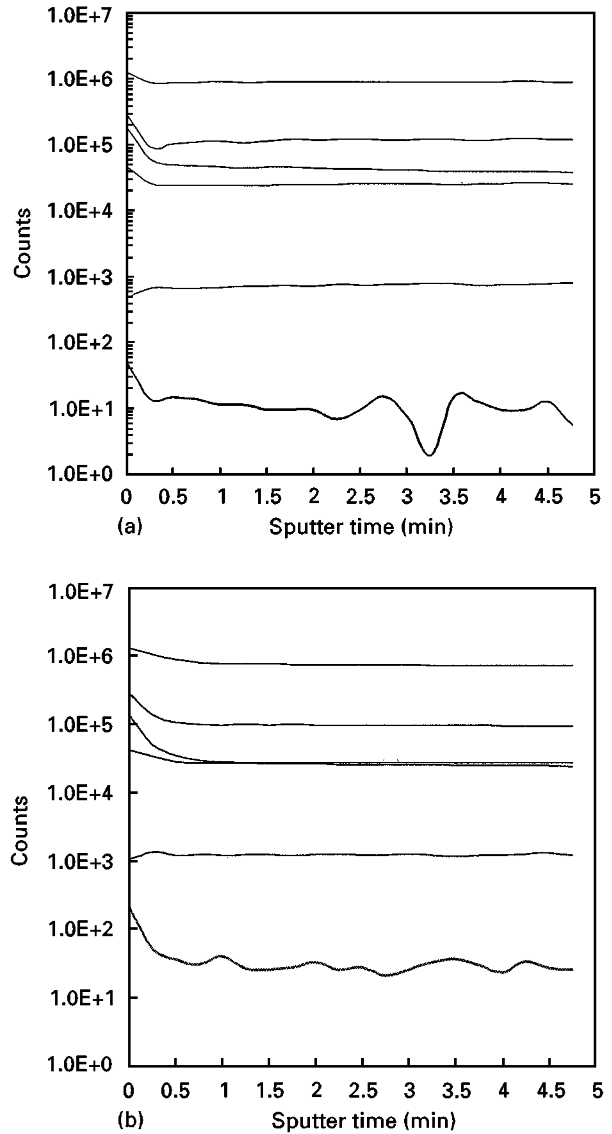


Figure 2 SIMS depth profilings of (a) 0.05 mol % and (b) 0.5 mol % Cr_2O_3 doped films. It was confirmed that Cr ions were distributed uniformly and doped as the target compositions.

The reduction reaction, Equation 1, is greatest at high temperature. If $n \gg [A']$, the combination of Equations 2 and 7 then lead to Equation 8. Assuming that the electron mobility, μ_n, is constant, the conductivity will be proportional to n

$$n \; \approx \; \{2K'(T)\}^{1/3} P_{O_2}^{-1/6} \qquad (8)$$

If [A′] cannot be neglected, however, either because of less oxygen vacancies from a stoichiometric film or because of a higher acceptor content (more than a few hundred p.p.m.), then Equations 2 and 7 lead to Equation 9 meaning that the conductivity can be controlled by acceptor concentration as a major source of defect

$$n \; \approx \; \left\{\frac{2K'(T)}{[A']}\right\}^{1/2} P_{O_2}^{-1/4} \qquad (9)$$

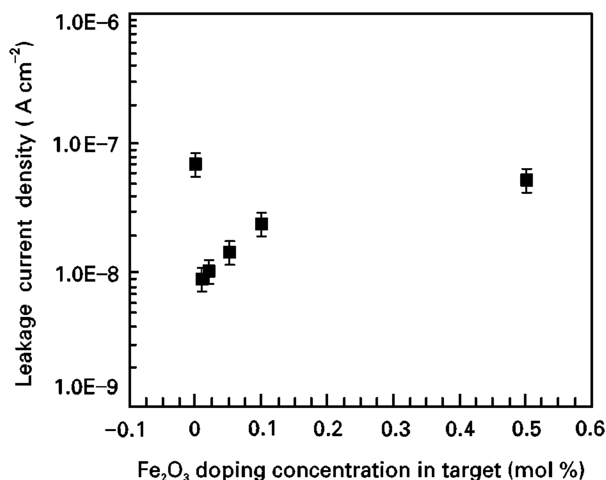


Figure 3 Dependence of leakage current density on Fe_2O_3 doping mol % in ($SrTiO_3$ + 5 mol % excess SrO) target. Substrate temperature 550 °C; O_2 ratio in (Ar + O_2) gases 50%.

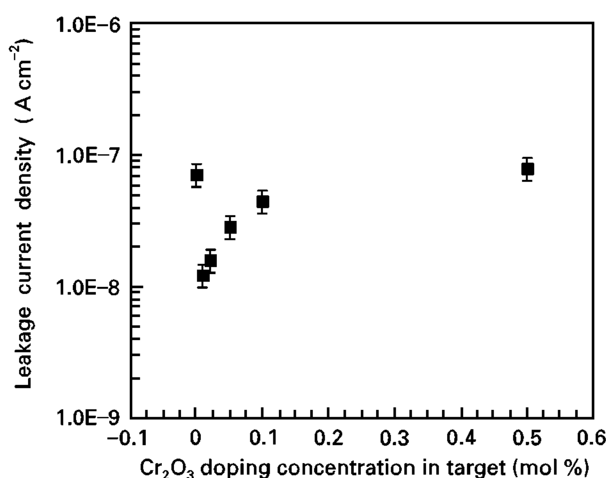


Figure 4 Dependence of leakage current density on Cr_2O_3 doping mol % in ($SrTiO_3$ + 5 mol % excess SrO) target. Substrate temperature 550 °C; O_2 ratio in (Ar + O_2) gases 50%.

Therefore, the Fe^{3+} or Cr^{3+} acceptor dopants in the stoichiometric films could electrically compensate oxygen vacancies which were generated thermodynamically at high temperature (called the "charge compensation effect") and thereby reduce the concentration of mobile carrier that would contribute to electrical conduction. However, at higher dopant concentration, introducing the hole carriers whose mobility is much less than electron carriers, resulted in the transition to p-type conduction from which the gentle increase in the leakage current resulted.

4. Conclusion

The leakage current of the films was dependent on the oxygen partial pressure as an ambient atmosphere during the deposition. It was confirmed that the oxygen vacancy was a key defect in STO films resulting in high leakage current. On the other hand, acceptor doping in Ti^{4+} sites, with Fe^{3+} or Cr^{3+}, successfully improved the leakage current property of the stoichiometric STO films. Near $0.01 \sim 0.02$ mol % doping of Fe_2O_3, Cr_2O_3, there was an improvement of about one order of magnitude which resulted from charge compensation effect between oxygen vacancies and acceptor ions. Therefore, the acceptor doping in STO films can be an alternative technique for the control of the leakage resistance in the film deposited in the process of high temperature in which the creation of oxygen vacancies are inevitable.

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