Effects of Pt diffusion barrier layer on the interface reaction and electric properties of PZT film/Si(111) sample

ZHU, Yong-Fa[*,a](朱永法) YAN, Pei-Yu[b](阎培渝) YI, Tao[c](易涛) CAO, Li-Li[a](曹立礼)
LI, Long-Tu[b](李龙土)

[a] *Department of Chemistry, Tsinghua University, Beijing 100084, China*

[b] *Department of Material Science and Technology, Tsinghua University, Beijing 100084, China*

[c] *State Key Laboratory of Rare Earth Materials Chemistry and Application, Peking University, Beijing 100871, China*

The effects of the Pt diffusion barrier layer on the interface diffusion and reaction, crystallization, dielectric and ferroelectric properties of the PZT/Si(111) sample have been studied using XPS, AES and XRD techniques. The results indicate that the Pt diffusion barrier layer between the PZT layer and the Si substrate prohibits the formation of TiC_x, $TiSi_x$ and SiO_2 species in the PZT layer. The Pt barrier layer also completely interrupts the diffusion of Si from the Si substrate into the PZT layer and impedes the diffusion of oxygen from air to the Si substrate greatly. Although the Pt layer can not prevent completely the diffusion and reaction between oxygen and silicon, it can prevent the formation of a stable SiO_2 interface layer on the interface of PZT/Si. The Pt layer reacts with silicon to form $PtSi_x$ species on the interface of Pt/Si, which can intensify the chemical binding strength between the Pt layer and the Si substrate. To play a good role as a diffusion barrier layer, the Pt barrier layer must be not thinner than 140 nm. The existence of the Pt layer not only promotes the crystallization of PZT layer to form a perovskite phase but also improves dielectric and ferroelectric performances of the PZT layer.

Keywords PZT, interface reaction, Pt diffusion barrier, XPS, AES

Introduction

In recent years, much attention has been paid to using PZT films for high density semiconductor memory devices and surface acoustic wave devices, pyroelectric type sensors and supersonic wave probes.[1-3] In general, PZT thin film is deposited directly on a semiconductor substrate such as silicon. It is very difficult to obtain a high quality ferroelectric PZT film on silicon successfully due to the interface reaction and diffusion between the PZT layer and the silicon substrate.[4-6] In order to prevent the interface diffusion and reaction between PZT layer and the silicon substrate, a buffer layer is necessary, which can improve the dielectric and ferroelectric performances greatly.[7-9] Due to low dielectric constant of oxide buffer layers such as CeO_2, MgO, Y_2O_3 and lattice mismatch, these buffer layers can not be accepted as perfect material until now. The study on the $SrTiO_3$ film/Si has revealed that platinum is a good diffusion barrier layer, and can improve the dielectric constant significantly.[10] The dielectric constant in the PZT film deposited on the Si substrate is about 13, but the dielectric constant of PZT film deposited on platinum substrate can reach 1500.[11] Platinum can be used not only as a diffusion barrier layer but also as a bottom electrode material in PZT films. So far it is still not very clear how platinum layer improve the performance of PZT film.

In this paper, the effects of Pt as a diffusion barrier layer on the interface diffusion and reaction have been studied. The results show that the Pt layer impedes the diffusion and reaction between Si and the PZT layer completely. It also decreases the diffusion of oxygen greatly and prevents the formation of TiC_x and $TiSi_x$ species in the PZT layer completely. In addition, the Pt

Received July 23, 1999; accepted December 25, 1999.

Project supported by the 1997 Grant-in Aid for Scientific Fundament Research of Tsinghua University and by State Key Laboratory of Rare Earth Materials Chemistry and Application.

barrier layer promotes the formation of PZT perovskite phase. After the Pt barrier layer is added, the dielectric properties of PZT film arrive at the level of bulk PZT materials and the ferroelectric properties are improved greatly.

Experimental

P-type Si(111) wafer with 2.4 Ω/cm resistance was cleaned using HF solution and used as substrates. A Pt layer was deposited on the Si(111) wafer by a DC magnetron sputtering, and the thickness was 50 nm for PZT/Pt(50)/Si and 140 nm for PZT/Pt(140)/Si samples, respectively. A PZT precursor film was deposited on the substrates of Pt/Si (111) using a sol-gel method.[12] The film was coated using the spin-coating method conducted at 500 rpm for 8 s followed by 4000 rpm for 15 s. The thickness of the PZT layer was about 80 nm. The PZT/Pt/Si samples that were used to measure the electric properties were coated five times, and the thickness of PZT layer was about 400 nm. The samples were dried and calcinated in air. First, the temperature was raised to 400℃ with the heating rate of 2℃/min and maintained for 30 min to promote the decomposition of organic compounds. Then, the temperature was raised to 800℃ with the same heating rate and maintained for two hours to form PZT perovskite phase. At last, the furnace was cooled naturally.

For determination of electrical properties of PZT films, a Pt layer was used as the base electrode and the top Au electrodes (1 mm diameter) were deposited to establish a parallel-plate capacitor geometry. The thickness of the PZT layer was 400 nm, which was measured by AES depth profile analysis. Dielectric properties of PZT films were measured by a HP4192A impedance analyzer at room temperature. Hysteresis loops were measured to evaluate the ferroelectric properties of PZT films using a modified Sawyer-Tower circuit with 50 Hz a.c. current.

The XPS spectra were measured in a PHI 5300 ESCA system. Mg K_α X-ray beam was used, and the power was set at 250 W. A hemispherical analyzer with a position sensitive detector at a pass energy of 37.75 eV was used. The base vacuumof chamber was maintained at 2×10^{-7} Pa during XPS analysis. During ion sputtering, the energy and the current of Ar ion beam were set at 3.0 keV and 20 μA, respectively. The beam was focused to a spot of 8 mm × 8 mm. The sputtering rate was about 2.0 nm/min for a thermal oxidized SiO_2 thin film.

The AES spectra were measured in a PHI 610 SAM system. The coaxial electron gun with a single pass cylindrical mirror analyzer (CMA) was used. The energy resolution of the CMA was set at 0.3%. The beam energy and the beam current were 3.0 keV and 0.5 μA, respectively. The electron beam was incident at an angle of 60° with respect to the specimen surface. During sputtering of Ar ion beam, the beam energy and current of Ar ion beam were 3.0 keV and 6 μA, respectively. The beam was focused to a spot of 1 mm × 1 mm, and the sputtering rate was about 40.0 nm/min for a thermal oxidized SiO_2 thin film.

Results and discussion

Effects of Pt *diffusion barrier layer on the formation of* PZT *species*

After PZT/Si sample was annealed at 800℃ for 1 h, $TiSi_x$ and TiC_x species were formed in the PZT layer.[13] Fig. 1 showed the Ti $2p$ spectra in the PZT layer of PZT/Pt(140)/Si samples. The peak shape of Ti $2p_{3/2}$ in PZT/Pt(140)/Si is narrow and symmetric. The binding energy is 458.7 eV, which can be attributed to PZT species. Compared with the results of PZT/Si sample, there is only one kind of Ti species in the PZT layer after a Pt diffusion barrier layer was inserted. Fig. 2 and 3 show the C $1s$ and Si $2p$ spectra in PZT/Si and PZT/Pt(140)/Si samples. In PZT/Si sample, two peaks appear on the C 1 s spectra. The binding energies are 285.0 eV and 280.8 eV, which can be attributed to carbonized carbon and carbide, respectively. After a Pt layer is inserted, only a single peak appears on the C $1s$ spectrum and the binding energy is 285.0 eV. The disappearing of shoulder peak at 280.8 eV implies that there is not any TiC_x species in the PZT layer of PZT/Pt(140)/Si sample. In PZT/Si sample, the Si $2p$ spectra show that there are two kinds of silicon species in PZT layer. The binding energies are 103.2 and 98.0 eV, which can be attributed to SiO_2 and silicide species, respectively. Si can not be detected in PZT layer using AES after the Pt barrier layer was added, indicating that Pt layer stopped the diffusion of Si from substrate into the PZT layer completely.

The above results indicate that the Pt diffusion bar-

rier layer prevents the by-reaction of Ti element with carbon and silicon. The main cause is that the Pt layer prevents the diffusion of silicon into the PZT layer and curbs the reaction between silicon and Ti element. Moreover, the Pt layer also impedes the diffusion of oxygen into interface and increases the concentration of oxygen in the PZT layer, which causes the residual carbon to be oxidized, and prevents the reaction of carbon and Ti element. The existence of the Pt layer reduces the by-reaction in the PZT layer and promotes the formation of PZT species.

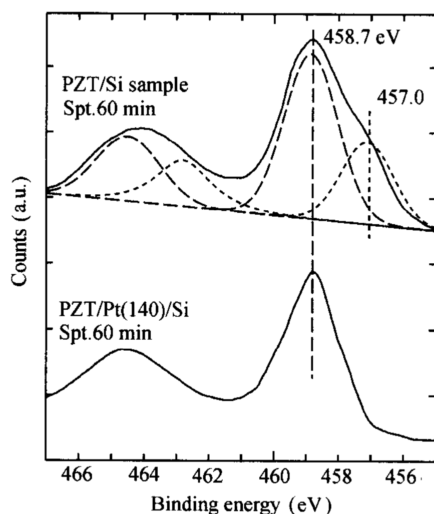

Fig. 1 Ti $2p$ spectra of PZT layer in PZT/Si and PZT/Pt (140 nm)/Si film sample.

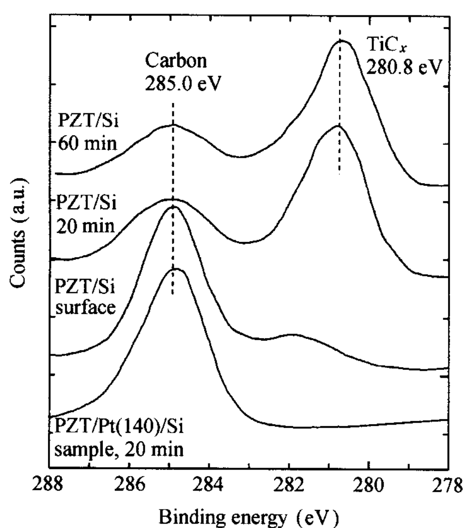

Fig. 2 C $1s$ spectra of PZT layer in PZT/Si and PZT/Pt (140 nm)/Si film sample.

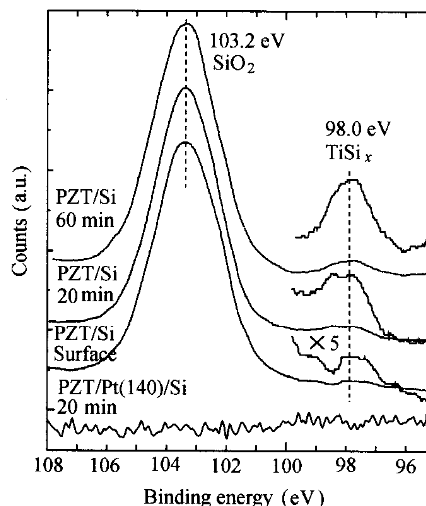

Fig. 3 Si $2p$ spectra of PZT layer in PZT/Si and PZT/Pt (140 nm)/Si film sample.

Effects of Pt layer on the interface diffusion and reaction

After PZT/Si sample was annealed at 800℃ for 1 h, the interface diffusion and oxidation were very serious.[13] A SiO_2 interface layer was formed on the interface of PZT/Si. The distribution of Pb, Zr, Ti elements in the PZT layer is not homogenous with depth. Fig. 4 showed the depth profile spectrum of PZT/Pt(140)/Si-(111) samples annealed at 800℃ for 1 h. After a Pt barrier layer was inserted, the distribution of Pb, Zr and Ti elements in the PZT layer becomes homogenous with depth. XPS and AES analyses also indicate that no detectable silicon was not found in the PZT layer. These results imply that the diffusion of silicon in the PZT layer is stopped completely. Although the Pt layer can not impede the diffusion of oxygen completely, the diffusion degree decreases greatly. Only a little oxygen can penetrate the Pt layer and diffuse into the Pt/Si interface to form a Gauss distribution. A stable SiO_2 interface layer can not be formed although oxygen reacts with silicon and forms SiO_2 species on interface of Pt/Si. The Pt layer also prevents the diffusion of PZT species into the Pt layer. Some diffusion and reaction existing on the interface of Pt/Si can improve the binding strength between Pt layer and the silicon substrate. In addition, the concentration of oxygen in the PZT layer of PZT/Pt(140)/Si sample is 70%, and is much higher than that of PZT/Si sample (50%).[13]

The Pt barrier layer prevents the diffusion of silicon from substrate to the PZT layer completely, and impedes the diffusion of oxygen from air to the interface of Pt/Si greatly. Due to the decrease of oxygen diffusion, the Pt layer impedes the formation of a stable SiO_2 interface layer. This will improve the dielectric properties of PZT/Pt/Si sample greatly. It suggests that the Pt layer is a good diffusion barrier layer for PZT/Si sample.

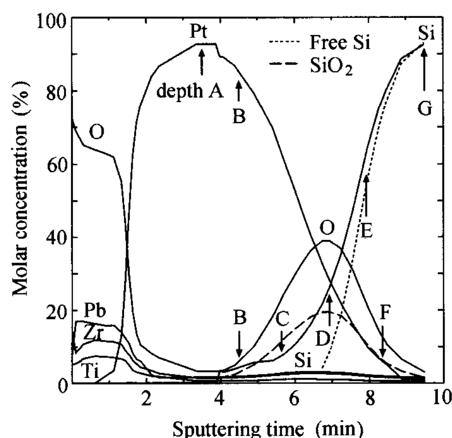

Fig. 4 AES depth profile of PZT/Pt (140 nm)/Si film sample treated at 800℃ for 1 h in air.

Effects of Pt *diffusion barrier layer on the interface reaction and species on* Pt/Si *interface*

The interface diffusion and reaction between a Pt layer and a Si substrate were studied here. The AES line shapes of Si LVV and Pt NVV are shown in Figs. 5 and 6. Fig. 5 indicates that there are two peaks of Si LVV near the interface of Pt layer and Si substrate. The kinetic energy is 72.5 and 88.5 eV, respectively. The former results from a SiO_2 species and the latter is a broaden peak which may be attributed to pure silicon and $PtSi_x$ species. When the depth is approaching the Si substrate, the peak at 72.5 eV disappears gradually. $PtSi_x$ species can be neglected due to a little Pt. The kinetic energy of the main peak is 88.5 eV corresponding to a pure silicon substrate. The SiO_2 species are formed by the oxidation between diffused oxygen and the silicon substrate, and the $PtSi_x$ species are produced by the reaction between the Pt layer and the silicon substrate. It can be found from Fig. 6 that the kinetic energy of Pt NVV is 60.1 and 58.1 eV in PZT/Pt interface, respectively, and it is 58.1 eV in the interface of Pt/Si. The peak at 60.1 and 58.1 eV can be attributed to pure Pt and $PtSi_x$ species, respectively.[14] This result implies that the Pt layer reacts with the silicon substrate to form $PtSi_x$ species on the interface of Pt layer/silicon substrate. It can be concluded that the Pt layer reacts with silicon substrate to form $PtSi_x$ species, which can enhance the binding strength between the Pt bottom electrode and the Si substrate.

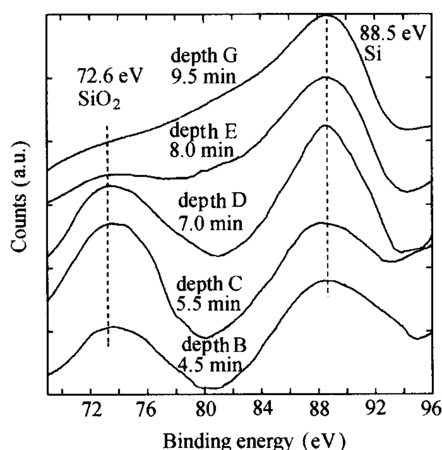

Fig. 5 Si LVV spectra in various depth of PZT/Pt (140 nm)/Si sample treated at 800℃ for 1 h in air.

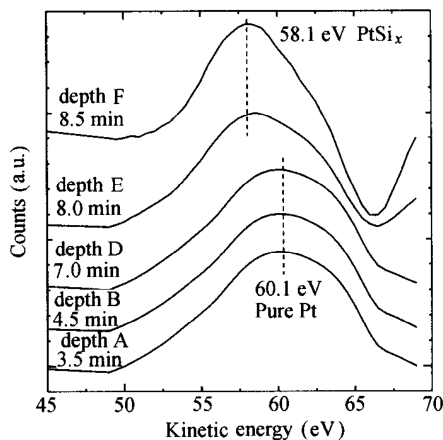

Fig. 6 Pt NVV spectra in various depth of PZT/Pt (140 nm)/Si sample treated at 800℃ for 1 h in air.

Effects of Pt *diffusion barrier layer thickness on interface reaction*

The effect of the thickness of Pt barrier layer on the interface diffusion and reaction is also studied here.

Fig. 7 shows the AES depth profile result of PZT/Pt (50)/Si(111) film sample. Here, the thickness of Pt diffusion barrier layer is as small as 50 nm. The concentration of oxygen in the PZT layer decreases from 65% to 40% when the thickness of Pt layer decreases from 140 to 50 nm. Silicon penetrates the Pt diffusion barrier layer and diffuses into the PZT layer. This result means that the thin Pt layer can not stop the diffusion of silicon completely. Oxygen diffuses into the silicon substrate and reacts with silicon to form SiO_2 species in the inner part of Pt layer. The kinetic energy of O KLL in the Pt layer is 502.3 eV, which indicates that oxygen in the Pt layer exists as SiO_2 species. The line shape of Si LVV also indicates that silicon exists as SiO_2 and $PtSi_x$ species in the Pt layer. However, the Pt layer can not impede the diffusion of oxygen into the silicon substrate. The diffused oxygen reacts with silicon to form a SiO_2 layer in the Pt layer. Meanwhile, the PZT species also diffuses into the Pt layer. When a Pt layer is deposited on the Si substrate, the Pt layer is constructed in Pt islands because it is formed at a Stranski-Krastanov mode not by layer-by-layer mode. As the thickness of Pt layer is less than 100 nm, there are many defects in the Pt thin layer.[15] These defects act as the diffusion channel of silicon and oxygen atoms. Thus, the thin Pt layer can not interrupt the diffusion and reaction between silicon and oxygen. The Pt layer that can play the role of a diffusion barrier layer must not be thinner than 140 nm.

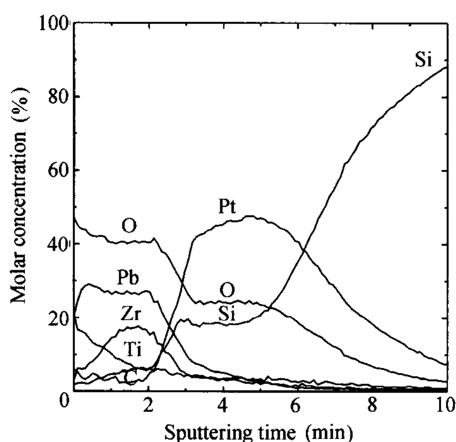

Fig. 7 AES depth profile of PZT/Pt(50 nm)/Si film sample treated at 800℃ for 1 h in air.

Effects of Pt *diffusion barrier layer on the structure and properties of* PZT *film sample*

XRD patterns of PZT/Si(111) and PZT/Pt(140)/Si(111) samples (Fig. 8) show that no characteristic diffraction peaks of PZT perovskite phase exist in the PZT/Si(111) sample. Several peaks of PZT perovskite phase appeared in the PZT/Pt(140 nm)/Si(111) sample after the sample annealed at 800℃ for 1 h. This result indicates that the Pt layer can promote the formation of perovskite phase in the PZT layer because the Pt layer impedes the existence and motion of silicon in the PZT layer.

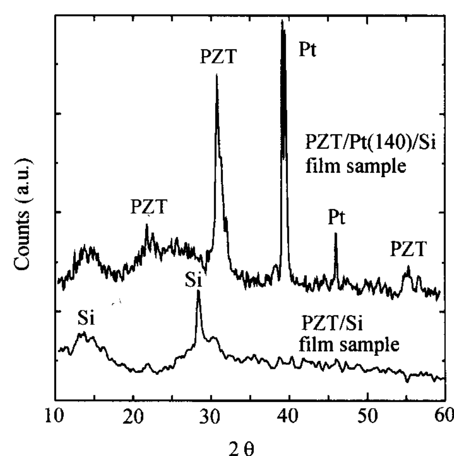

Fig. 8 XRD spectra of PZT/Si and PZT/Pt(140 nm)/Si film sample.

The Pt layer improves the dielectric properties of PZT thin film significantly. Figs. 9a and 9b show the comparison of PZT film and bulk PZT material in dielectric constant and dissipation factor. The dielectric constant of PZT film/Si(111) sample is 13 due to the formation of a SiO_2 layer on interface. After the Pt barrier layer is inserted, the dielectric constant can reach 620, which is close to that of bulk PZT material. The dissipation factor of PZT film is about 0.06 which is also close to that of bulk material. In addition, the ferroelectric properties are improved greatly after the Pt layer is inserted. A hysteresis loop can be observed in annealed PZT/Pt(140)/Si(111) sample as shown in Fig. 10. The remnant polarization P_r and coercive field E_c are estimated to be 28 $\mu C/cm^2$ and 65 kV/cm, respectively, but the PZT/Si(111) sample does not show the hystere-

sis loop because perovskite structure of PZT layer can not be formed.

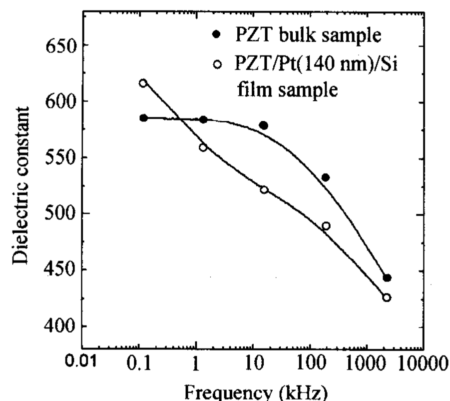

Fig. 9a Dielectric constant of bulk PZT ceramic and PZT/Pt (140 nm)/Si thin film sample.

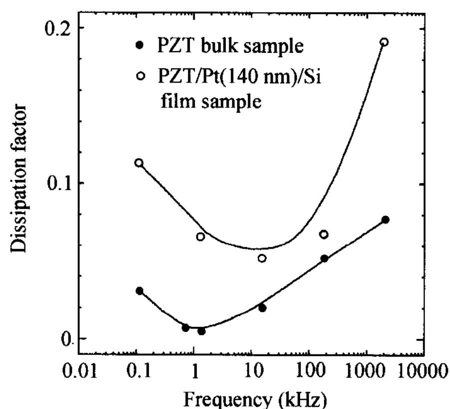

Fig. 9b Dissipation factor of bulk PZT ceramic and PZT/Pt (140 nm)/Si film sample.

In the PZT/Si sample, a SiO_2 interface layer is formed after being treated at 800℃ for 1 h. The formation of the SiO_2 layer between a PZT layer and a silicon substrate makes the PZT layer connect itself with the SiO_2 layer as a serial circuit. This serial connection causes great decrease of dielectric constant in the PZT/Si sample because the dielectric constant of SiO_2 is as low as about 10. After the Pt barrier layer was added, the diffusion and reaction between silicon and oxygen is curbed and the SiO_2 layer is not formed. As a result, only the PZT layer governs the dielectric properties of PZT/Pt/Si sample. Because the Pt layer can promote the crystallization of perovskite PZT phase and curb the by-reaction, the excellent ferroelectric properties can be obtained in PZT/Pt(140)/Si sample. It can be concluded that the insertion of the Pt barrier layer greatly improves the properties of PZT film/Si sample.

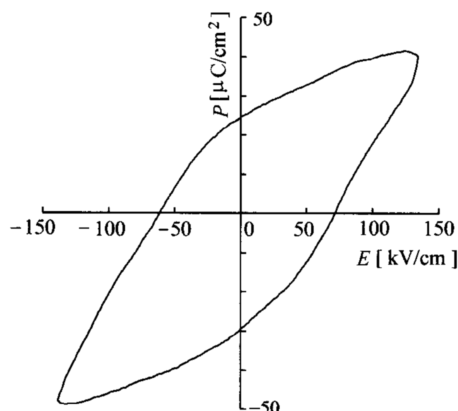

Fig. 10 Hysteresis loop of PZT/Pt(140 nm)/Si film sample.

Conclusion

1. The Pt diffusion barrier layer curbs the formation of TiC_x and $TiSi_x$ species in the PZT layer and promotes the formation of PZT species.

2. The Pt layer prevents the diffusion of silicon from substrate to the PZT layer completely and impedes the diffusion of oxygen from air to the silicon substrate significantly. A stable SiO_2 interface layer is not formed at the interface, and silicon can neither exist nor diffuse into the PZT layer.

3. The Pt layer promotes the crystallization of PZT perovskite phase and improves the dielectric properties of PZT/Pt(140)/Si(111) film sample to be close to those of bulk PZT material. The existence of Pt layer results in a good ferroelectric property of the PZT/Pt(140 nm)/Si film sample.

4. To interrupt the diffusion and reaction between oxygen and the silicon substrate, the thickness of Pt barrier layer must be not less than 140 nm. The Pt layer can react with silicon substrate to form $PtSi_x$ species and improve the binding strength between Pt layer and substrate.

References

1. Larsen, P. K; Cuppens, R.; Spierings, G. A. C. M., *Ferroelectrics*, **128**, 256(1992).

2. Hirai, T.; Teramoto, K.; Nagashima, K.; Koike, H.; Tarui, Y., *Jpn. J. Appl. Phys.*, **34**, 4163(1995).
3. Moulson, A.J.; Herbert, J.H., *Electroceramic, Materials, Properties and Applications*, Chapman and Hall, London, U.K., 1990.
4. Kalkur, T.S.; Argos, G.; Kammerdiner, L., *MRS Proc.*, **200**, 313(1991).
5. Shhichi, Y.; Tanimoto, S.; Goto, T.; Kuroiwa, K.; Tarui, Y., *Jpn. J. Appl. Phys.*, **33**, 5172(1994).
6. Otani, S.; Kimura, M.; Sasaki, N., *Appl. Phys. Lett.*, **63**, 1889(1993).
7. Ea-Kim, B.; Varniere, F.; Hugon, M.C.; Agius, B.; Bisaro, R.; Olivier, J., *Mater. Res. Soc. Symp. Proc.*, **433**, 163(1996).
8. Park, B.E.; Sakai, I.; Tokumitsu, E.; Ishiwara, H., *Appl. Surf. Sci.*, **117/118**, 423(1997).
9. Horita, S.; Naruse, T.; Watanabe, M.; Masuda, A.; Kawada, T.; Abe, Y., *Appl. Surf. Sci.*, **117/118**, 429 (1997).
10. Sakuma, T.; Yamamichi, S.; Matsubara, S.; Yamaguchi, H.; Miyasaka, Y., *Appl. Phys. Lett.*, **57**, 2431(1990).
11. Scott, J.F.; Kammerdiner, L.; Parris, M.; Trayner, S.; Ottenbacher, V.; Shawabkeh A.; Oliver, W.C., *J. Appl. Phys.*, **64**, 787(1988).
12. Yan, P.Y.; Li, L.T.; Zhang, X.W.; Zhu, Y.F.; Cao, L.L., *Bomo Kexue Yu Jishu* (in Chinese), **8**, 110 (1995).
13. Zhu, Y.F.; Cao, L.L., *Zhenkong Kexue Yu Jishu*, **16** (in Chinese), 18(1996).
14. Smith, M. A.; Levenson, L.L., *Phys. Rev. B*, **16**, 1365(1997).
15. Lelay, G.; Kern, R., *J. Crys. Growth*, **44**, 197(1978).

(E9907093 ZHOU, X.M.; DONG, L.J.)