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METALORGANIC CHEMICAL VAPOR DEPOSITION OF FERROELECTRIC $Pb(Zr_XTi_{1-X})O_3$THIN FILMS

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Abstract – Ferroelectric $Pb(Zr_XTi_{1-X})O_3$ (PZT) thin films were successfully deposited on $Pt/Ti/SiO_2/Si$ substrates by metalorganic chemical vapor deposition (MOCVD). $Pb(C_2H_5)_4$, $Zr(O\text{-}t\text{-}C_4H_9)_4$, and $Ti(O\text{-}i\text{-}C_3H_7)_4$ were used as metalorganic precursors. Variations in crystalline structure, surface morphology, and grain size of deposited films were systematically investigated as a function of process parameters by using X-ray diffraction and scanning electron microscopy. The deposition temperature and gas composition in the reactor are the main parameters that control the microstructure and composition of films. An interrelationship between the grain orientation and surface roughness of the films was found. Films with (111) preferred orientation are significantly smoother than films with other preferred orientations. The ferroelectric properties of the films were also measured by RT66A ferroelectric tester for hysteresis loop and fatigue property. Electrical measurements revealed that the films had good ferroelectric characteristics with the high remanant polarization (32 $\mu C/cm^2$) and low coercive voltage (1.1 V).

Key words: *MOCVD, PZT, Thin Film, Ferroelectric, FRAM*

INTRODUCTION

Ferroelectric materials possess the perovskite crystal structure in their ferroelectric state. The presence of dual polarization states in these materials gives rise to interesting and useful properties such as ferroelectricity, pyroelectricity, piezoelectricity, and optoelectronic properties. Recently the great attention in these materials has been attracted for the applications to nonvolatile ferroelectric random access memories (FRAM's) and high density dynamic random access memories (DRAM's) [Parker and Tasch, 1990].

Lead zirconate titanate is one of the promising candidates for these applications because it has large remanant polarization with a relatively small coercive voltage, and a high dielectric constant. Many techniques are available for the deposition of PZT thin films including sol-gel method [Schwartz et al., 1995], metalorganic decomposition (MOD) [Tuttle et al., 1992], sputtering [Ansari and Safari, 1995], and various evaporation processes [Saenger et al., 1990]. None of these techniques provides the step coverage needed to fabricate the high density memory devices. MOCVD of PZT thin films has exhibited the distinctive advantages of excellent step coverage and flexible composition control [Shimizu et al., 1993; Keijser et al., 1993]. Shimizu et al. could form perovskite PZT films by a two step growth process on 6 inch Si wafer. The study by Keijser et al. was focused on the deposition of PZT films at optimized process conditions and the accompanying changes in the ferroelectric properties.

In this work, home-made PZT MOCVD system was introduced and the process parameters for deposition of PZT thin films were systematically investigated by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) in order to develop the process for the formation of perovskite PZT thin films. Microstructure of the deposited films was analyzed in terms of crystalline structure, surface morphology and grain size for the control of orientation of PZT films. In addition, the electrical properties of the deposited films were measured by using RT66A ferroelectric tester after the fabrication of the ferroelectric capacitors.

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EXPERIMENTAL

In order to perform the deposition of PZT thin films, a MOCVD system which could mount up to 4 inch Si wafer was built. Schematic diagram of the MOCVD system is shown in Fig. 1. The MOCVD system consists of a gas delivery system, a reaction chamber with a loadlock, and an evacuation system. In the gas delivery system, the bubbling system including bubblers, valves and pressure controlling components was placed in the temperature controlled ovens and all the source delivery lines were placed in the silicon oil baths. In this way the uniform heating system was achieved for the precise precursor delivery to a reaction chamber. In addition, this system has its capability of using solid, liquid and gaseous precursors. To prevent the source materials from condensing on the wall of the transporting systems, the feed lines were maintained at 10 °C higher than those of bubblers. Additional heating tapes were applied to the valves to prevent clogging caused by temperature drop due to fast flow of the gas in valve body. Each bubbler was equipped with a pressure controlling system, enabling the bubbler pressure to be regulated independently of the carrier-gas flow. The temperature of precursor delivery system could be controlled from room temperature to 300 °C with precision of less than 1 °C. This enabled us to precisely control the individual

precursor flow to the reactor so that any composition of PZT films could be reliably deposited over the range of deposition temperature under investigation.

The reaction chamber was equipped with a horizontal rectangular cell. A rotating 4 inch graphite susceptor coated with silicon carbide was placed in the center of this cell. The cell was enclosed in a rectangular outer body of the reactor chamber made of stainless steel. Wafers are transported in and out of the reactor cell from the loadlock by means of a manually operated transport system. The substrate heating was done by pancake-shaped RF coil which was located above the graphite susceptor. In the evacuation system, a mechanical booster pump and a mechanical pump were used to evacuate the reactor chamber. The pressure in the reactor could be kept constant using an automatic throttle valve. The exhaust was released to the air through the gas scrubber.

In this experiment, $Pb(C_2H_5)_4$ (tetraethyllead, TEL), $Zr(O\text{-}t\text{-}C_4H_9)_4$ (zirconium tetratertiarybutoxide, ZTB), and $Ti(O\text{-}i\text{-}C_3H_7)_4$ (titanium isopropoxide, TIP) were used as metalorganic precursors for the deposition of PZT films. The partial pressures of precursors in the reactor cell were varied by adjusting the pressures and temperatures of the bubblers as well as the flow rates of carrier gases. Bubbler temperatures were in the range of 30-60 °C and bubbler pressures were regulated between 200 and 300 Torr. The substrates used for the PZT deposition were Pt(270 nm)/Ti(30 nm)/SiO_2(250 nm)/Si. The crystalline structures and textures of the films were examined by XRD. The surface morphology of the film was observed using FESEM. For the measurement of electrical properties, platinum (Pt) top electrodes were sputter-deposited on the PZT films by utilizing a shadow mask with well defined openings of $5\times10^{-5}-7\times10^{-5}$ cm^2. A ferroelectric tester, RT66A, was used for the measurements of ferroelectric properties containing hysteresis loop and fatigue property. For fatigue study, an external square pulse generator providing ±5 V at 1 MHz was used.

RESULTS AND DISCUSSION

In MOCVD of PZT thin films, there are various process parameters including precursor, bubbler temperature, bubbler pressure, carrier-gas flow rate, substrate, substrate temperature, reactor pressure, etc. Among these parameters, in this study, deposition temperature, Pb precursor flow rate, and ratio of [Zr]/([Zr]+[Ti]) precursor flow rates were chosen as the main process parameters. The effects of these process parameters on PZT thin films were studied for the understanding of deposition mechanism in MOCVD of PZT films and for the process window for the deposition of perovskite PZT thin films. The electrical properties including hysteresis loop and fatigue property were also examined for the characterization of ferroelectric properties of the deposited PZT films.

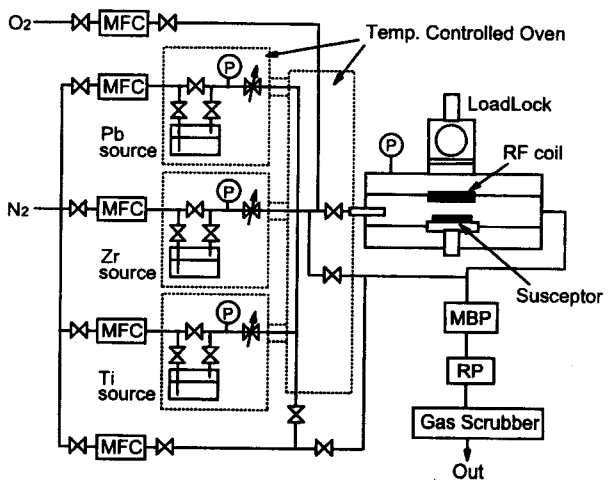

Fig. 1. Schematic diagram of the MOCVD system.

1. Effect of Deposition Temperature

The X-ray diffraction patterns of PZT films deposited at various deposition temperatures (540-600 °C) with [Zr]/([Zr]+[Ti])= 0.35 (hereafter denoted as Zr=0.35) are shown in Fig. 2. No other phases other than tetragonal perovskite phases [see the tetragonal splitting of (200) peak] can be seen in these films. As the deposition temperature increases, the grain orientation has been progressively changed from (110) to (100) to (111). Fig. 3 depicts the variations of peak intensities as a function of deposition temperature. At least two distinct regions can be seen in Fig. 3. For deposition temperatures below 580 °C (region I in Fig. 3) the dominant change in film orientation was from (110) to (100), whereas the (111) peak height remained relatively constant. In region I, it is assumed that the effective arrival rate of the species to surface and the relative surface free energy of tetragonal PZT play an important role in determining the orientation of the PZT films. At present, we are investigating this region in more detail to understand the reasons for the orientation change from (110) to (100). However, in region II (above 580 °C) the dominant orientation of PZT films is (111). It should be noted that the Pt bottom electrode was predominantly (111) oriented.

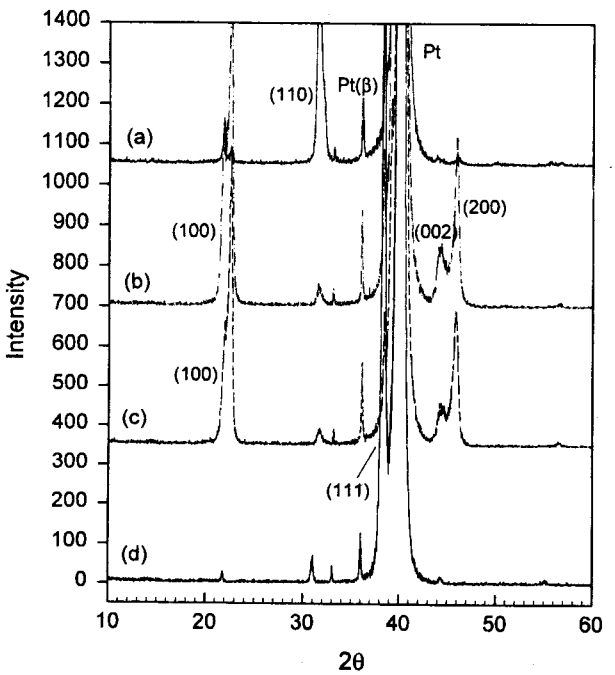

Fig. 2. X-ray diffraction patterns of Ti-rich PZT films (Zr=0.35) deposited at various temperatures: (a) 540 °C, (b) 560 °C, (c) 580 °C, (d) 600 °C.

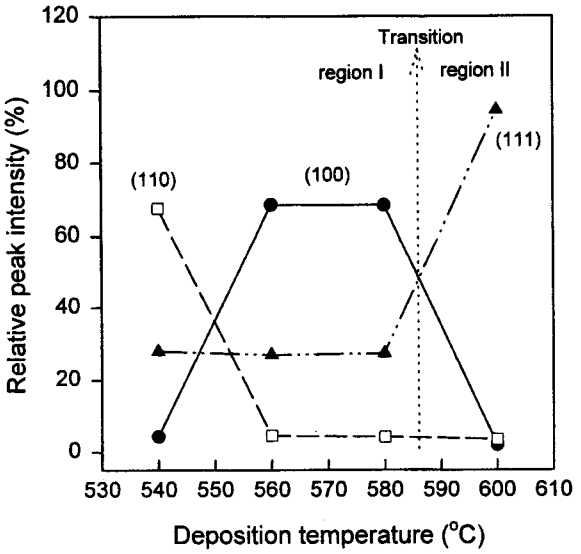

Fig. 3. Comparison of relative peak intensities [(100), (110), (111)] of Ti-rich PZT films (Zr=0.35) as a function of deposition temperature.

Moreover, the variation in deposition rate is little; it varied from 5.4 to 5.0 nm/min when the deposition temperature increased from 540 °C to 600 °C. It is well known that for the epitaxy to occur the surface mobility of the ad-atoms has to be higher than the effective arrival rate of the species to the surface. In other words, in region II the orientation of bottom electrode plays a key role in determining the orientation of the PZT films; it means that pseudo-epitaxial conditions exist for temperatures above 580 °C. In fact, the epitaxial PZT films have been grown on single crystal substrate right around 650 °C. Furthermore, the grain size in region II is approximately two to three times larger than that in region I, which implies the increased surface mobility in region II compared to region I. Also it should be noted that the surface of PZT film grown in region II is much smoother than that grown in region I (see Fig. 4).

SEM photographs of PZT films with Zr=0.35 are shown in Fig. 4 as a function of deposition temperature from 540 to 600 °C. The (100) preferentially oriented PZT films grown at 560-580 °C reveal that top surfaces consist of mainly pyramid-like islands with the size between 100 and 200 nm. On the other hand, the surface of the (111) oriented film grown at 600 °C shows densely packed triangular-like islands with the size of 200-300 nm, and this is in accordance with the previous report [Shimizu et al., 1994]. Considering that the Pt electrode used is (111) oriented, it is reasonable that the films with (100) orientation have shapes of pyramid-like islands and the films with (111) orientation have flat and triangular-like islands of the crystallites. From the observation of the surface morphology of the (100) and (111) textured films, it is concluded that the films with (111) major texture have smoother surface than those with (100) texture.

2. Effect of Pb Precursor Flow Rate

For a given deposition temperature, the flow rate of N_2 gas for carrying. Pb precursor (TEL) has been systematically increased to examine its influence on the film structure. The lower limit of Pb precursor flow rate (30 sccm) was set at the on-

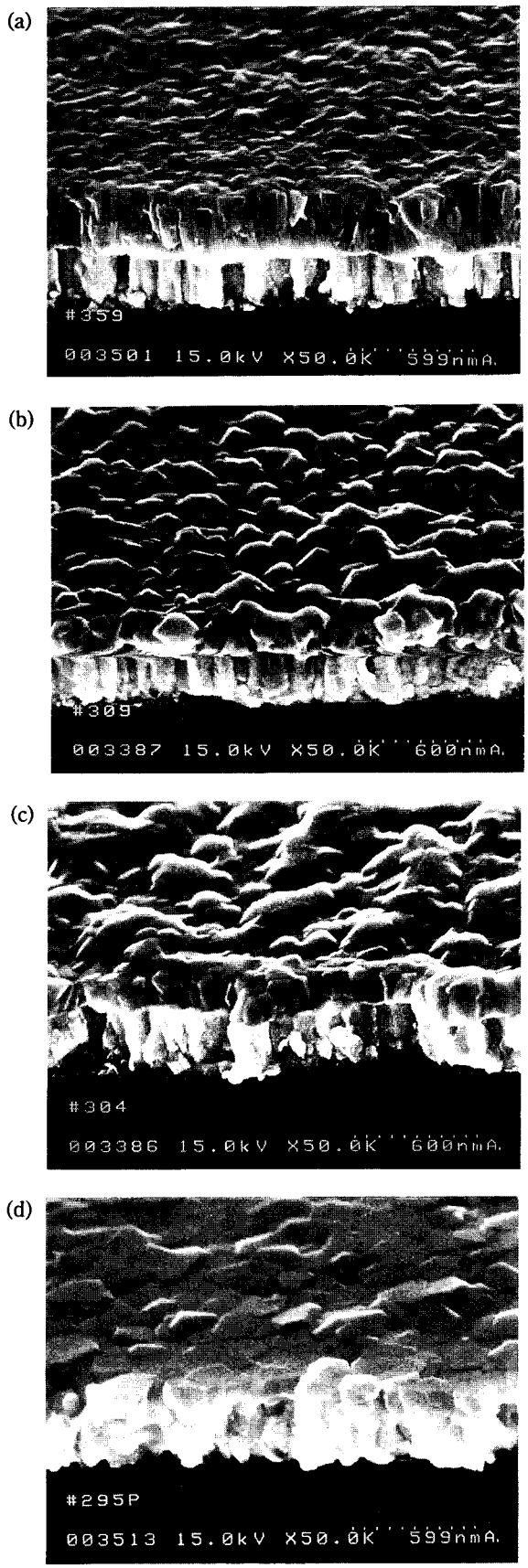

Fig. 4. SEM photographs of Ti-rich PZT films (Zr=0.35) deposited at various temperatures: (a) 540 °C, (b) 560 °C, (c) 580 °C, (d) 600 °C.

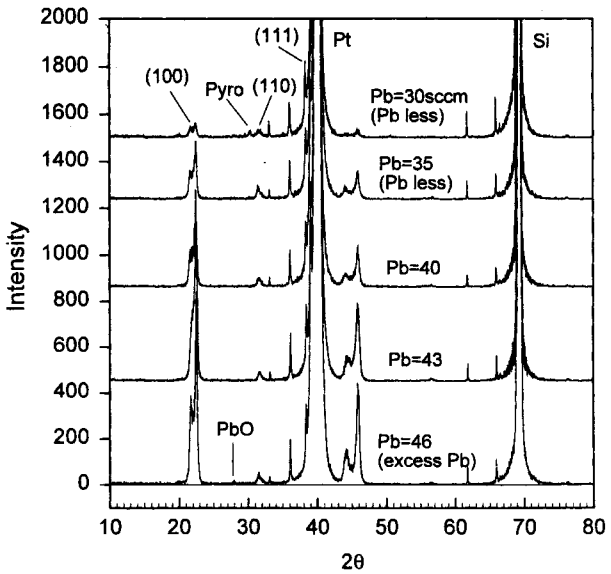

Fig. 5. X-ray diffraction patterns of PZT films deposited at 580 °C with Zr=0.35 as a function of Pb precursor flow rate.

set of pyrochlore phase formation in the film, whereas the upper limit (46 sccm) was set at the onset of lead oxide formation in the film. Fig. 5 shows XRD patterns of PZT films grown at 580 °C with Zr=0.35 as a function of Pb precursor flow rate. In general, as the Pb precursor flow rate increases, there is a gradual increase in the intensity of XRD peak. It is because the formation of stoichiometric PZT film begins to increase without pyrochlore phase which is second phase (deficient PZT in stoichiometry) of PZT film with increasing the Pb precursor flow rate. However, no significant changes in the relative intensities of various peaks was observed indicating little or no effect on the preferred orientation of the films.

3. Effect of Ratio of [Zr]/([Zr]+[Ti]) Precursor Flow Rates

It is mentioned above that pseudo-epitaxial conditions exist at temperatures above 580 °C for the deposition of PZT films with [Zr]/([Zr]+[Ti])=0.35 (denoted as Zr=0.35) because of the relatively high surface mobility of the species. Since $PbZrO_3$ is more refractive than $PbTiO_3$, the surface mobility of the species would decrease for the fixed deposition temperature with increasing Zr content in the films. In other words, the relative peak height ratio of (111)/(100) would decrease as Zr content increases because of the increase of (100) oriented grains. Furthermore, one can also expect pyramid-like surface microstructure for films with higher Zr content.

Fig. 6 shows SEM photographs of the PZT films deposited at 600 °C with varying Zr content. As expected, the amount of pyramid-like grains that are correlated to (100) orientation increases as the Zr content in the film increases. This is in agreement with our hypothesis that the surface mobility plays a significant role in determining the orientation of films at the deposition temperature of 600 °C. It is concluded that the surface mobility decreases with increasing the Zr content in the film; this results in the reduction of the (111) oriented grains and the increase of pyramid-like grains.

4. Electrical Properties of the Deposited PZT Films

Fig. 7 shows the typical D-E hysteresis loop and fatigue property of PZT film grown at 600°C with Zr=0.5. The thickness of the film was 240 nm. The spontaneous polarization (P_S), remanant polarization (P_r) and coercive voltage (V_C) had values of 63 $\mu C/cm^2$, 32 $\mu C/cm^2$ and 1.1 V, respectively. The remanant polarization, which is the critical parameter in FRAM operation, is the remaining polarization when the power is off. The coercive voltage is the voltage necessary to switch the domain. The obtained value of remanant polarization was high enough and the value of coercive voltage was low enough for the application to FRAM device. Fatigue property indicates the degree of the en-

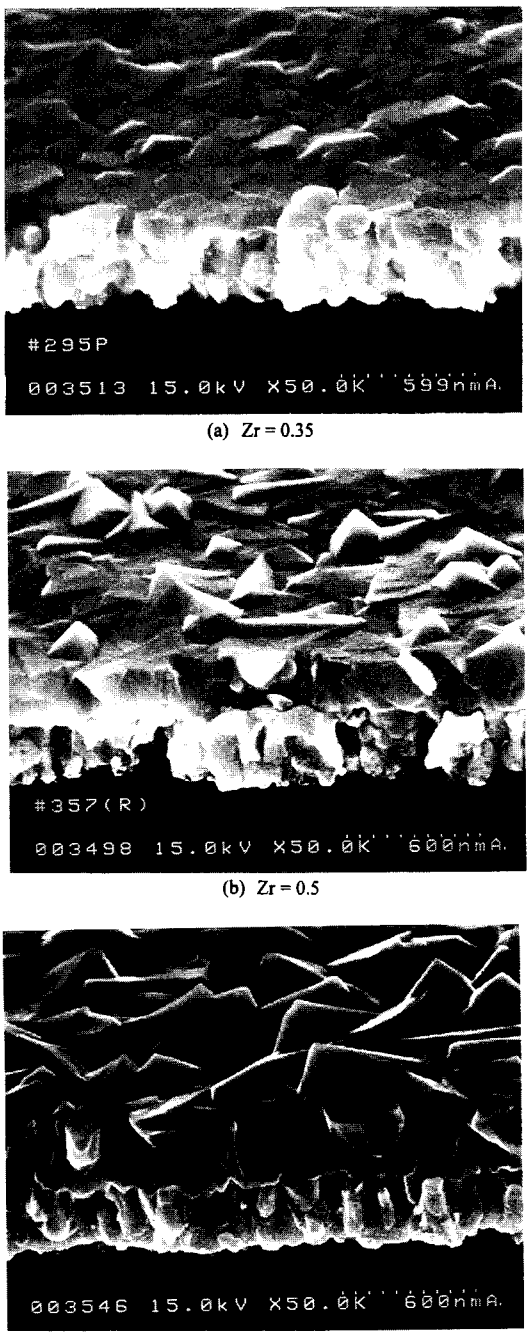

Fig. 6. SEM photographs of PZT films deposited at 600 °C with various Zr contents: (a) Zr=0.35 , (b) Zr=0.5, (c) Zr=0.65.

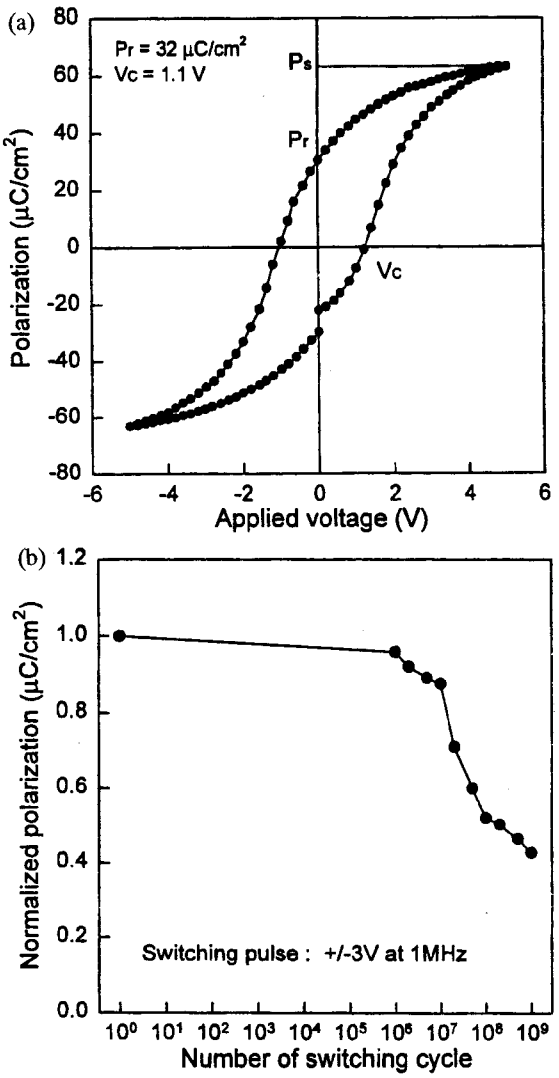

Fig. 7. Electrical properties of PZT films deposited at 600 °C with Zr=0.5: (a) Hysteresis loop, (b) Fatigue property.

durance of the film upon the repeated bipolar switching which corresponds to reading and writing the information in FRAM operation. The remanant polarization was changed little up to 10^6 switching cycle and then started to decrease gradually. This phenomenon is typical in PZT film and it needs to be improved for the longer operation.

CONCLUSION

PZT thin films were successfully fabricated by MOCVD on $Pt/Ti/SiO_2/Si$ substrate at deposition temperature of 540-600 °C with varying [Zr]/([Zr]+[Ti]) ratio from 0.35 to 0.65. The deposition temperature and gas composition of each precursor in the reactor are the major process parameters which have a great influence on the microstructure of the film, including the grain orientation, surface morphology and grain size.

As the deposition temperature increases from 540 °C to 600 °C, the grain orientation has been changed from (110) to (100) to (111). The (111) oriented films with the grain shape of triangular-like island had smoother surface morphology than the (100) oriented films having the shape of pyramid-like island. For deposition temperature close to 600 °C, it was observed that the grain orientation in PZT films was controlled by the quasi-epitaxial conditions and the orientation of the Pt electrode played the key role. As the ratio of [Zr]/([Zr]+[Ti]) increases, the (111) oriented grain decreases and the surface morphology becomes rough. There is the optimum flow rate of Pb precursor which forms the perovskite PZT films without the formation of pyrochlore phase and lead oxide. It was considered that the change in the flow rate of Pb precursor had no effect on the preferred orientation of the films. The well defined hysteresis loop was observed with the ferroelectric properties of P_S =63 μC/cm², P_r=32 μC/cm² and V_C=1.1 V.

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