



Fabrication of PZT Thick Films on Silicon Substrates for Piezoelectric Actuator

YONGBAE JEON, JAESHIK CHUNG & KWANGSOO NO

Korea Advanced Institute of Science and Technology, Department of Materials Science and Engineering, Taejeon, 305-701, Korea

Submitted March 12 1999; Revised September 7, 1999; Accepted September 22, 1999

Abstract. In recent years, there has been an increased interest in ferroelectric lead zirconate titanate (PZT) films for applications in piezoelectric devices. Many potential applications require a film thickness of about $10\ \mu\text{m}$ for higher force, better sensitivity and stability. In this study we fabricate lead zirconate titanate (PZT) thick films by screen printing on silicon substrates with a platinum bottom electrode. Various substrates were studied. The longitudinal piezoelectric coefficient, d_{33} , was measured by the normal load testing method. Breakdown voltage, $\tan \delta$, P-E hysteresis loop and permittivity were measured on the PZT thick films. The results are promising for the use of PZT thick films in various applications, for example, in silicon micromachined micro-pump.

Keywords: films, X-ray method, piezoelectric properties, PZT, actuators

1. Introduction

Piezoelectric thick film integrated circuits or components are useful as microsensors and actuators in various areas of application: medical, military, telecommunications, motor vehicle and office automation. In particular, the combination of screen printed PZT thick film and silicon substrate allows for inexpensive fabrication technology and provides the possibility of depositing a wide thickness range of films for various devices.

It is almost impossible to produce film thicknesses of about $10\ \mu\text{m}$ using thin film processing methods, such as sol-gel, sputtering and CVD [1]. It is very difficult to fabricate PZT thick films on the silicon substrates because of volatility of PbO and the interdiffusion of Si and Pb through the bottom electrode during sintering at normal temperatures (such as above 1200°C). Consequently many researchers use Al_2O_3 substrates [2]. In this study, PZT materials, which can be sintered at low temperature [3] (under 1000°C), were printed on Pt. Various diffusion barrier layers such as SiO_2 , ZrO_2 , $\text{SiN}_x/\text{SiO}_2$ and MgO thin films were coated on Si

substrates to minimize interdiffusion between the Si and Pb.

2. Experimental Procedure

The screen printing paste was made by mixing the PZT powder and an organic vehicle (DJB-7401) using conditioning mixer (MX-201, Thinky Co., Ltd). We studied different diffusion barrier layers: sol-gel ZrO_2 ($1500\ \text{\AA}$), thermal SiO_2 ($5000\ \text{\AA}$), sputtered MgO ($3000\ \text{\AA}$) and LPCVD $\text{SiN}_x/\text{SiO}_2$ thin films ($1800\ \text{\AA}/500\ \text{\AA}$), etc. Platinum bottom electrodes ($4000\ \text{\AA}$) were deposited by dc magnetron sputtering at 400°C with 25 W on the different diffusion barrier layers. For $30\ \mu\text{m}$ thick films, we coated the PZT paste on the Pt bottom electrodes 5 times, dried the paste each time for 10 min at 120°C , and then fired the samples in a tube furnace at a peak temperature of 925°C for 30 min. The normal sintering temperature of PZT powder is above 1250°C . At this high temperature, it was almost impossible to prevent the interdiffusion between the Pb and Si, and the vaporization of Pb. Therefore, we used the PZT

powder with specified glass frit (5 wt% Bismuth doped) as a sintering aid [3] in order to decrease the sintering temperature significantly. A prior study showed that almost fully dense bulk PZT samples could be prepared as low as 950°C. This is the main reason we sintered our thick films at 925°C. Finally, the Pt top electrodes were deposited at room temperature on the PZT layers by sputtering.

3. Results and Discussions

Figure 1 shows the typical XRD patterns of the as-deposited Pt bottom electrode on the various buffer layers. All of the XRD patterns show that the Pt films are highly oriented to (111) being parallel to the substrate surfaces, and the buffer layers consist of amorphous phases within the limit of XRD. We also studied Pt layers having different thicknesses up to 1 micron but found that there is no difference in the XRD patterns of the Pt layers of different thicknesses.

Figure 2 shows the typical XRD patterns of the PZT thick films (30 microns) on the Pt layers with various buffer layers. It is difficult to establish the PZT crystal structure near the interface region because PZT layers are too thick, but (110) peaks of PZT are distinguished in the MgO and ZrO₂ buffer layer cases. The polycrystalline perovskite phase was formed in the PZT thick films when deposited on SiO₂ or SiN_x/SiO₂ buffer layers. The films were sintered at 925°C for 30 min. We also sintered the films at 1100°C but observed that the films consisted of no perovskite phase. We found that severe diffusion between the Pb and Si occurred in all of the films sintered at 1100°C.

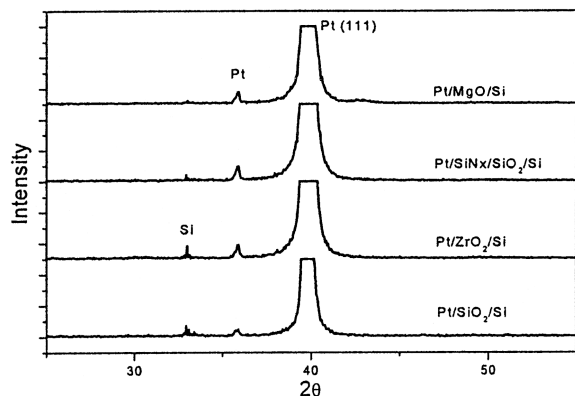


Fig. 1. XRD patterns of Pt on the various buffer layers.

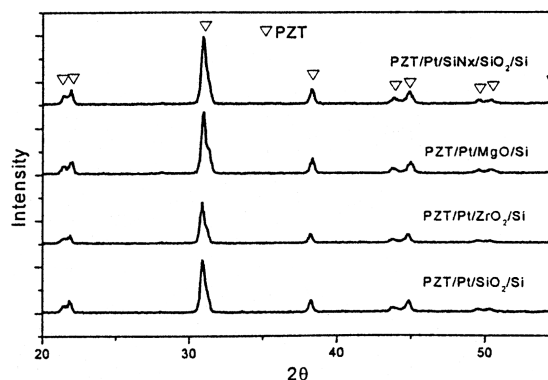


Fig. 2. XRD patterns of PZT films on Pt with various buffer layers.

Figure 3 shows SEM images and EDXS line scans of the Pb and Si of the fractured and polished surfaces of the PZT/Pt/buffer layers/Si sample. The films show a fairly dense microstructure consisting of a few micron grains. Because only Pt electrodes without Ti buffer layers were applied in this study, there are portions of the films at which the Pt electrode separated from the SiO₂ layer. This kind of separation may be solved by applying a thin Ti layer between the Pt and SiO₂. The ZrO₂ buffer layer had a good adhesion, but some interdiffusion occurred between Si and PZT. SiN_x/SiO₂ buffer layers had the worst adhesion, and many hillocks and cracks were observed on the Pt surface. The MgO buffer layer did not have enough adhesion and did not serve as a good interdiffusion barrier. The buffer layer of the ZrO₂(1500)/SiO₂(6000 Å) produced enough adhesion and diffusion barrier. Figure 4 (a),(b) show XRD patterns and SEM image of the PZT/Pt/ZrO₂/SiO₂/Si. The best crystal structure, diffusion barrier and adhesion were obtained for this sample.

Figure 5 shows a typical SEM image of the fractured surface of the PZT film (one layer coated). Large voids of a few microns are observed. These voids resulted from micron air bubbles which formed during the mixing and screen printing processes and were trapped inside the green films. The screen mesh mark also caused some defects on the surface of the films. After sintering, the mesh mark and the trapped air bubble turned to voids passing through the thickness of the films and causing an electrical short circuit between the top and bottom electrodes, thereby significantly lowering the breakdown field. We systematically analyzed the process, step by step, to

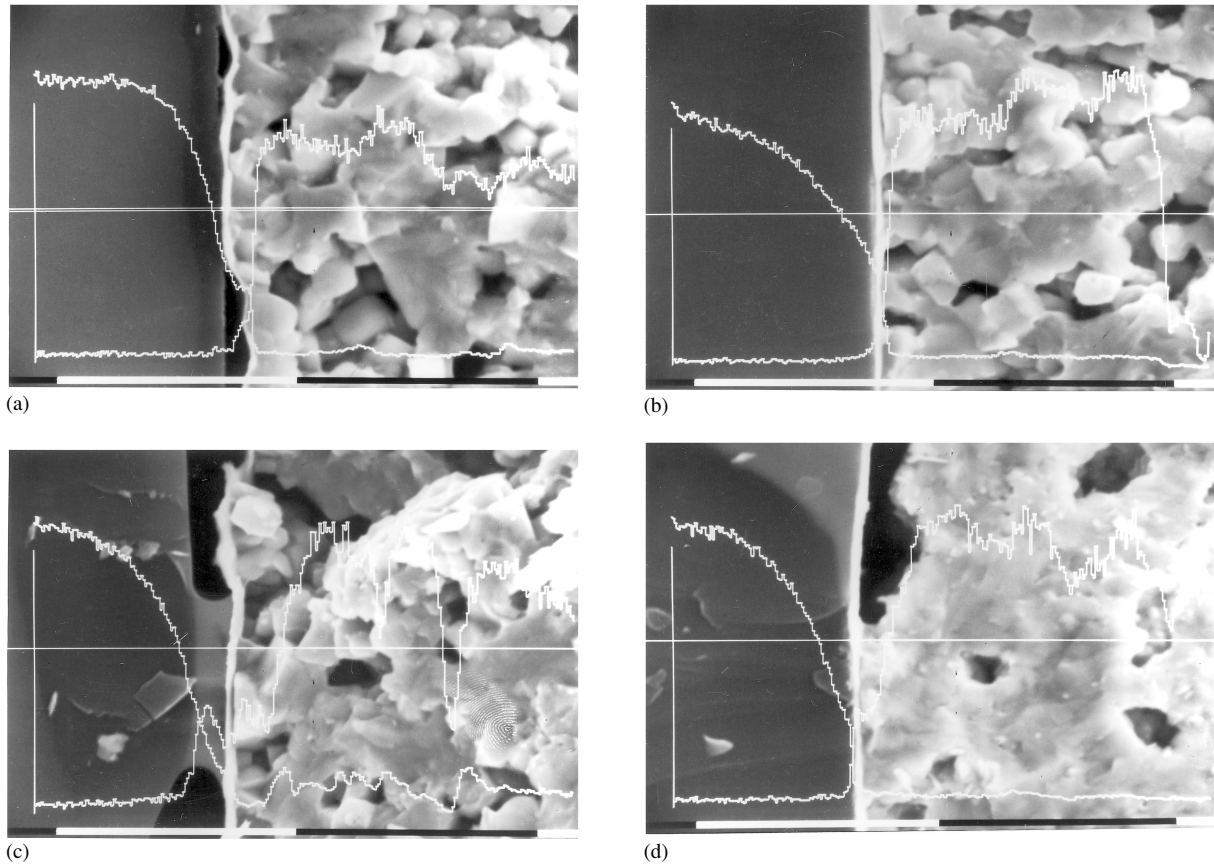


Fig. 3. The SEM images and EDS scanning data (a) PZT/Pt/SiO₂/Si, (b) PZT/Pt/ZrO₂/Si, (c) PZT/Pt/SiN_x/SiO₂/Si, (d) PZT/Pt/MgO/Si (left side is Si substrates, right side is PZT thick films, EDS lines are Si, and Pb, bar = 10 μm).

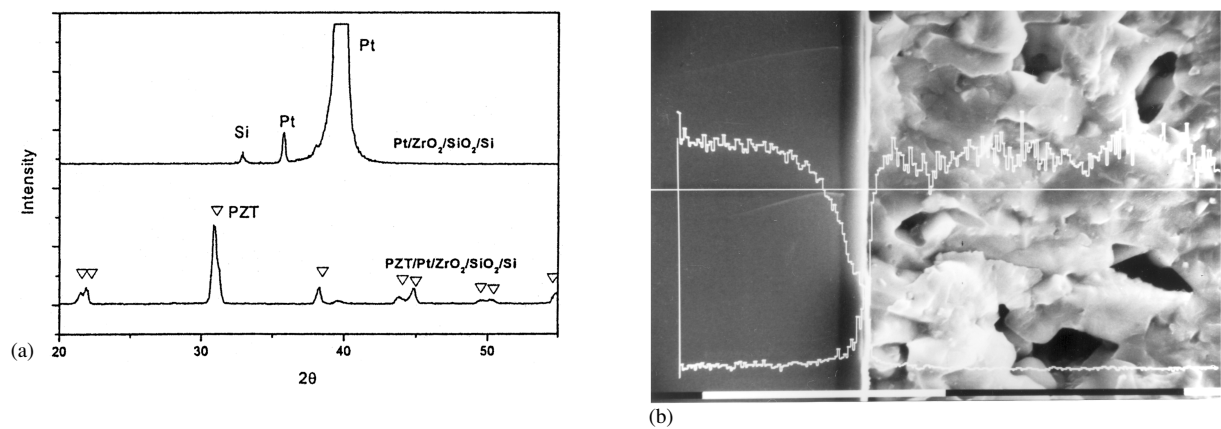


Fig. 4. (a) XRD patterns of the PZT thick film with ZrO₂/SiO₂ buffer layer, (b) SEM image and EDS scanning data of the PZT thick film with the ZrO₂/SiO₂ buffer layer (bar = 10 μm)

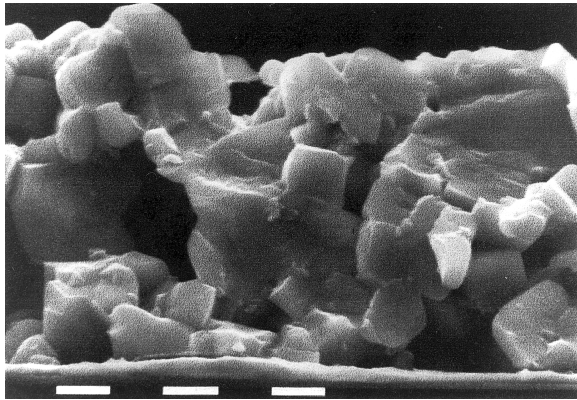


Fig. 5. The SEM image of the fracture surface of the porous PZT film. (bar = 1 μm)

improve the mesh mark and trapped air bubble. Lowering the viscosity of the paste and the aging of the films at room temperature under ultrasonic vibration helped to decrease the voids.

Figure 6 shows the fracture surface of the PZT film (one layer coated) fabricated by the additional process described above. The portion of the microstructure was selected for the worst case. The density was improved compared to the microstructure in Fig. 5, but connected voids passing through between the top and bottom surfaces were still observed. Multiple coating improved the short circuit between the top and bottom electrodes. Now a further improvement is being studied.

Figure 7 shows an hysteresis loop of the PZT thick film on Pt/ZrO₂/SiO₂ buffer layer with 6.57 uC/cm²

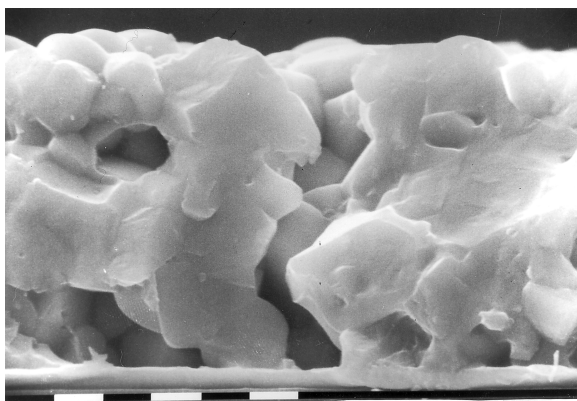


Fig. 6. The SEM image of the fracture surface of the PZT film (bar = 1 μm)

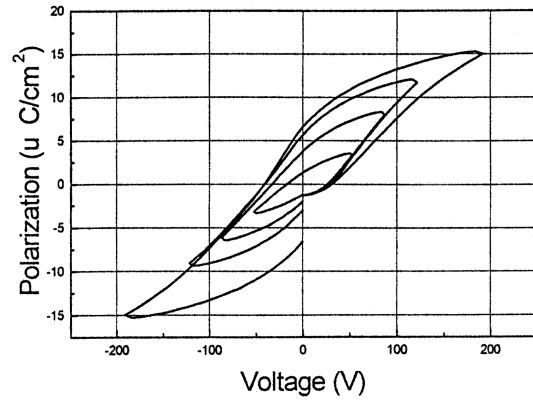


Fig. 7. The hysteresis curve of polarization-electric voltage.

and 13 kV/cm for the remanent polarization and coercive field respectively. The dielectric permittivity ϵ_r , the dissipation factor δ , the breakdown voltage and piezoelectric constant d_{33} of the PZT thick film with ZrO₂/SiO₂ buffer layer are then measured and the results recorded in Table 1. ϵ_r and $\tan \delta$ are measured under the conditions of applied voltage 1 KHz–0.1 V. The PZT thick films are poled at 150°C with 3 MV/m for 0.5 h. The piezoelectric coefficient, d_{33} was measured by the normal load method [5] that is applying 0.3 N on the PZT thick film and reading the induced voltage. These values are not worse compared with the bulk ceramic materials [3] and other thick films [1]. The piezoelectric constant [4,5], d_{33} , was lower than bulk ceramics but was larger than other PZT thick films [1]. It is not clear yet whether the observed low d_{33} is due to either or both the low density and/or the sintering additives applied in this study. It is impossible to get rid of the sintering additive due to the low sintering temperature for the integration. The density of the films improves with additional processing steps, but it is too early to make any definite conclusions.

Table 1. The dielectric and piezoelectric properties of the final PZT thick film

| ϵ_r | Tan δ | Breakdown field (MV/m) | d_{33} [pC/N] |
|--------------|--------------|------------------------|-----------------|
| 1260 | 0.015 | 11 | 343 |

Acknowledgment

The authors express sincere appreciation for G7 project's fund of Ministry of Science and Technology (MOST), Ministry of Commerce, Industry and Energy (MOCIE) and Samsung Electronics Inc. And we would like to thank Dr. Seong-Jin Kim, Dr. Jaewoo Chung of SAIT, and Dr. Hak-In Hwang, Mr. Jun-Shik Park of KETI for supplying the substrates and PZT paste, and Mr. Dong Guk Kim of KAIST for his help with measuring d_{33} .

References

1. M. Koch, N. Harris, A.G.R. Evans, M. White, and A. Brunnschweiler, *1997 International Conference on Solid-State Sensors and Actuators*, Chicago, 353–356 (1997).
2. J. Vechembre, L. Sagalowicz, and N. Setter, submitted *JMR*, (1998).
3. Gui, Zhllun, Li Logntu, Gao Suhua, and Zhang Xiaowen, *J. Am. Ceram. Soc.*, **72**(3), 486–491 (1989).
4. K. Lefki and G.J.M Dormans, *J. Appl. Phys.*, **76**(3), 1764 (1994).
5. C.J. Kim, Fabrication, *Analysis of Growth Mechanism and Electrical Properties of Aligned PZT Thin Films*, PhD thesis, Korea Advanced Institute of Science and Technology, (1995), p. 158.