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THE EFFECTS OF ACTIVATED OXYGEN ON REDUCTION IN LEAKAGE CURRENT OF PZT THIN FILMS.

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The crystallization behavior of PZT thin films during RTA were examined. The film with excess Pb content found to crystallize uniformly. To reduce the leakage current for the PZT film with excess Pb, activated oxygen annealing was used and it decreased to 1/4000 (3×10^{-7} A/cm^2).

1. INTRODUCTION

Thin films of ferroelectric materials with ABO_3 - type structure such as $PbTiO_3$, $Pb(Zr,Ti)O_3$, $(Pb,La)(Zr,Ti)O_3$, $SrTiO_3$ and $(Ba,Sr)TiO_3$ have attracted much attention for memory applications. Because lead has low affinity for oxygen, many efforts have been made to realize good insulating properties for PZT thin films. Post-deposition annealing in O_2 ambient at high temperature (>700°C) are often employed, but this process will cause problems such as inter-diffusion of electrode materials and PZT thin films [1], oxidation of barrier layer materials (Pt/Ta) [2], and re-evaporation of lead from the PZT film. Furthermore, processing temperature should be as low as possible to insure compatibility with underlying MOS transistor process for memory applications. In this study, atomic oxygen produced by RF discharge were used to diminish the oxygen vacancy at low processing temperature.

2. FILM PREPARATION

The films studied in the present work were prepared by RF magnetron sputtering on platinum coated (100) Si substrate [Pt(100 nm)/SiO_2(100 nm)/Si]. The details of sputtering procedure were reported in earlier report [3]. The films were sputtered at 200°C substrate temperature, and then rapidly thermal annealed to obtain perovskite phase.

The crystallization behavior was examined by XRD. The heating rate and annealing time was kept constant at 10°C/sec and 60 seconds respectively.

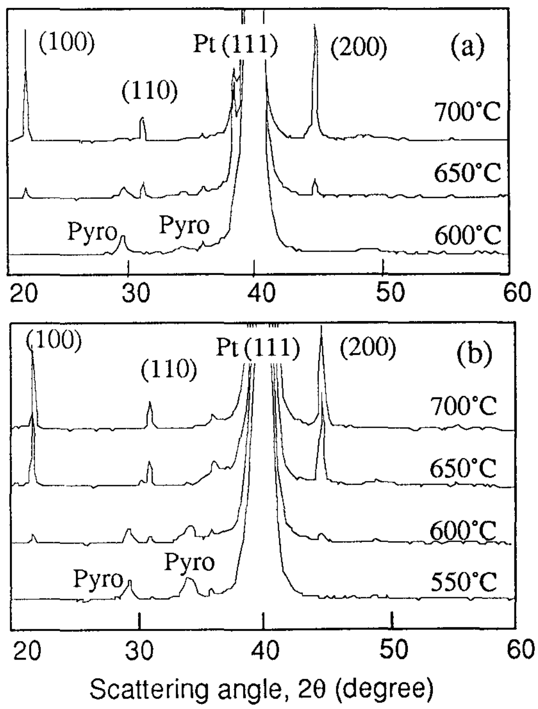

Figure 1. XRD patterns of PZT thin films for different annealing temperature.
(a) near-stoichiometric lead content, (b) 10% excess lead

As can be seen in Fig. 1(a), the PZT film with near-stoichiometric lead content starts to crystallize to perovskite structure at 650°C. However there still exists a small fraction of pyrochlore phase even at 700°C.

For the film with 10% excess lead., crystallization starts at 600°C. At an annealing temperature of 700°C, pyrochlore phase disappeared and the film exhibited pure perovskite phase, as shown in Fig. 1(b).

Figure 2 shows the optical microscope views for PZT film that was crystallized by RTA at 700°C. Crystalline islands appear on the surface of the PZT film with near-stoichiometric lead content. These islands are 5 -10 microns in size. The surrounding areas are not crystallized, and have grain size around 50 nm.

In contrast to the film with stoichiometric lead content, the film with 10% excess lead crystallized uniformly. According to these results, excess lead supposed to promote the nucleation.

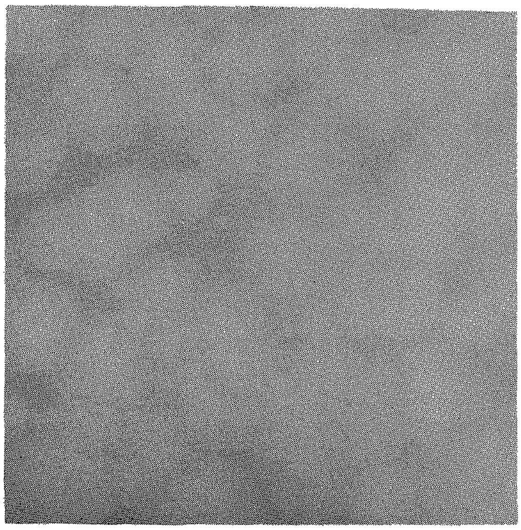

Figure 2 Optical microscope views for PZT film with near-stoichiometric lead content.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Leakage Current Characteristics of RTA crystallized PZT thin films

The leakage current density for RTA crystallized PZT film with near stoichiometric lead content was as low as $2X10^{-7}$ A/cm^2 without atomic oxygen annealing, however, the yield of capacitor is only 20 - 30 % because of island structure described in previous section.

For a PZT film with 10% excess lead, the leakage current density was large because excess lead existed as metal, and there were many oxygen vacancies in PZT itself.

3.2 Activated Oxygen Treatment

To reduce leakage current, PZT films with excess Pb were annealed in the activated oxygen atmosphere. RTA crystallized films were placed in vacuum chamber, and it evacuated to $1X10^{-7}$ torr before the oxygen gas introduced. It takes about 20 minutes to stabilize RF plasma, and films were heated to 550°C during this period. When the stable temperature had been reached, atomic oxygen was supplied and annealed for 30 min. The background oxygen pressure is $5X10^{-5}$ torr. Films were cooled to 200°C at a rate of 20°C/min. with the plasma source turned on.

The species supplied from the discharge chamber were examined by plasma emission spectroscopy. As shown in Fig. 3, the atomic oxygen line (777.5 nm) is much more intense than the other lines. This line corresponds to the emission by the transition from 3p ^5P state to 3s $^5S^0$ state. Thus the main particles supplied from rf plasma is atomic oxygen that is activated about 11 eV from the ground state. The other weak peaks at 394.7 nm, 436.9 nm, 532.9 nm, 615.8 nm, 645.7 nm, 700.2 nm, and 725.5 nm are also

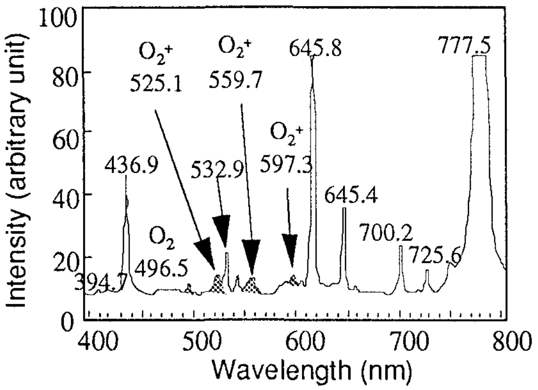

Figure 3. Plasma emission spectra of atomic oxygen source.

atomic oxygen lines. Oxygen ion bombardments have been reported to cause damage to film [4]. Since the lines associated with oxygen ion (525.1 nm, 559.7 nm, 597.3 nm) are much less intense, few charged particles are bombard on PZT thin films.

After the atomic oxygen annealing, the film has an improved crystallinity as shown in Fig. 4.

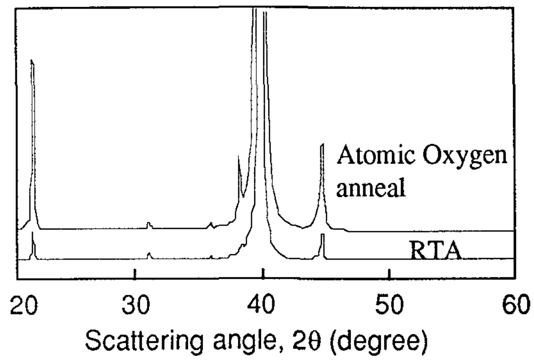

Figure 4. XRD patterns of PZT thin films before and after atomic oxygen annealing

3.3 Oxygen concentration

Figure 5 shows the depth profiles of PZT film concentration obtained by secondary ion mass spectroscopy (SIMS). The PZT film deposited with 10% excess lead was examined. The oxygen concentration is increased and lead content is decreased after atomic oxygen annealing. The oxygen atoms might be incorporated into crystal lattice and excess lead re-evaporated during atomic oxygen annealing.

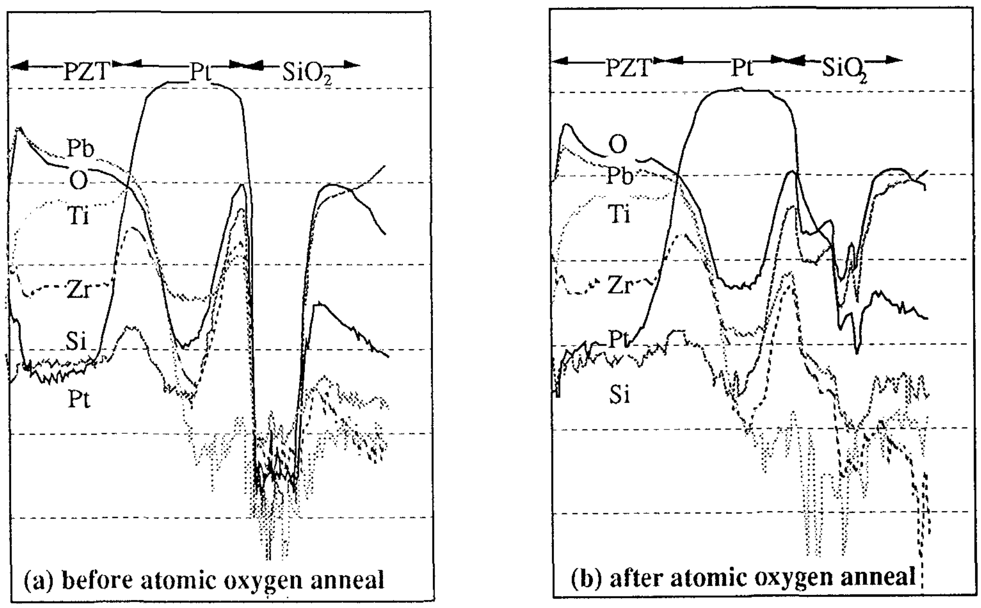

Figure 5. The dipth profiles of concentration by SIMS for a RTA crystallized PZT thin film (a) before, and (b) after atomic oxygen anneling.

Although the annealing temperature was as low as 550°C, platinum found to diffuse into PZT thin films and SiO2.

3.4 Electrical properties of activated oxygen annealed PZT thin films

The typical leakage current characteristics of PZT film with 10% excess lead before and after atomic oxygen annealing is shown in Fig. 6.

For a 100 nm-thick PZT film, it can be reduced to 1/4000 (3×10^{-7} A/cm^2 at 100 kV/cm) by atomic oxygen treatment. The yield of capacitor improved to 70 - 80 % for atomic oxygen annealed film with excess lead.

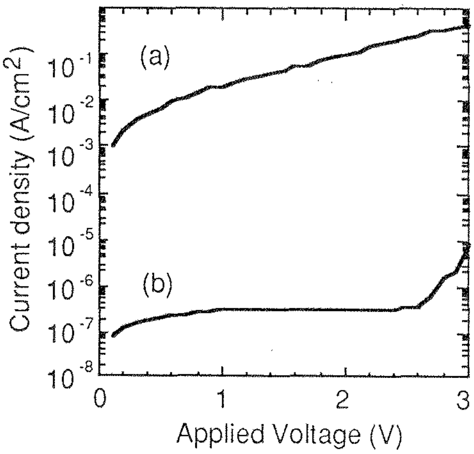

Figure 6. Leakage current densities for a PZT thin film (a) before, and (b) after atomic oxygen anneling.

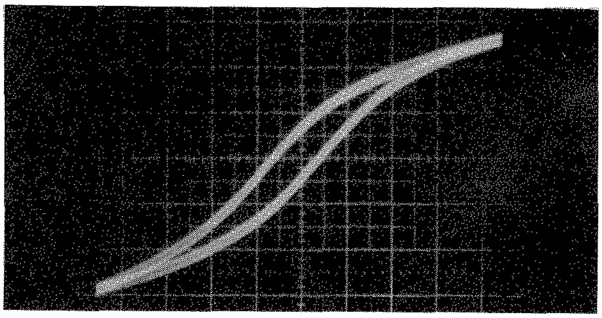

Figure 7 Polarization hysteresis loop for an activated oxygen annealed PZT thin film

The ferroelectric behavior was investigated by observing the polarization hysteresis, which is shown in Fig. 7, for the atomic oxygen annealed PZT film with 10% excess lead. This film has a high storage charge density of 90 fC/cm^2 for 1.5V voltage swing.

4. CONCLUSIONS

The excess lead of about 10% need to obtain the PZT film that is crystallized uniformly without island structure. The oxygen vacancies in PZT thin films were successfully reduced by atomic oxygen annealing. The leakage current density for a 100-nm PZT thin film decreased to 1/4000 (3×10^{-7} A/cm^2 at 100 kV/cm) and yield of ferroelectric capacitor was improved.

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