

行政院國家科學委員會專題研究計畫 成果報告

以網印法合成相對厚 PZT 壓電薄膜之研究

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以網印法合成相對厚鉛鈦酸鉛壓電薄膜之研究

計畫編號：92-2216-E-032-005

主持人：林諭男

執行期限：92/8/1 ~ 93/7/31

摘要：

本研究以網印法製作 PNN-PZT 厚膜，並利用雷射轉印法將其轉印至 Pt/Ti/SiO₂/Si 基板。所得到的 PNN-PZT/Si 厚膜具有優越鐵電特性；其殘留極化值為 $P_r = 16.5 \mu\text{C}/\text{cm}^2$ 而矯頑電場為 $E_c = 24.6 \text{ kV}/\text{cm}$ 。

關鍵字：壓電薄膜、網印合成法

Abstract

PNN-PZT thick films on silicon substrate were prepared by the screen printing method on sapphire and then were transferred from sapphire substrate to Pt/Ti/SiO₂/Si substrate. The PNN-PZT green films which screen-printed on sapphire were sintered at 1200 °C for 3 hours. These films were attached to Pt/Ti/SiO₂/Si substrate using a silver-bonding process. Then, a single 248 nm KrF excimer laser pulse was used to irradiate through the sapphire substrate. The 38 ns pulse at 400 mJ/cm² fluence melted PNN-PZT layer at the interface, expelling the sapphire and leaving the PNN-PZT film bonded to the silicon substrate. Silver-bonding and laser lift-off process can successfully transfer the PNN-PZT films from the sapphire to silicon substrates, maintaining ferroelectric properties. The resulted PNN-PZT/Si thick films possess good ferroelectric properties: $P_r = 16.5 \mu\text{C}/\text{cm}^2$ and $E_c = 24.6 \text{ kV}/\text{cm}$.

一、研究背景：

Lead zirconate titanate (PZT) with excellent piezoelectric properties, a high Curies temperature, high spontaneous polarization and high electromechanical coupling coefficient, had been found tremendous opportunity in device application. Thin films of Pb(Zr_{1-x}Ti_x)O₃-series materials with marvelous piezoelectric constant are suitable for

synthesizing microsensors, such as surface acoustic wave device, force sensor, gas sensor and accelerometer^(1~4). However, in order to apply these materials as microactuators, a critical component in micro-electro-mechanical system (MEMS), thick PZT films are required.^(5~7) While the sputtering, sol-gel, MOD and laser ablation process^(8~10) are suitable for synthesizing Pb(Zr_{1-x}Ti_x)O₃ films of sub-micron thickness, they have tremendously difficulty in growing the films with thickness 5 μm. The major problem is the accumulation of residual stress with film thickness, which easily induces the cracking for the films.

In this paper, we synthesized relatively thick PNN-PZT films in a totally different approach. We first modified the PZT materials with 45 mol.% Pb(Ni_{1/3}Nb_{2/3})O₃ so as to reduce the firing temperature necessary for the densification of materials and then screen printed^(11,12) PNN-PZT thick film on sapphire substrate, followed by sintering at high temperature to reach a high density. We then transferred the PNN-PZT films from sapphire to silicon substrates by using laser lift-off^(13,14) technique. Relatively thick PZT films (20 μm) possessing good ferroelectric properties can thus be obtained.

二、研究方法：

The $x\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-(1-x)\text{Pb}(\text{Zr}_{0.39}\text{Ti}_{0.61})\text{O}_3$ ($x=0.45$) materials, which were designated as PNN-PZT, were prepared by a conventional mixed oxide process using two-step calcination technique to circumvent the formation of undesired pyrochlore phase. NiO and Nb₂O₅ powders with 1:1 molar ratio were first mixed and calcined at 850 °C (32 h) to form Columbite phase, which were then mixed with PbO, ZrO₂ and TiO₂ of nominal composition, followed by calcinations at 850 °C (2 h). Thus obtained PNN-PZT powders were pulverized down to sub-micron size and then mixed with ethyl cellulose and α-terpineol at 140°C for 10

minutes to form the printed paste.

The PNN-PZT green films were screen-printed on sapphire. It was printed 5 times and each green layer was dried at 100°C. After printing, the thick film was pressed uniaxially under 2000 psi for 1 min to make the film denser. Finally, the green film was debindered at 600 °C for 2 h, and then fired at 1200 °C for 3 h, resulting in thick PNN-PZT layer (~25 µm) on sapphire.

Without using the PdIn₃-bonding process (11, 12), we tried using the silver as the bonding materials. Both the surfaces of PNN-PZT and silicon substrate were screen printed with a thin layer of silver-paste, about 7 µm for each layer, and then bonded together at 100 °C for 6 hr. Then, a single 248 nm KrF excimer laser pulse was used to irradiate through the sapphire substrate. The 38 ns pulse at 400 mJ/cm² fluence melted PZT buffer layer at the interface, expelling the sapphire and leaving the PNN-PZT film bonded to the silicon substrate. The ferroelectric properties of the films were measured by modified Sawyer-Tower circuits.

三、研究結果與討論

All the sintered PNN-PZT films possess perovskite structure with no secondary phase (Fig. 1). Evolution of microstructure with sintered temperature is shown in Fig. 2, the grains are small (< 1 µm) when the PNN-PZT films are sintered at 1000 °C (3 hr) and grow appreciably (to 2-5 µm) when the films are sintered at 1200 °C (3 hr). There exists large proportion of pores for these samples, which is apparently due to the constrain of the sapphire on the lateral shrinkage of the films. Fortunately, the pores are not interconnected such that good ferroelectric properties are observed.

Figure 3 indicates that the 1000 °C-sintered PNN-PZT films possess large remanent polarization (P_r) = 10 µC/cm² and coercive field (E_c) = 30 kV/cm. The P_r -value increases with sintering temperature, reaching P_r = 16.4 µC/cm², whereas the E_c -value decreases with the sintering temperature, approaching E_c = 12.6 kV/cm, for 1200 °C-sintered ones. The increase in remanent polarization with sintering temperature can apparently be ascribed to the increase in sintered density and the decrease in coercive field is owing to the increase in grain size of the films.

To transfer the PNN-PZT films from sapphire to the silicon substrate, both the surfaces of PNN-PZT and silicon substrate

were coated with a thin layer of Ag-paste (15 µm) and then bonded together. Laser beams were then irradiated through the sapphire to locally vaporize the PNN-PZT-to-sapphire interface layer, separating the PNN-PZT/Si films from the sapphire. Figure 4(a) illustrates the top-view and cross-sectional view of the PNN-PZT sapphire films prior to the transferring process, whereas Fig. 4(b) shows the top and cross-sectional view of the PNN-PZT/Si films after transferring from sapphire to silicon substrates by laser lift-off process. Moreover, X-ray diffraction patterns for the two PNN-PZT films shown in Fig. 4 and Fig. 5(a). reveals that the films possess pure perovskite structure, before and after the laser lift-off process. There is no damaged layer observable. These results indicated that although the laser irradiation vaporized the PNN-PZT films in film-to-sapphire interface, the melted layer crystallize instantaneously after cooling. The damage due to laser irradiation process is minimal. However, Fig. 5(b) illustrates that the remanent polarization (P_r) of the PNN-PZT films are not degraded, but the coercive field (E_c) of the films increases markedly due to the laser lift-off process. Apparently, the laser irradiation process induces some damage on a thin layer of materials, which is non-ferroelectric, even though the SEM and XRD examination can not resolve the existence of the damaged layer.

四、結論：

Thick PNN-PZT films, about 25 µm, were successfully prepared by combining the screen printing and laser lift-off techniques. PNN-PZT films screen printed on sapphire substrate are of secondary free perovskite, possessing good ferroelectric properties (P_r = 16.4 µC/cm², E_c = 12.6 kV/cm), after sintering at 1200 °C (3 hr), although there exist large proportion of pores on the thick films. Silver-bonding and laser lift-off process can successfully transfer the PNN-PZT films from the sapphire to silicon substrates, maintaining ferroelectric properties. The resulted PNN-PZT/Si thick films possess good ferroelectric properties: P_r = 16.5 µC/cm² and E_c = 24.6 kV/cm.

伍、參考資料：

1. Shibata, Y.; Kuze, N.; Kaya, K.; Matsui, M.; Kanai, M.; Kawai, T. IEEE, Volume: 1, 3-6 Nov. 1996 Page(s): 247 -254
2. Itoh, T.; Lee, C.; Sasaki, G.; Suga, T., Materials Chemistry and Physics Volume: 44,

- Issue: 1, April, 1996, pp. 25-29
3. Dorojkine, L.M.; Volkov, V.V.; Doroshenko, V.S.; Lavrenov, A.A.; Mourashov, D.A.; Rozanov, I.A. *Sensors and Actuators B: Chemical*, Volume: 44, Issue: 1-3, October, 1997, pp. 488-494
 4. Nemirovsky, Y.; Mural, P.; Setter, N.; Nemirovsky, A. *Sensors and Actuators A: Physical*, Volume: 56, Issue: 3, September, 1996, pp. 239-249
 5. V.Kaajakari, S.Rodgers, A.Lal, The Thirteenth Annual International Conference on Micro Electro Mechanical Systems, MEMS 2000, 23-27, 40 (2000).
 6. S. Matsumoto, A. Klein, R. Maeda, Twelfth IEEE International Conference on Micro Electric Mechanical systems, MEMS'99. 141, (1999).
 7. J.Y.Park, Y.J.Yee, H.J.Nam, J.U.Bu, , Microwave Symposium Digest, 2001 IEEE MTT-S International , 3 , 2111 (2001).
 8. G. Yi, M. Sayer, *Ceram. Bull.*,70(7)1173-1179(1991).
 9. J. D. Mackenzie, and Y. Xu, *J. Sol-Gel Sci.&Tech.*, 8,673-679(1997)
 10. M. H. Yeh, K. S. Liu, I. N. Lin, *J. Appl. Phys.*, 77(10), 5335 (1995).
 11. Tomoaki Futakuchi, Kunitaka Nakano, Masatoshi Adachi, *Jpn. J. Appl. Phys.*, **39**, 5548 (2000)
 12. Tomoaki Futakuchi, Hiroshi Yamano and Masatoshi Adachi, *Jpn. J. Appl. Phys.* **40**, 5687 (2001)
 13. W. S. Wong, Y. Cho, E. R. Weber, and T. Sands, *Appl. Phys. Lett.*,75,1887 (1999).
 14. L. Tsakalakos, T. Sands, *Appl. Phys. Lett.*, 76, 227 (2000).

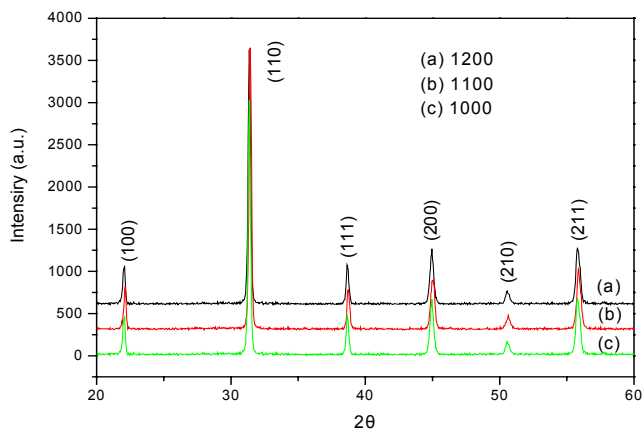


Fig.1 X-ray diffraction of the PNN-PZT thick films, which were screen printed and the sintered at (a)1000 , (b)1100 , and (c)1200 for 3hr.

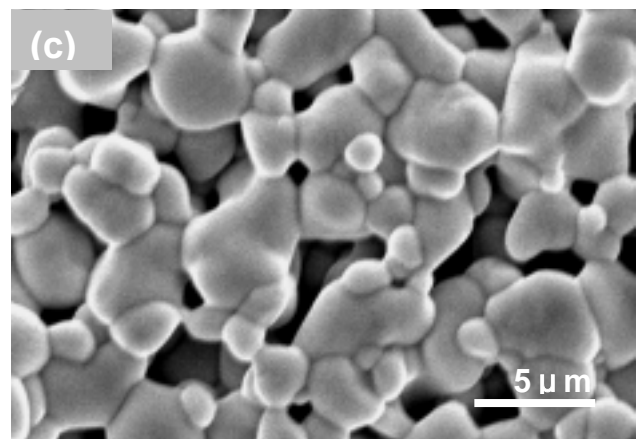
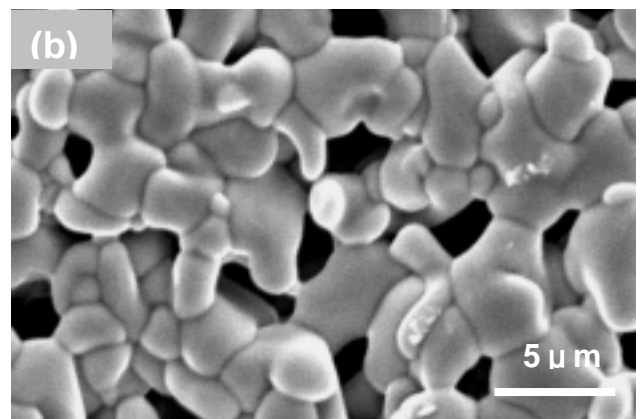
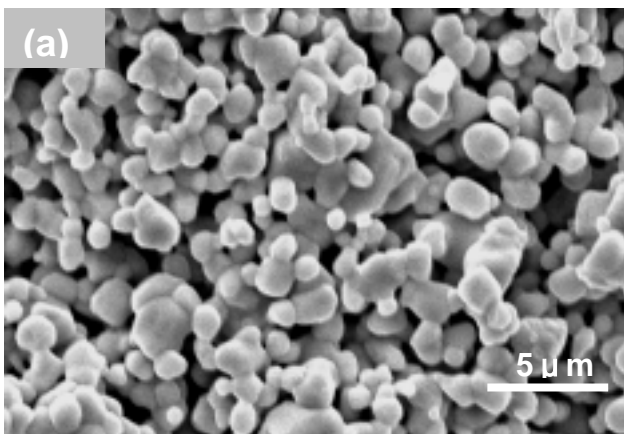
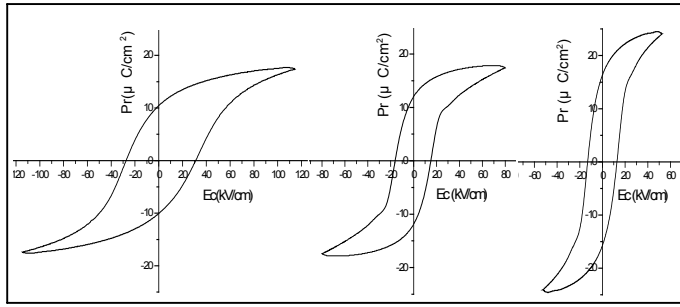


Fig.2 SEM microstructure of the PNN-PZT thick films, which were screen printed and the sintered at (a)1000 , (b)1100 , and (c)1200 for 3hr.



1000 (3 hr)	1100 (3 hr)	200 (3 hr)
$Pr=10 \mu C/cm^2$	$Pr=12.1 \mu C/cm^2$	$Pr=16.4 \mu C/cm^2$
$Ec=30 kV/cm$	$Ec=15.2 kV/cm$	$Ec=12.6 kV/cm$

Fig.3 The electrical polarization-field (P-E) characteristics of the PNN-PZT thick films, which were screen printed and the sintered at ()1000 , ()1100 , and ()1200 for 3hr.

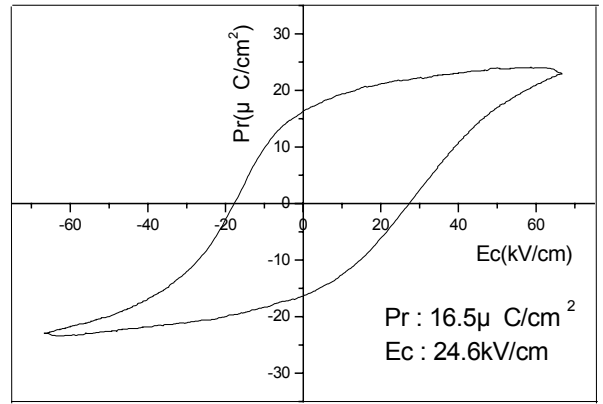
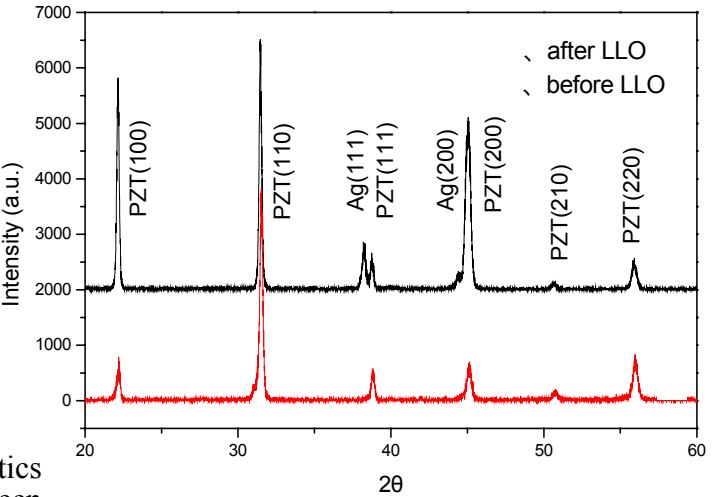
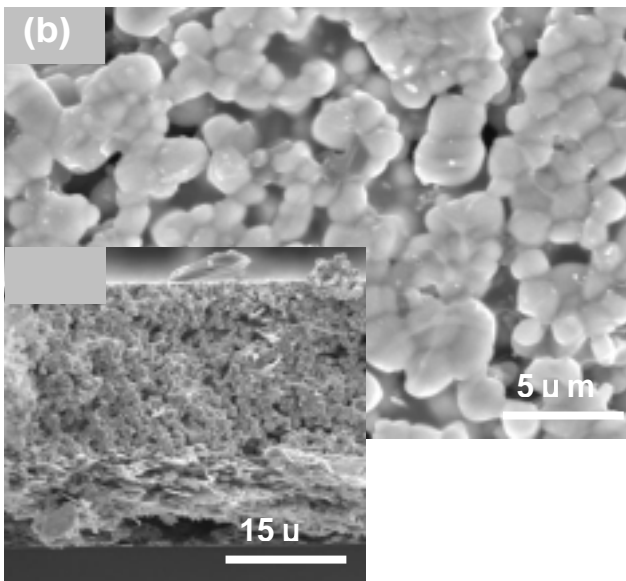
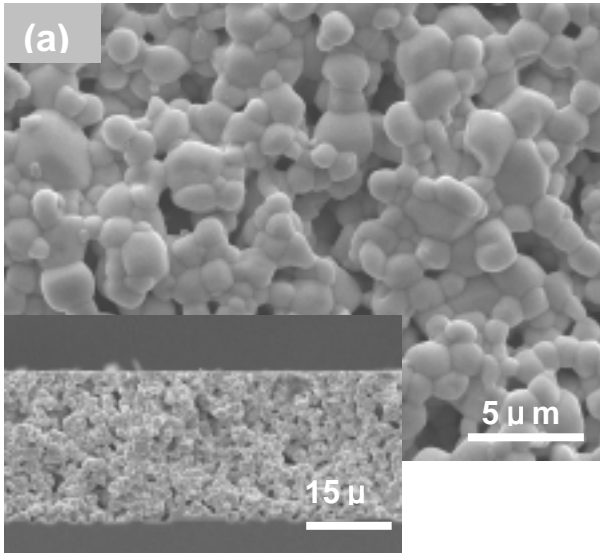


Fig.5 (a) X-ray diffraction patterns and (b) ferroelectric properties of the PNN-PZT thick films after laser transferring from sapphire to silicon substrates. The films were screen printed and then sintered at 1200 (3hr).

Fig.4 Plan-view and cross-sectional-view SEM micrographs of the PNN-PZT/sapphire thick films (a) before and (b) laser transferring process. The films were screen printed and then sintered at 1200 (3hr).