

THE INFLUENCE OF CHEMICAL PASSIVATION ON THE PZT/Pt ELECTRODE INTERFACE

Byung Soo Jeon and Jae Soo Yoo[†]

Dept. of Chemical Engineering, Chung-Ang University, 221 Huksuk-Dong, Dongjak-Ku, Seoul 156-756, Korea
(Received 7 October 1997 • accepted 26 December 1997)

Abstract – It has been recognized that the interdiffusion of atomic species between a PZT film and the Pt bottom electrode leads to the gradual degradation of a PZT capacitor. In order to prevent this interdiffusion, experimental studies on chemical passivation to the bottom electrode surface were carried out by the sulfurization method. It was observed that a sulfur layer was built up on the Pt substrate with small grains, which resulted in a structural change at the Pt surface. Atomic force microscopy (AFM) showed that the film roughness of the Pt surface was increased by sulfur treatment. $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (PZT) thin films were prepared on a Pt/Ti/SiO₂/Si bottom electrode by spin-coating techniques. The microstructure and the preferred orientation of the PZT films were shown to depend on the sulfur-treated electrode. The PZT capacitor on a clean Pt electrode was confirmed to be ferroelectric with $\text{Pr}=17.7 \mu\text{C}/\text{cm}^2$ and $E_c=65 \text{ kV}/\text{cm}$ from the P-E hysteresis curves. The fatigue behavior of a PZT film capacitor prepared on a sulfur-treated one was observed to be relaxed, but the absolute value of Pr was paid off.

Key words: Ferroelectric PZT Film, Sol-Gel Method, Chemical Passivation, Fatigue Property

INTRODUCTION

PZT thin films, which have applications in many fields, have recently been extensively investigated for use in non-volatile memories [Chung et al., 1997; Nakamura et al., 1994; Mihara et al., 1994]. However, several problems, such as ferroelectric fatigue, have remained unsolved for successful application to electronic devices. The fatigue behavior of ferroelectric film by repeated polarization switching cycles has been a central issue in reliability and is currently of much concern [Dormans et al., 1992]. The formation of a PZT capacitor requires thermal treatment, which causes interdiffusion of atomic species between the PZT film and the bottom electrode substrate. Thus, the choice of the bottom electrode is restricted to suppress the interaction between ferroelectric and electrode materials under the processing temperatures involved, which might result in the degradation of these films during polarization reversals. Many attempts have been made to reduce the degradation properties of PZT thin film capacitors. Desu and Yoo [1992] have reported that oxygen vacancy plays an important role through the fatigue model based on defect chemistry. They have proposed that the fatigue could be alleviated either by reducing the concentration of intrinsic defects or by controlling the film interface states. Scott et al. [1992] showed that PZT layers adjacent to both the top and the bottom electrodes have an oxygen deficiency and the fatigue may be from the diffusion of oxygen into the electrode.

Hence, the interface region where there may exist improper phase development and a chemical reaction between ferroelec-

tric and electrode materials should be stabilized. Recently, chemical and photochemical treatments have been found to successfully improve the quality of a GaAs surface [Maeda et al., 1993; Ohno et al., 1993]. In particular, ammonium sulfide $[(\text{NH}_4)_2\text{S}]$ treatments have proven to be effective in stabilizing the surface.

In this work, $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ thin films were prepared by the sol-gel method on Pt/Ti/SiO₂/Si substrate obtained using sputtering and CVD. The microstructural changes and the crystallographic properties of the Pt electrode surfaces treated by hydrogen sulfide were analyzed by x-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The influence of sulfur treatment was evaluated by studying the electrical properties of a PZT capacitor prepared on a sulfur-treated electrode.

EXPERIMENTAL

Sol-gel derived PZT films were prepared from metalorganic solutions of lead acetate trihydrate, zirconium n-propoxide and titanium isopropoxide precursors. Each concentration was controlled to be a ratio of Pb:Zr:Ti=1:0.5:0.5. The Pb-Zr-Ti solutions were diluted with acetic acid and methoxyethanol to form a 0.4 M PZT precursor solution. PZT films were finally deposited onto substrates of a Pt (270 nm)/Ti (30 nm) layer, which were sputter-deposited on a thermally oxidized Si wafer, using a spin coater operated at 2,500 rpm for 40 second, and subsequently dried on a hot plate at 200 °C for 5 min. Multilayer depositions (three coatings) were performed to increase the film thickness (about 250 nm). These films were subsequently converted to crystallized $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ films by annealing at 650 °C for 30 min. For the measurement of electrical properties, the Pt top electrodes were sputter-deposit-

[†]To whom all correspondence should be addressed.
E-mail: jsyoo@cau.ac.kr

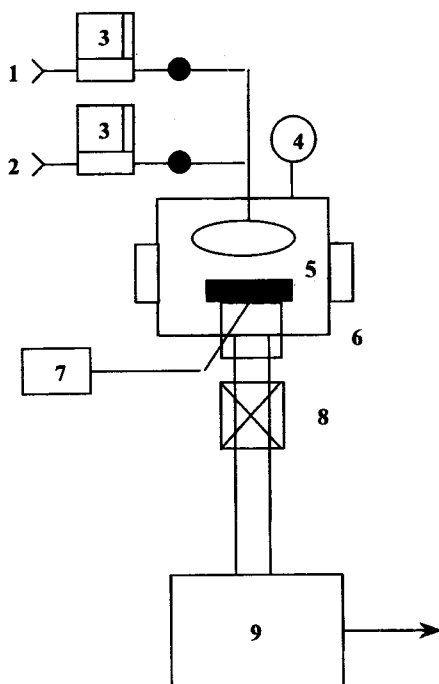


Fig. 1. Schematic diagram of sulfur-treatment system.

- | | |
|-------------------------|---------------------------|
| 1. H_2S gas | 6. Reactor |
| 2. N_2 gas | 7. Temperature controller |
| 3. Mass flow controller | 8. Butterfly valve |
| 4. Pressure gauge | 9. Rotary pump |
| 5. Shower-ring | |

ed using a shadow mask. The area of the Pt top electrode was about $1 \times 10^{-4} \text{ cm}^2$ and the thickness was about 100 nm.

Fig. 1 shows a schematic diagram of the experimental apparatus for the sulfur-treatment of the Pt electrode substrate. In this experiment, the sulfur-treatment of the Pt/Ti/SiO₂/Si substrate used above was carried out at 700 K, which is a decomposition temperature of H_2S (hydrogen sulfide 99.5%) gas. Sulfur is adsorbed mainly in the molecular form at room temperature and in dissociated form at higher temperature (700 K). It is therefore highly probable that the molecules are already dissociated at the surfaces. H_2S gas as treatment agent was supplied to the vertical reactor with N_2 gas used as dilution gas under a pressure of 300 torr.

Crystallization behavior of the films was studied with an X-ray diffractometer (Model Scintag XDS 2000). The surface morphology of the films was evaluated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The hysteresis loops in this experiment were measured under an applied voltage of ± 5 V using a Radiant Technologies RT-66A system. The fatigue measurements were carried out by applying 1 MHz square waves with ± 5 V.

RESULTS AND DISCUSSION

The crystallinity of the PZT films prepared by the sol-gel technique under the various parameters was investigated. X-ray diffraction profiles with the annealing temperatures for the $Pb(Zr_{0.5}Ti_{0.5})O_3$ films coated onto Pt/Ti/SiO₂/Si substrates are shown in Fig. 2. These films were of the same thickness

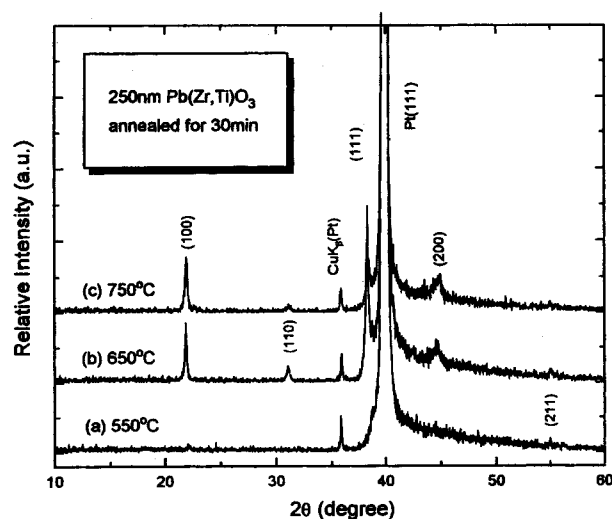


Fig. 2. XRD patterns of $Pb(Zr_{0.5}Ti_{0.5})O_3$ films annealed at (a) 550°C, (b) 650°C, and (c) 750°C.

(250 nm) and were annealed for 30 min. The film annealed at 550°C shows a pattern of amorphous material, and a single phase with the perovskite structure is shown above an annealing temperature of 650°C. Although the main orientation (110) of the polycrystalline PZT phase was slightly detected above 650°C, there was no metastable pyrochlore phase at this temperature range. The appearance of the (110) peak in the PZT film is due to the (110) orientation of the Pt nuclei on the substrate. It is also found that PZT films with Zr:Ti = 50:50 show very weak (110) peaks due to their composition ratio.

It is also observed from Fig. 3 that the diffraction intensity of the (100) peak increases relative to the other peaks with an increase of film thickness as well as annealing temperature. The results show that the crystalline orientations of the films strongly depend on their thickness. The thickness of the PZT film increased with an increase in coating cycles, but the sequence coating process produced the peeling phenomenon of PZT film. The films with 250 nm thickness show typ-

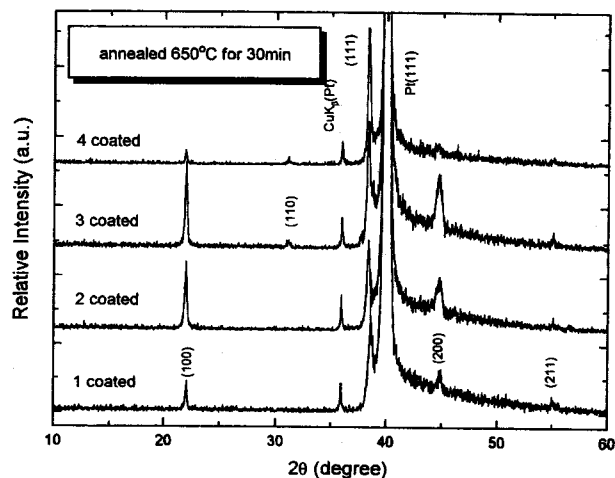


Fig. 3. XRD patterns of $Pb(Zr_{0.5}Ti_{0.5})O_3$ films prepared with coating cycles.

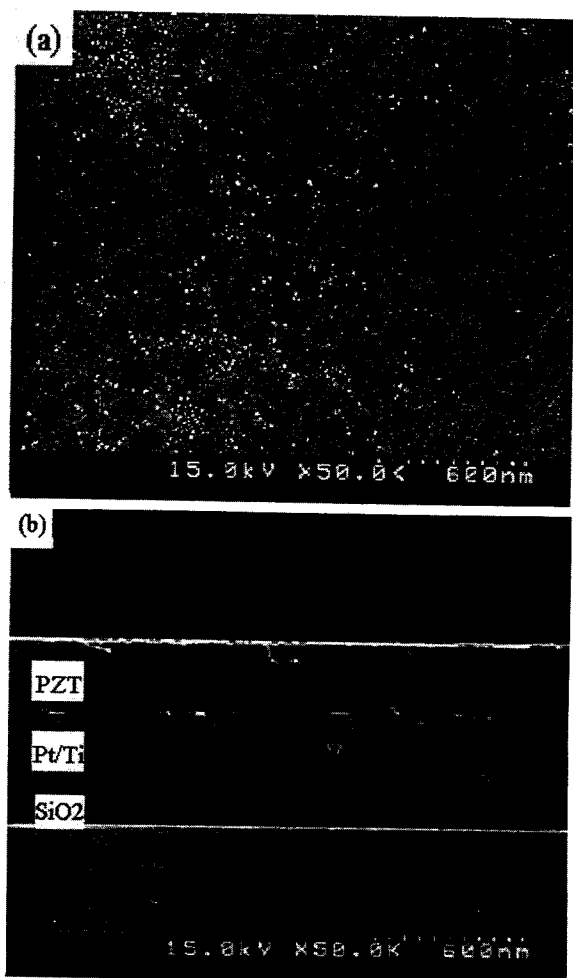


Fig. 4. SEM images of surface morphology (a) and cross-section (b) of PZT film (250 nm).

ical XRD patterns from the oriented polycrystalline PZT. Fig. 4 shows SEM images of the surface morphology and the cross-section of 3-coated PZT film (250 nm). The film has a rosette-like structure and dense uniform structure with a grain size of about 100 nm. The Pt/Ti layer was sputter-deposited on the thermally oxidized Si wafer.

For chemical passivation, hydrogen sulfide gas was supplied to the vacuum chamber at 700 K, which is known as its decomposition temperature. Sulfur-treatment time as process variable ranged from 30 sec to 5 min. In order to investigate the chemical bonding at the electrode surface treated by hydrogen sulfide, XRD measurements were carried out. Fig. 5 shows XRD profiles of the Pt electrode surface as a function of the sulfur-treatment time. The surface of the Pt/Ti/SiO₂/Si substrate treated by hydrogen sulfide exhibits the XRD peak of the Pt-S bond around $2\theta=26^\circ$. This indicates that the dissociation adsorption of hydrogen sulfide gas induces a surface reconstruction that corresponds to a structural change at the Pt surface. It can be therefore expected that an exchange reaction between the Pt electrode and the sulfur atoms occurs at the Pt surface.

However, assuming that the overlayer of sulfur has a layered structure, the thickness of sulfur should be roughly con-

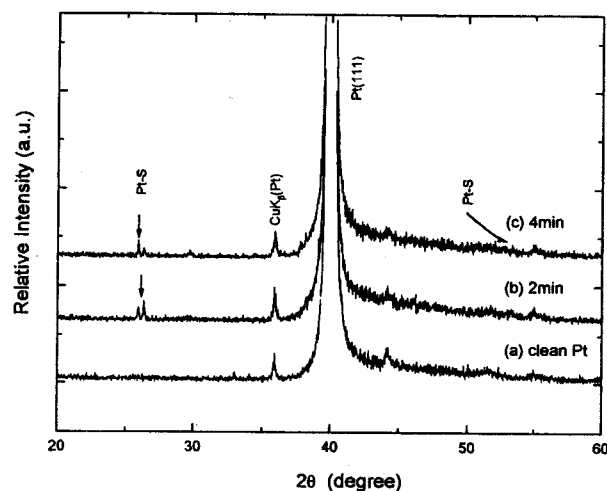


Fig. 5. XRD patterns of Pt electrode substrate with sulfur-treatment: (a) clean Pt, (b) and (c) sulfur-treated one for 2 min and 4 min, respectively.

trolled to be near one or two monolayers [Oigawa et al., 1991]. It is also well known that sulfur-treatment is partially effective for the reduction of surface defect density [Maeda et al., 1993]. Nannichi et al. [1990] have presented a simplified model of the sulfur-treated surface. In the case of Na₂S-treatment on a GaAs surface, the surface is covered with an amorphous sulfur layer of about 10 nm-thickness (or Na₂S). Hence, sulfur atoms in a vacuum correspond one to one with the substrate alignment and form any bonding on the surface. It is therefore inferred that the sulfur-treatment time on the Pt surface should be reduced to form a thinner sulfur layer because the thick sulfur layer might act as an insulator against the Pt electrode.

Three-dimensional AFM measurements were performed to examine the surface morphologies of the Pt electrode treated by hydrogen sulfide. Fig. 6 shows AFM surface images of a clean Pt surface and a sulfur-treated one for 2 min. In order to quantitatively compare the surface morphologies, the average root-mean-squares roughness was calculated directly from the AFM images. The roughness for the clean Pt surface and the sulfur-treated one is 1.2 nm and 2.8 nm, respectively. It is seen that the surface flatness decreases with an increase of sulfur-treatment time.

An important issue that is mentioned in this work is the interaction of the ferroelectric film with the electrode substrate during growth or further processing. This interaction can take the diffusion form of a film species into the substrate. Fig. 7 shows the effects of sulfur-treatment on the crystallization of PZT films. The preferred orientation of as-deposited PZT films on the sulfur-treated electrode shows some dependence on the surface treatment. The preferred crystal growth process on a clean Pt electrode results in the (111) oriented PZT crystals, while the (100) peak intensity of as-deposited PZT film on a sulfur-treated electrode increases more than that of PZT on a clean one. It is here very likely that even though the sulfur-treated surface as a nucleation site for the perovskite phase gives rise to a rough morphology in terms of AFM surface images, Pt (100) hillocks are not exhibited. It is therefore

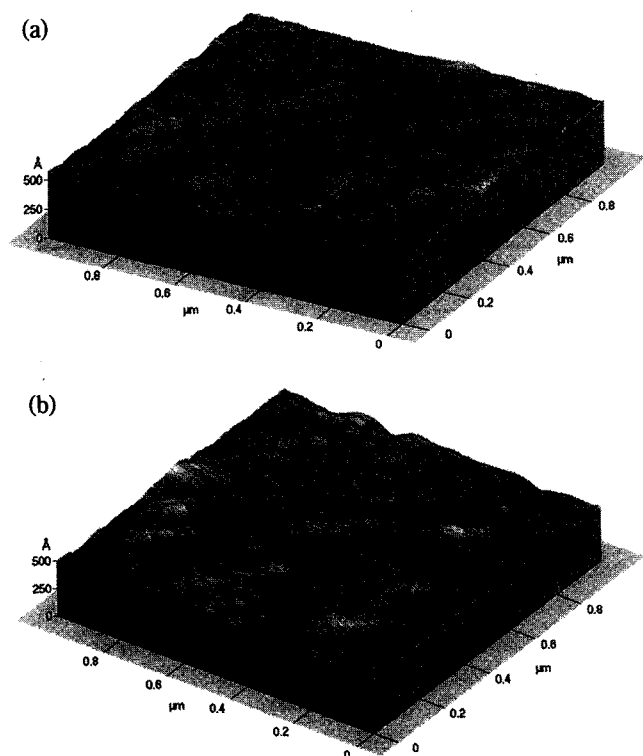


Fig. 6. Three dimensional AFM surface images of clean Pt surface (a) and sulfur-treated one (b) for 2 min.

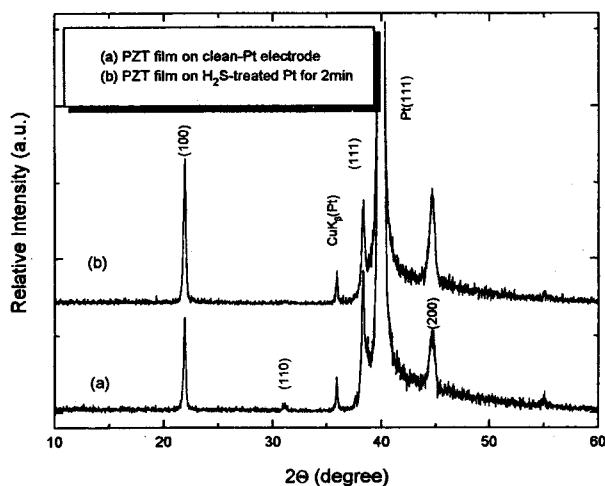


Fig. 7. XRD patterns of $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ films grown on clean electrode and sulfur-treated one for 2 min.

worth noting that a porous Pt surface, which is the main cause for the diffusion of PZT film species into the bottom electrode, might be suppressed by a sulfur layer. Spierings et al. [1991] explained that the (100)-oriented growth might be the natural growth behavior of lead perovskite on smooth unannealed-Pt electrodes.

Fig. 8 shows hysteresis curves of PZT thin films grown on a clean electrode surface and a sulfur-treated one. The initial state before fatigue and the fatigued states after 10^9 switching cycles with pulse height were compared. The remnant polarization, P_r , and the coercive field, E_c , of a PZT capacitor

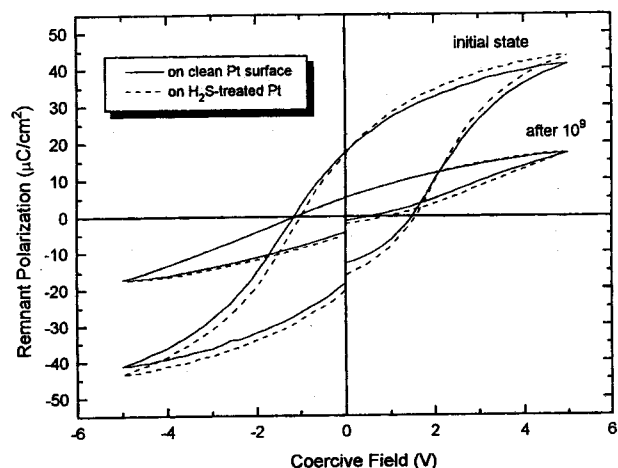


Fig. 8. Hysteresis loops depicting initial states and fatigued states of PZT (50/50) films grown on a clean electrode and a sulfur-treated one at 10^9 polarization switching cycles.

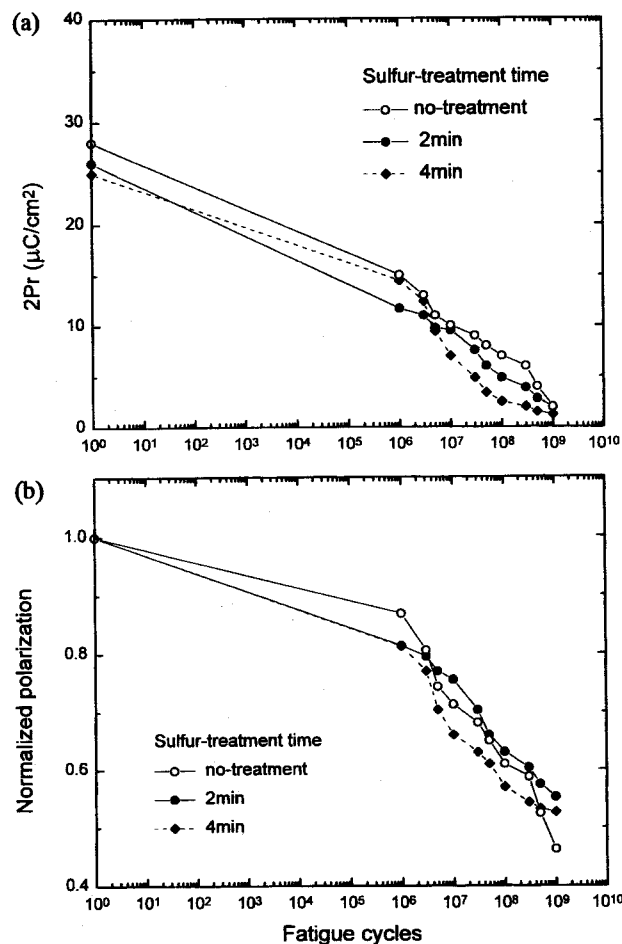


Fig. 9. Fatigue behavior of PZT film capacitor prepared on clean electrode and sulfur-treated one.

on a clean electrode are $17.7 \mu\text{C}/\text{cm}^2$ and $65 \text{ kV}/\text{cm}$, respectively. Also, the initial states of the PZT film capacitor prepared on the sulfur-treated electrode had a well-saturated hysteresis loop, which exhibited a slight difference due to the ef-

fects of sulfur-treatment on P-E hysteresis properties. However, the fatigue behavior does not change appreciably in comparison with films on the sulfur-treated electrode.

The fatigue behavior of PZT thin films grown on a clean electrode and a sulfur-treated one is shown in Fig. 9(a). The difference between switched and unswitched polarizations ($2P_r$) drops to a low level above 10^6 cycles. The initial $2P_r$ values of as-deposited PZT film on a sulfur-treated electrode are less than that of PZT film on a clean one. After fatigue of 10^9 cycles, the $2P_r$ is saturated to about $5 \mu\text{C}/\text{cm}^2$, which is about 16% of the initial value. It can be found from the normalized data (Fig. 9b) that the degradation rate of PZT film grown on a sulfur-treated electrode is slightly relaxed with switching cycles compared with that on a clean one. An important emphasis is the relaxation of degradation rate by preventing the interaction of PZT/Pt interface regions. The normalized data [Fig. 9(b)] indicates that the degradation rate of PZT film on a clean electrode is higher than that of PZT film on a 2 min-treated one. However, $2P_r$ decreases with an increase in sulfur-treatment time. It is therefore expected that the thick sulfur layer might form an interface region between the PZT film and the Pt electrode. New interface regions through thick sulfur layers can also form space charge layers along the PZT/Pt interface. This results in an increase of the interfacial resistance and a decrease of the interfacial capacitance.

CONCLUSIONS

PZT (50/50) thin films were prepared by the sol-gel technique, and the effects of sulfur-treatment on the surface of the Pt/Ti/SiO₂/Si substrate were experimentally investigated. It was also found from X-ray diffraction measurements that sulfur adsorption on a Pt surface induces a structural change at the surface. The surface morphologies as well as the preferred orientation of the PZT films were affected by the sulfur-treatment on a Pt electrode surface. The remnant polarization, P_r , and the coercive field, E_c , of the PZT capacitor are $17.7 \mu\text{C}/\text{cm}^2$ and $65 \text{ kV}/\text{cm}$, respectively. The experimental observation that sulfur-treatment of the Pt electrode surface can play a positive role as a diffusion barrier in integration of the ferroelectric film into devices was presented.

ACKNOWLEDGEMENT

The authors gratefully acknowledge that this research was supported by the Korea Science and Engineering Foundation under Grant No. (951-1105-038-2). They would like to thank

Mr. Jun Ki Lee of the Samsung Advanced Institute of Technology for AFM analysis, and measurement of electrical properties.

REFERENCES

- Chung, C. W. and Kim, D., "Metalorganic Chemical Vapor Deposition of Ferroelectric Pb(Zr_xTi_{1-x})O₃ Thin Film", *Korean J. Chem. Eng.*, **14**(2), 136 (1997).
- Desu, S. B. and Yoo, I. K., "Ferroelectric PbZr_xTi_{1-x}O₃ Thin Films Grown by Organometallic Chemical Vapor Deposition", *Proc. 4th Int. Symp. Integrated Ferroelectrics, Monterey*, 640 (1990).
- Dormans, G. J. M., Keijer, M. de and Veldhoven, P. J. Van., "Ferroelectric PbZr_xTi_{1-x}O₃ Thin Films Grown by Organometallic Chemical Vapor Deposition", *Proc. Symp. Mat. Res. Soc.*, 203 (1992).
- Maeda, F., Watanabe, Y. and Oshima, M., "Surface Chemical Bonding of (NH₄)₂S-treated InP(001)", *Appl. Phys. Lett.*, **62**(3), 297 (1993).
- Makamura, T., Nakao, Y., Kamisawa, A. and Takasu, H., "Preparation of Pb(Zr,Ti)O₃ Thin Films on Ir and IrO₂ Electrode", *Jpn. J. Appl. Phys.*, **33**, 5207 (1994).
- Mihara, T., Watanabe, H. and Araujo, Carlos A. Paz De, "Polarization Fatigue Characteristics of Ferroelectric Pb (Zr, Ti)O₃ Thin Film Capacitors", *Jpn. J. Appl. Phys.*, **33**, 3996 (1994).
- Nannichi, Y. and Oigawa, H., "The Effects of Sulfur on the Surface of III-IV Component Semiconductors", *Extended Abstracts of 22nd Int. Conf. on Solid State Devices and Materials, Sendai*, 453 (1990).
- Ohno, H., Kamanishi, H., Akagi, Y., Nakajima, Y. and Hijikata, T., "AES and XPS Studies of Surface of Al_xGa_{1-x}As (110) Treated by Ammonium Sulfide", *Jpn. J. Appl. Phys.*, **29**(11), 2473 (1990).
- Oigawa, H., Fan, J., Nannichi, Y., Sugahawa, H. and Oshima, M., "Universal Passivation Effects of (NH₄)₂S_x Treatment on the Surface of III-IV Component Semiconductors", *Jpn. J. Appl. Phys.*, **30**, L322 (1991).
- Scott, J. F., Melnick, B. M., Araujo, C. A., McMillan, L. D. and Zuleeg, R., "d.c. Leakage Currents in Ferroelectric Memories", *Integrated Ferroelectrics*, **1**, 323 (1992).
- Spierings, G. A. C. M., Ulenaers, M. J. E., Kampschoer, G. L. M., van Hal, H. A. M. and Larsen, P. K., "Preparation and Ferroelectric Properties of PbZr_{0.53}Ti_{0.47}O₃ Thin Films by Spin Coating and Metalorganic Decomposition", *J. Appl. Phys.*, **70**(4), 2290 (1991).