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Effects of Oxygen Annealing of MgO Thin Films on the Phase Formation and the Electrical Properties of PZT/MgO/Si Structure

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The effects of oxygen annealing on the carbon content in MgO thin films were investigated. MgO thin films were deposited on Si(100) substrate at different temperatures of 400 to 700°C and different deposition rates of 3.4 to 11.6 Å/min. Using rf magnetron sputtering method. Carbon content change on the surface of MgO thin films with the oxygen annealing at different temperatures was investigated using various method. The carbon content decreased as the annealing temperature increased. $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT) thin films were deposited on the MgO/Si(100) substrates. The effects of carbon content on the phase formation and the electrical properties of PZT thin films were also investigated.

Key words: PZT/MgO/Si thin films, Ferroelectrics, Oxygen annealing, Phase formation, Electrical properties

I. Introduction

It is well known that the epitaxy and the properties of films strongly depend on the underlying films such as buffer layers and the substrates. For example, the ferroelectric thin films grown epitaxially to a certain direction had shown much better electrical properties than the films grown randomly.[1] Moreover, the quality of the buffer layers, such as crystallinity and impurities, affects the epitaxy and the properties. Hayakawa *et al.*[2] observed that the crystallinity and the superconducting properties of $YBa_2Cu_3O_{7-x}$ (YBCO) thin films grown on MgO substrates were evidently improved by annealing the substrate. Consequently, the preparation of high quality buffer layers and substrates is a key issue for the epitaxial growth and the properties of the films on the buffer layers and the substrates. Recently, MgO single crystal has been used for the deposition of $Pb(ZrTi)O_3$ (PZT) and YBCO films because MgO single crystal is very stable and has only a small lattice mismatch with both PZT and YBCO films, which ensures the epitaxial growth. With the same reason, MgO thin films have been widely used for the buffer layers between the films and Si substrates because of the device integration and the economic reason. It has been reported that MgO thin films adsorb carbon at the ambient atmosphere, and carbon contamination affects negatively the epitaxial growth and the properties of the films deposited on MgO films.[3,4] So it has been a key issue for the epitaxial growth of upper PZT and YBCO films to prevent the carbon contamination of underlying MgO thin films.

The effects of oxygen anncaling on the carbon content and the crystallinity of MgO films and the electrical properties of PZT films deposited on MgO films were investigated in this study.

II. Experimental Procedure

1. Deposition of MgO Films

MgO thin films were deposited using rf magnetron sputtering. The major experimental parameters being changed in this study were substrate temperature and deposition rate. The substrate temperature was varied from 400°C to 700°C, and the deposition rate were from 3.4 Å/min. to 11.6 Å/min. to find an optimum processing condition for the formation of (100) oriented MgO thin films which are required for the (100) oriented growth of PZT thin films. A relationship between the deposition rate and the orientation of the films deposited at 600°C was investigated by varying the sputtering power. 600°C was chosen because the films deposited at that temperature showed a mixed orientation in a prior study.[5] MgO target of 99.9% purity was used. P-type Si(100) single crystal were used as substrates. Experimental processing parameters for the deposition of MgO films are summarized in Table 1. After MgO deposition, oxygen annealing was carried out at different temperatures from

Table 1. Experimental Processing Parameters for the Deposition of MgO thin Films

Material	MgO
Substrate	Si p-type(100)
Substrate temperature	400~700°C
Working pressure	1.2×10^{-2} torr
Deposition rate	3.4/min.~11.6/min
OA temperature	700~900°C
OA time	3 hrs

Table 2. Experimental Processing Parameters for the Deposition of PZT thin Films

Substrate	MgO/Si
Deposition temperature	Room temperature
Deposition Time	60 min
Annealing Temperature	700
Annealing Time	20 min

700°C to 900°C for 3 hrs. in the furnace. The crystallinity and the orientation of deposited films were analyzed using x-ray diffraction method (XRD) with Cu Kα radiation and XRD pole figure, and the microstructure was observed using scanning electron microscopy (SEM) and Auger electron spectroscopy (AES).

2.2. Deposition of PZT Films

PZT films were deposited on the MgO/Si(100) substrates using rf magnetron sputtering. The films were amorphous when they were deposited at room temperatures and were crystallized in oxygen ambient at 700°C for 20 min. using rapid thermal annealing (RTA). The crystallization temperature and RTA process were chosen in this study to minimize the annealing effect on the MgO films which were annealed at the same or higher temperature and longer duration. A typical thickness of the PZT thin films was about 450 nm. Experimental processing parameters are summarized in Table 2. The crystallinity and the orientation of the deposited film were analyzed by XRD with Cu Kα radiation, and the interface between the PZT thin film and the buffer layer was observed by SEM and AES. The polarization vs. electric field (P-E) hysteresis curve of PZT/MgO/Si was measured by RT66A.

Table 3. Comparison between the Properties of MgO(100) and MgO(111)

Plane	(100)	(111)
Surface energy(eV/nm^2)	21.5	31.3
Lattice mismatch with Si(100)	3.2%	0.7%

III. Results and Discussion

3.1. Deposition of MgO Films

The deposition temperature and the deposition rate have dominant effects on the orientation of MgO thin films and changed them in this study. The XRD patterns of MgO thin films deposited at different temperatures are shown in Fig. 1. (111) oriented MgO thin film was grown at 400°C while (100) oriented MgO thin film was at 700°C. We may speculate that this orientation change was due to the competition between the surface energy of MgO and the lattice mismatch with Si(100)[5] during the crystallization process. Comparison between the properties of MgO(100) and MgO(111) are shown in Table 3. At relatively low temperature such as 400°C, (111) oriented MgO thin film was observed because the attached atoms and molecules have not sufficient thermal energy to rearrange to (100). At relatively high temperature such as 700°C, (100) oriented MgO thin film was grown because the attached atoms and molecules have sufficient thermal energy to rearrange. The surface energy of (100) is lower than that of (111), and (100) of MgO is easier to grow than (111) when enough thermal energy is provided at high temperature. But the lattice mismatch between (111) of MgO and Si(100) is smaller than that between (100) and Si(100) and (111) is easier to grow when insufficient thermal energy is provided for atomic rearrangement.

The XRD patterns of MgO thin films at 600°C with differ-

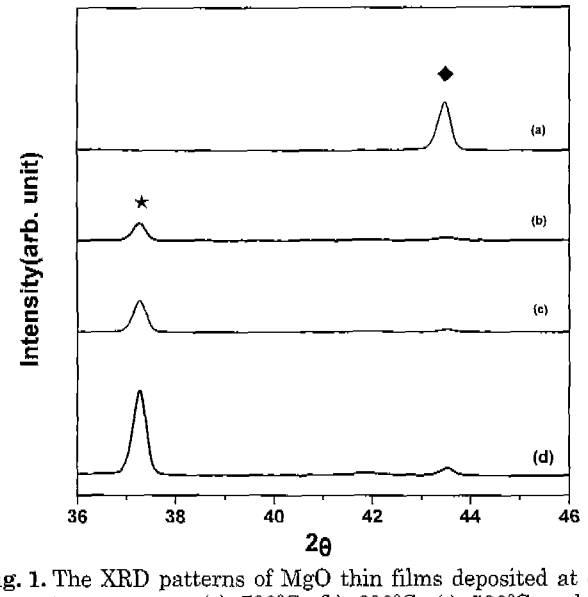

Fig. 1. The XRD patterns of MgO thin films deposited at different temperatures (a) 700°C, (b) 600°C, (c) 500°C and (d) 400°C (★: MgO(111) and ◆ : MgO(200)).

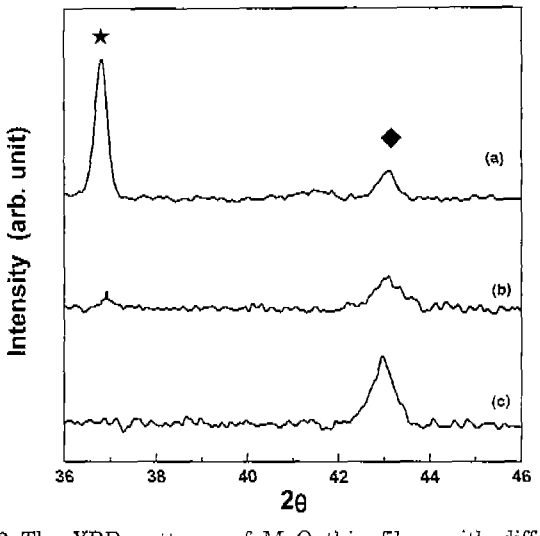

Fig. 2. The XRD patterns of MgO thin films with different deposition rates (a) 11.6 Å/min., (b) 6.5 Å/min. and (c) 3.4 Å/min. (★: MgO(111) and ◆ : MgO(200)).

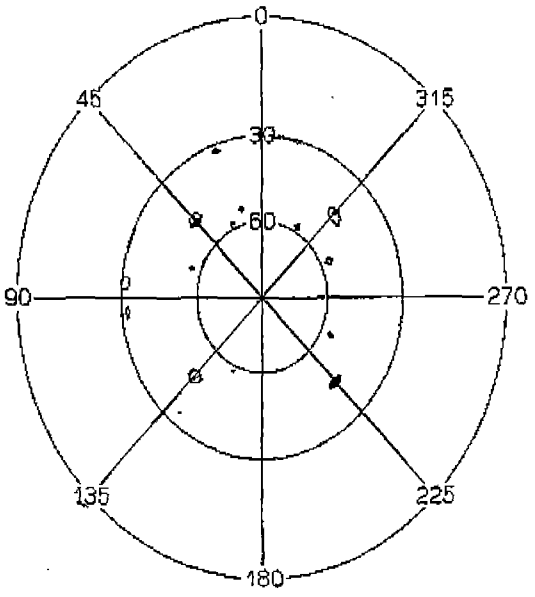

Fig. 3. Pole figure taken from the MgO(100) deposited at 600°C and 3.4 Å/min.

ent deposition rates are shown in Fig. 2. At high deposition rate, the mixture of (111) and (100) oriented MgO thin film was grown. At low deposition rate, (100) oriented MgO thin film was grown. It may be also speculated that observed orientation change was due to the time when the attached atoms and molecules rearrange.[5] Fig. 3 shows the pole figure of MgO(100) deposited at 600°C and 3.4 Å/min.. Strong 4-fold symmetrical (100) contours with a few minor spots were observed, which indicates that the film orientation is also extended being parallel to the surface of substrate.

3.2. Oxygen Annealing Effects on Carbon Content in MgO Films

Fig. 4(a), (b) and (c) show SEM images of the surface of MgO thin films stored in air atmosphere for various durations. Surface of MgO thin films degraded as the exposure time increased. As deposited, clean surface without significant carbon contamination is observed We thought that the black dots in Fig. 4 were due to the surface carbon adsorption of MgO thin films. So we tried to reduce this carbon contamination using annealing in oxygen.

Fig. 5(a), (b) and (c) show SEM images of the surface of MgO thin films annealed in oxygen at various temperatures. The number and size of black spots were decreased, but they are still observed after oxygen annealed in oxygen at 700°C and 800°C for 3 hrs. At 900°C for 3 hrs, the black spots were disappeared, but the surface morphology was not same as the deposited film. The carbon was removed by oxygen annealing, which was conformed by AES depth study. For crystallinity, there was no difference between films before and after annealing in oxygen. From this result, we thought that the carbon contamination of MgO thin films was confined only to the surface.

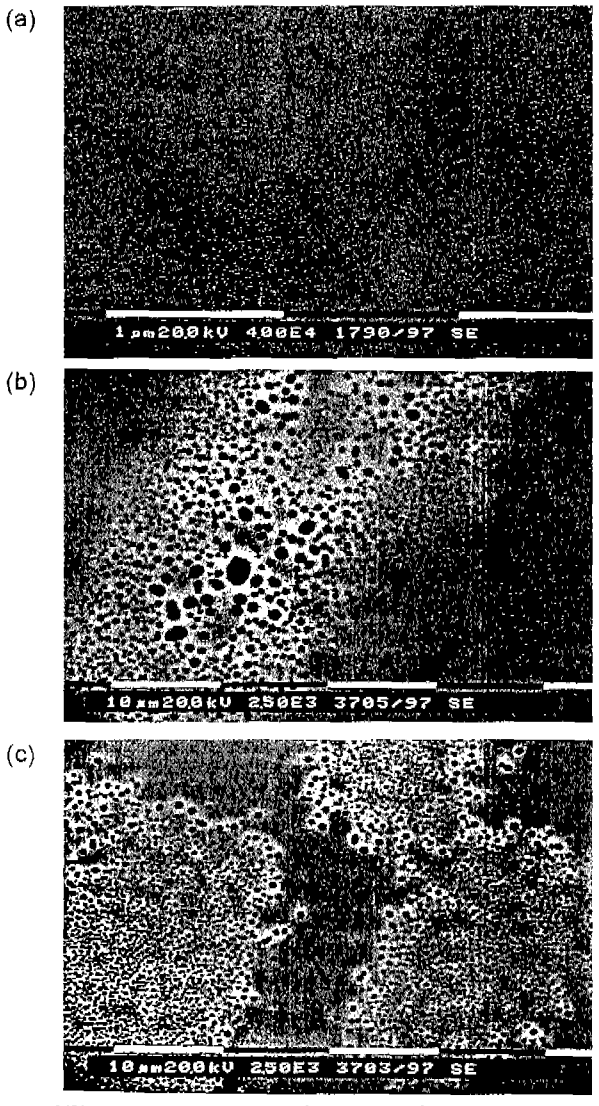

Fig. 4. SEM images of the surface of MgO thin films stored in air for various durations (a) as deposited, (b) 1 day and (c) 3 days

3.3. The effects of carbon contamination of MgO on the PZT thin film

At first we compared two cases, PZT thin films deposited by the in-situ processing and PZT thin films deposited on MgO thin films stored in air atmosphere for 1 day.

The XRD patterns of PZT thin films on MgO/Si substrates are shown in Fig. 6. Fig. 6(a) is the XRD pattern of PZT film deposited without breaking vacuum (in-situ) after the deposition of MgO film. Fig. 6(b) is the XRD pattern of PZT film on MgO film stored in air atmosphere for 1 day. As shown in this figure, PZT thin film by in-situ processing shows the perovskite peaks, while PZT thin film on MgO thin films stored in air atmosphere for 1 day dose not show the perovskite peaks. Poor crystallinity of the PZT film deposited on MgO film stored in air atmosphere for 1 day may be specu-

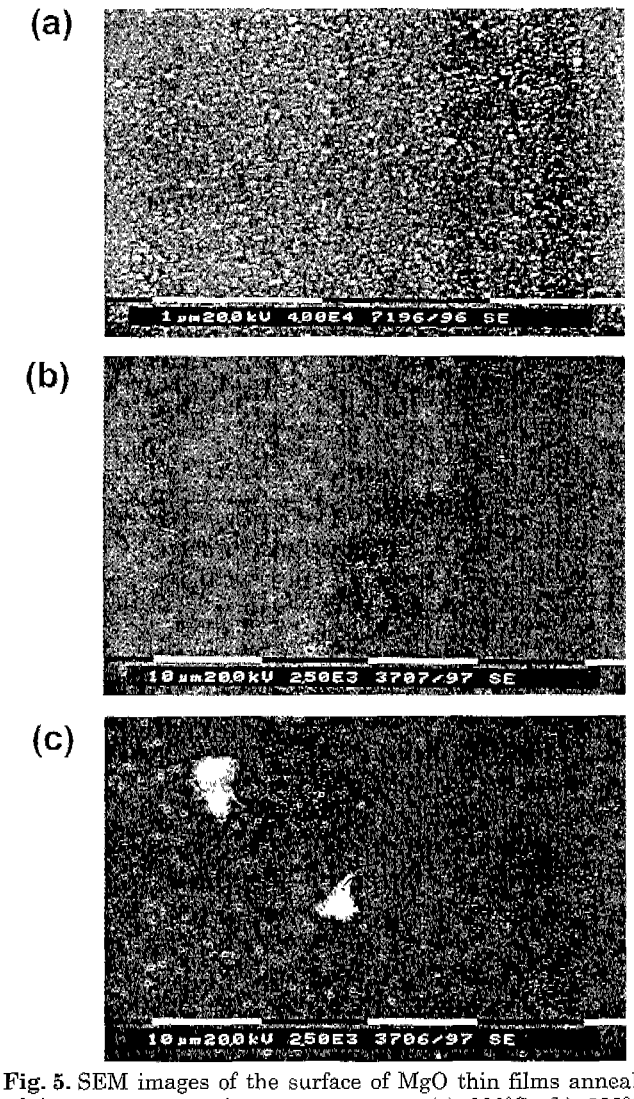

Fig. 5. SEM images of the surface of MgO thin films annealed in oxygen at various temperatures (a) 900°C, (b) 800°C and (c) 700°C for 3 hrs.

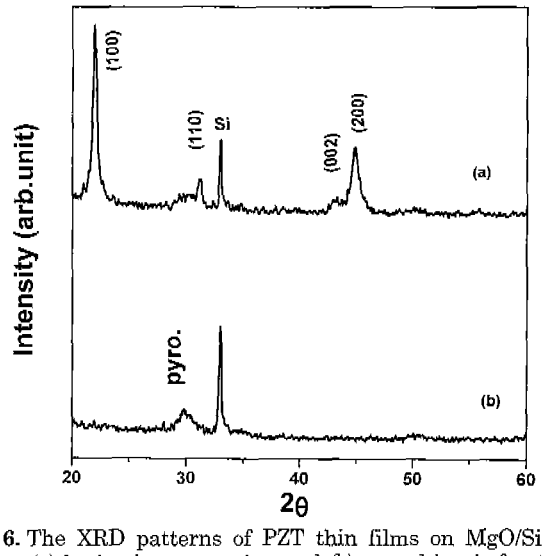

Fig. 6. The XRD patterns of PZT thin films on MgO/Si substrates (a) by in-situ processing and (b) stored in air for 1 day.

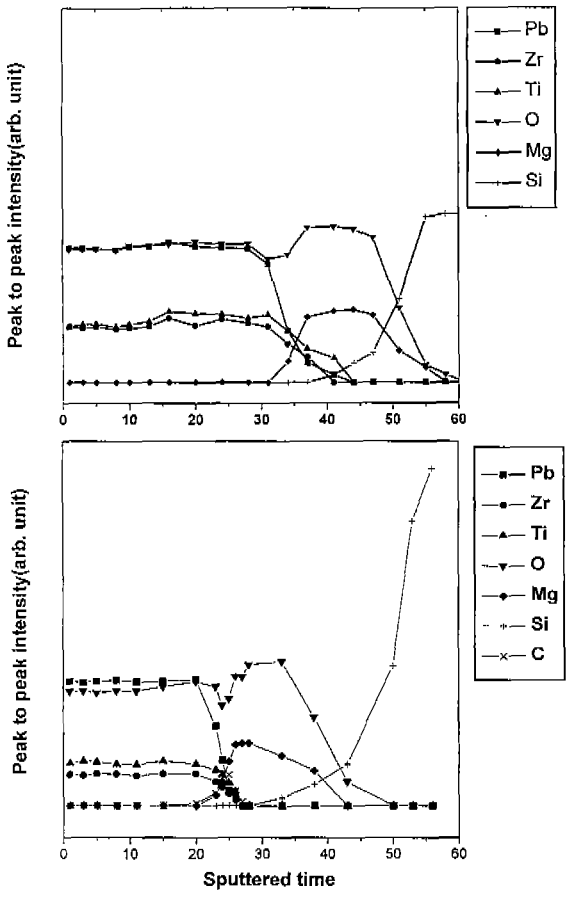

Fig. 7. The Auger depth profiles of PZT/MgO/Si structure (a) by in-situ processing and (b) stored in air for 1 day.

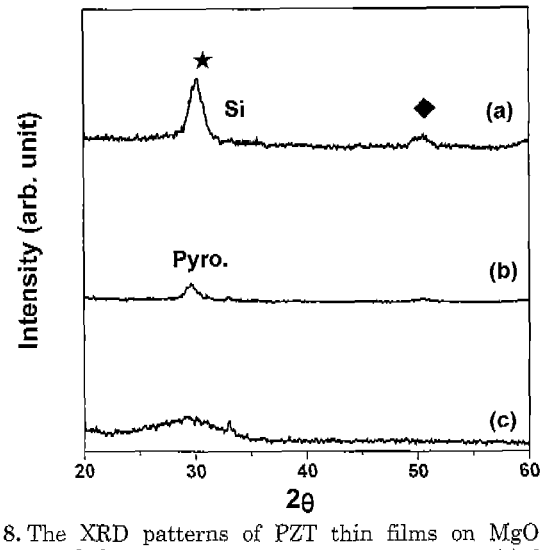

Fig. 8. The XRD patterns of PZT thin films on MgO thin films annealed in oxygen at various temperatures (a) 900°C, (b) 800°C and (c) 700°C for 3 hrs (★: PZT(110) and ◆: PZT(211)).

lated to the poor crystallinity of degraded surface of MgO film and/or the lattice distortion due to the carbon contamination.

The Auger depth profiles of PZT/MgO/Si structure are

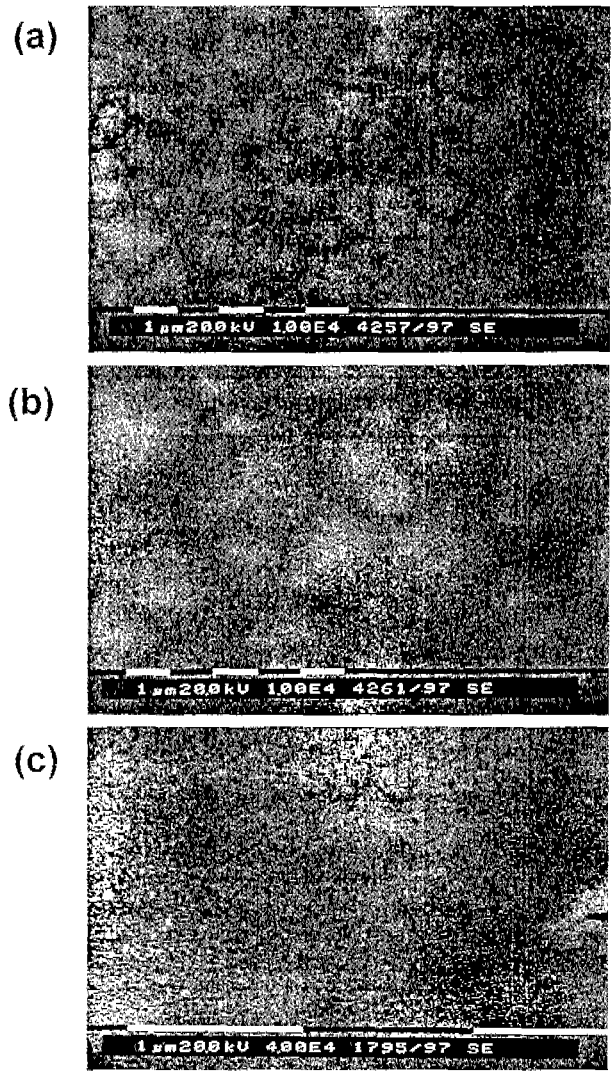

Fig. 9. SEM images of the surface of PZT thin films on MgO thin films annealed in oxygen at various temperatures (a) 900°C, (b) 800°C and (c) 700°C for 3 hrs.

shown in Fig. 7(a) and (b). For the PZT thin films on MgO thin films exposed to air, carbon exists at the interface between PZT and MgO while carbon is not shown for PZT thin film by in-situ processing.

We deposited PZT thin films on MgO thin films annealed in oxygen at various temperatures. Fig. 8 shows the XRD patterns of PZT thin films on MgO thin films annealed in oxygen at various temperatures. There are no perovskite peaks in the PZT thin film on MgO film annealed at 700°C and 800°C, but at 900°C, the perovskite peaks are shown. Carbon contamination still existed in the MgO film annealed at 700°C and 800°C, but was removed in the film annealed at 900°C. So the PZT thin film on MgO film annealed at 900°C consists of the perovskite phase, but the films annealed at 800°C and 700°C do not.

The surface SEM images of PZT thin films on MgO thin films annealed in oxygen at various temperatures are

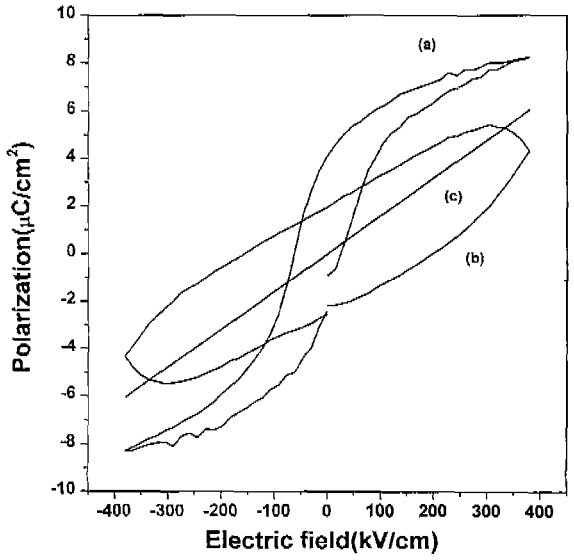

Fig. 10. The P-E hysteresis curve of PZT/MgO/Si structure annealed in oxygen at various temperatures (a) 900°C, (b) 800°C and (c) 700°C for 3 hrs.

shown in Fig. 9 (a), (b) and (c). The PZT films on the MgO films annealed in oxygen at 700°C and 800°C consist of the amorphous phase and the PZT film at 900°C consists of the perovskite phase.

The electrical properties of PZT/MgO/Si structure were measured. Fig. 10 shows the P-E hysteresis curve of PZT/MgO/Si structure. Carbon contamination still existed in the MgO film annealed at 700°C and 800°C, but was removed in the film annealed at 900°C. So the PZT thin film on MgO film annealed at 900°C consists of the perovskite phase and shows the typical P-E hysteresis , but the films annealed at 800°C and 700°C does not.

IV. Conclusions

The effects of oxygen annealing at various temperatures on the carbon contamination of MgO thin films were examined. The SEM and AES results indicated the evident improvement. The improvement of the crystallinity and the electrical properties of PZT thin films on MgO by oxygen annealing was also examined. The PZT thin film on MgO film annealed in oxygen at 900°C consists of the perovskite phase and shows the typical P-E hysteresis.

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