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Electrical characteristics of $SrTiO_3$ films by acceptor doping

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불순물 주입에 의한 $SrTiO_3$ 박막의 전기적 특성 개선

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Abstract Electric and dielectric properties of the $SrTiO_3$ films have been studied. The influence of impurities on $SrTiO_3$ films was evaluated to reduce the leakage current density. 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. The experimental results can be explained by a model in which oxygen vacancies are the key defects responsible for the leakage current. The $SrTiO_3$ film 200 nm in thickness with 5 mol% excess SrO fabricated in Ar/O_2 at 550℃ obtained the lowest leakage current density 1.0×10^{-9} A/cm^2. The improved results can be introduced into the capacitor dielectric of giga bit DRAM memories.

요 약 불순물 주입에 의한 $SrTiO_3$ 박막의 전기적 특성 개선에 관하여 연구하였다. 잉여 SrO가 첨가되고 Fe, Cr 이온이 불순물 도핑된 박막은 550℃, Ar/O_2비를 변화시키면서 형성되었다. 어셉터 이온 도핑에 의한 누설전류 특성이 개선됨을 알 수 있었다. 5 mol% SrO가 첨가되고, 550℃, Ar/O_2비가 5 : 5에서 형성된 $SrTiO_3$ 박막의 유전상수 값은 320, 누설전류 밀도는 1.0×10^{-9} A/cm^{2}까지 개선될 수 있었다. 이러한 결과는 고유전 박막의 전기적 특성을 향상시킴으로써 차세대 메모리 유전체 물질 개발에 응용될 수 있을 것으로 기대한다.

1. Introduction

High dielectric constant materials such as $SrTiO_3$ and $(Ba, Sr)TiO_3$ are considered the

most promising candidates for the capacitor dielectric of giga bit DRAMs. $SrTiO_3$ is one of the perovskite oxides that have recently become the subject of intensive research for their DRAM capacitor due to the excellent dielectric properties. STO is a more attractive dielectric than other oxides because it is in paraelectric phase at the range of operating temperature and therefore is independent of fatigue and aging. In 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, 2]. Among them, a low leakage current is particularly important because a leakage current is often used to monitor the electrical charateristics of integrated circuit systems [3]. 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 [4]. STO films have been reported to exhibit the n-type conductivity which is resulted 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 have also 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℃ (leading to "in-situ" crystallization) on $Pt/Ti/SiO_2/Si$ substrate using a rf-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 0.02~1.0 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 1. 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 250 nm were dc sputter deposited at 200℃ and at room temperature on the (100) p-silicon wafers with a thermally oxidized layer, 100 nm in thickness respectively. Base perssure for sputtering was prepared below 10^{-6} torr using the diffusion pump and the working pressure of $(Ar+O_2)$ gases was kept at the pressure of 1.0×10^{-2} torr. The presputtering prior to the deposition of the STO films was performed in the atmosphere

Table 1
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℃
RF power density	2.63 W/cm^2
Base pressure	$< 10^{-6}$ torr
Sputtering gas	Ar and O_2 (various O_2/Ar ratios)
Sputter working pressure	1.0×10^{-2} torr
Substrate-target distance	4 cm
Film thickness	200 nm

of Ar only for about one hour, shuttering the substrate. Ar and O_2 gas were used for sputtering gases and O_2 % 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 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 in the pressure of below 10^{-6} torr to establish a parallel-plate capacitor geometry with the Pt bottom electrode. I-V characteristic was analyzed with a HP4145B DC parameter analyzer and leakage current density was defined as a current density when (+) 1.5 V biased to Al top electrode. Leakage measurements were conducted on several test capacitors of each samples to verify that the observed behaviors were representatives 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 SEM im-

ages, the thickness of STO film was fixed 200 nm through the present work. The chemical composition of the films and the distribution of the dopant was analyzed by RBS (Rutherford Backscattering Spectroscopy) and SIMS (Secondary Ion Mass Spectroscopy) respectively.

3. Results and discussion

Correlation between the leakage current density and the O_2 % ratios in $(Ar+O_2)$ sputtering gases were shown in Fig. 1. The leakage current density decreased with the inclusion of O_2 gas and with the increasing O_2 gas % ratio. It is obvious that oxygen vacancies play quite an important role in the leakage current mechanism in STO films, indicating n-type conductivity [2,4-7].

Many researchers have studied the defect chemistry of the titanate ceramics over many years [2,5-9]. According to defect chemistry, an oxygen atom is removed from

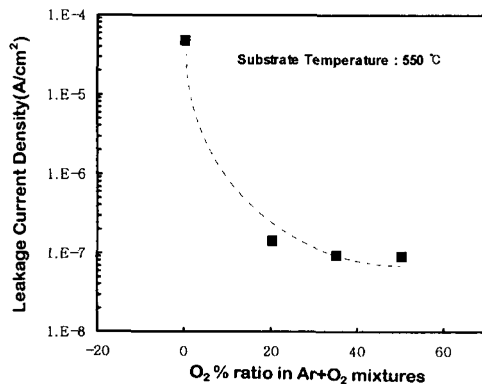
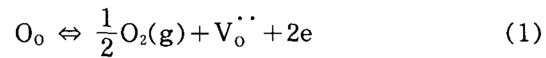


Fig. 1. Dependence of leakage current density on the O_2 % ratio in $(Ar+O_2)$ plasma gases.

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 is left behind (Eq. (1)). As a result of this, the n-type conductivity has observed in STO films. Its mass-action relation is expressed in terms of the thermodynamic parameter, P_{O2}, T, ΔH (Eq. (2)). The term of n is 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_{O2}.



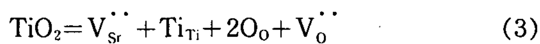
$$O_O \Leftrightarrow \frac{1}{2}O_2(g)+V_O^{\cdot\cdot}+2e \quad (1)$$

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

As shown in Fig. 1, with the inclusion of oxygen in sputtering gases, oxygen partial pressure changed from 10^{-6} torr to the order of 10^{-2} torr which is the working pressure and therefore the leakage current could decrease markedly.

As a result, this experimental results could be explained by a model in which oxygen vacancies are the key defects responsible for the leakage current and the tleakage 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 $V_O^{\bullet\bullet}$ creation independent of P_{O2}. 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



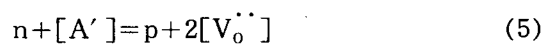
$$TiO_2 = V_{Sr}^{\bullet\bullet} + Ti_{Ti} + 2O_O + V_O^{\bullet\bullet} \quad (3)$$

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

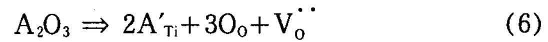
However, it is reported that the solubility of excess TiO_2 or SrO are extremely small in STO films and the presence of excess TiO_2 or SrO in the solubility limit has almost no effect on the conductivity of the films, while the excess Sr or Ti out of the solubility limit, in the forms of Sr-O or Ti-O_2 planes, deform the crystal structure, resulting in the electrical degradation [10].

The other mechanism for $V_O^{\bullet\bullet}$ creation would result from acceptor impurities [11]. 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 left behind (Eq. (4)). Combined with Eq. (1), for charge neutrality (Eq (5)), the incorporation of acceptor ion lead to the creation of oxygen vacancies (Eq. (6)) during the crystallization. p is the concentration of conducting holes. A′ is trivalent cation whose oxide A_2O_3 replaces $2TiO_2$ leaving the oxygen vacancy. If [A'] could not be neglected, the $[V_O^{\bullet\bullet}]$ 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.

$$A \Leftrightarrow (A')3+)h \quad (4)$$



$$n + [A'] = p + 2[V_O^{\bullet\bullet}] \quad (5)$$



$$A_2O_3 \Rightarrow 2A'_{Ti} + 3O_O + V_O^{\bullet\bullet} \quad (6)$$

As expressed Eq. (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 as eq. (7).

$$2[V_O^{\bullet\bullet}] \approx n + [A'] \quad (7)$$

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 [11]. Figure 2 is 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 Fig. 3,4 respectively. The leakage current decreased to 10^{-9} order near 0.01~0.02 mol% doping concentration of Fe_2O_3 or Cr_2O_3 independent of dopant species and as the concentration of dopant increase above that, the leakage current density increase.

The reduction reaction, Eq. (1), is great-

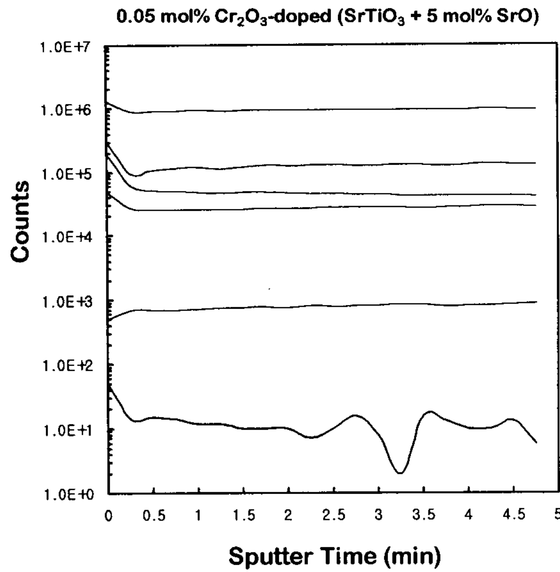


Fig. 2. SIMS depth profilings of 0.05 mol% Cr_2O_3.

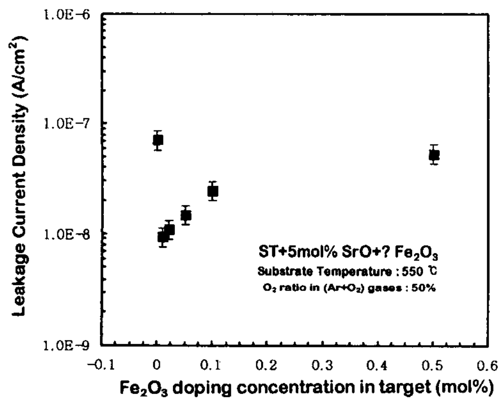


Fig. 3. Dependence of leakage current density on Fe_2O_3 doping mol% in ($SrTiO_3$+5 mol % excess SrO) target.

est at high temperature. If n ≫ [A'], combination of Eq. (2) and (7) then lead to Eq. (8). Assuming that the electron mobility, μ_n, is constant, the conductivity will be proportional to n.

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

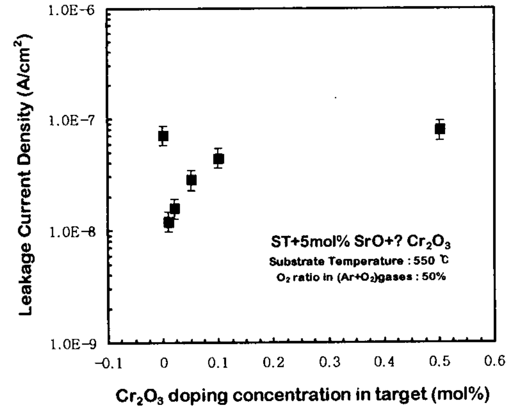


Fig. 4. Dependence of leakage current density on Cr_2O_3 doping mol% in ($SrTiO_3$+5 mol % excess SrO) target.

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

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

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 "charge compensation effect") and thereby reduced the concentration of mobile carrier that would contribute to electrical conduction. However, 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. Conclusions

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 the 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 0.01~0.02 mol% doping of Fe_2O_3, Cr_2O_3, there was an improvement of about 1 order of magnitude which resulted from charge compensation effect between oxygen vacancies and acceptor ions. The $SrTiO_3$ film 200 nm in thickness with 5 mol% excess SrO fabricated in Ar/O_2 at 550℃ obtained the lowest leakage current density 1.0×10^{-9} A/cm^2. The improved results can be introduced into the capacitor dielectric of giga bit DRAM memories.

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