Extended Abstracts of the 2014 International Conference on Solid State Devices and Materials, Tsukuba, 2014, pp208-209

# Enhancement of pyroelectric PZT thick film sintered at low temperature on Pt-Si substrate by adding $Pb_5Ge_3O_{11}$

C. G. Wu, Q. X. Peng, J. Meng, X. Y. Sun, Y. Shuai, J. Q. Cao, W. B. Luo, W. L. Zhang

State Key Lab of Electronic Thin films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China
Phone: +86-28-83202140 E-mail: cgwu@uestc.edu.cn

**Abstract**

**Effects of $Pb_5Ge_3O_{11}$ (PGO) sintering additive on the sintering temperature (Ts) and the pyroelectric properties of 1×1mm$^2$ Lead-zirconate-titanate (PZT) thick films on Pt/Ti/$SiO_2$/Si substrate were studied. The pattern of PGO-added PZT thick films were directly formed by electrophoresis deposition (EPD). The PGO percentage and Ts were optimized at the range of from 0wt% to 9wt% and 700°C to 900°C, respectively. The 800°C-sintered PZT films with 3wt% PGO exhibited room-temperature pyroelectric coefficient (Pc) of $1.73\times10^{-8}$C/cm$^2$K, permittivity of 330 and dielectric loss of 1.5%, figure of merit for detectivity (FD) of $1.7\times10^{-5}$Pa$^{-0.5}$, respectively. These results demonstrate that the patterned PGO-added PZT thick films show potential applications in Si MEMS infrared detectors.**

## 1. Introduction

PZT thick film shows great promising application in ferroelectric devices such as sensors, actuators, ultrasonic motors. It is crucial to deposit and pattern the PZT thick films to fabricate MEMS devices. Many methods, such as screen printing, composite film technology, EPD and direct writing, are used to deposit PZT thick films onto the desired substrates [1]. EPD is regarded as a potential way to deposit and pattern the PZT thick films on Si substrate, because of the advantages of direct patterning, simple equipment, low cost and compatibility with complex geometries [2].

Sintering process is necessary to transform the green body to ceramic thick film. Conventionally, the PZT ceramics were sintered at temperature higher than 1250°C [3]. However, the high sintering temperature was unacceptable for PZT films on Si substrate because of the severe Pb/Si inter diffusion.

PGO powder was selected as sintering additive in this paper based on the following advantages: Firstly, PGO was a pyroelectric material with low melting point (about 740°C) and Pc (1-3×$10^{-9}$C/cm$^2$K). Secondly, the low dielectric constant of PGO was beneficial to FD [4]. Finally, compared to mixed powder such as $LiBiO_2$-CuO, the electrophoresis process would be more easily controlled. However, the effect of PGO sintering aid on pyroelectric properties of EPD deposited PZT thick films on Si substrate have not been studied.

In the present paper, we describe the preparation processing and characterization of PZT thick films with various PGO percentages as sintering additive. The influences of Ts and Si diffusion on pyroelectric properties of the PZT thick films were investigated.

## 2. Experiments

PGO was synthesized by solid reactive method using PbO (99.9%) and $GeO_2$ (99.999%) mixture powders at 680°C for 10h. PZT (Hayashi Chemical Industry Company, commercial, $Pb(Zr_{0.3}Ti_{0.7})O_3$)/PGO powders suspension was prepared for the fabrication of the thick films.

Patterned Pt(200nm)/Ti(30nm) electrode was sputtered on $SiO_2$/Si substrate by DC magnetron sputtering before PZT deposition. 10V/cm DC voltage was applied between the Pt/Ti cathode and graphite counter electrode in suspension. The deposition rate was about 10μm/min. 30μm thick PZT films were deposited by EPD in 3min.

The organic binder was removed by thermal treatment at 400°C with rising rate 1°C/min. The samples were sintered at temperature from 700°C to 900°C for 1h in air atmosphere. The heating and cooling rate were 4°C and 2.5°C per minute respectively.

The phase identification of PGO and the thick films were performed by X-ray diffraction (XRD) and cross sectional microstructures were characterized using Scan Electron Microscope (SEM). The silicon diffusion was monitored by Energy Disperse Spectroscope (EDS). For electrical measurements, 100nm Pt layer with 40nm intermediate adhesive Ti layer were DC sputtered as top-electrode. All the films were poled at 150°C for 15min using 6V/μm electric filed. The Pc properties of the films were tested by auto-measurement system [5]. The relative dielectric constant and loss of the composites were measured by an impedance analyzer (Agilent-4284A).

## 3. Result and Discussion

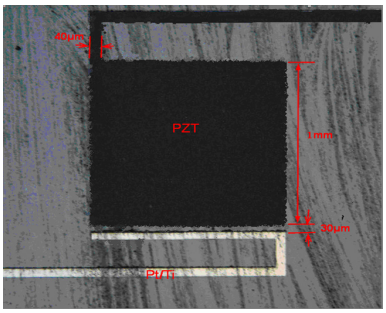


Fig.1 optical microscopy image of the patterned PZT thick film on $SiO_2$/Si substrate

Fig.1 showed the optical microscopy image of the patterned PZT thick film deposited on Si substrate by EPD. The clear gap between PZT film and the blank Pt/Ti elec-

trode is about 30μm, indicating that EPD has promising potential application in pyroelectric and piezoelectric device fabrication.

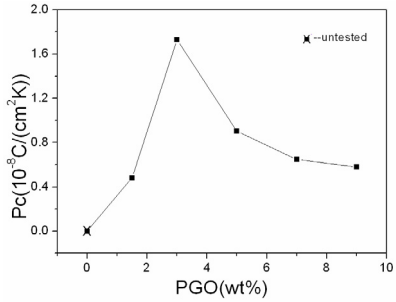


Fig.2 $P_c$ of PZT thick films with various GPO percentages

Various PGO percentages (0wt%, 1.5wt%, 3wt%, 5wt% 7wt%, 9wt%) added PZT thick films were sintered at 800°C for 1h. Fig.2 shows the curve of $P_c$ versus PGO percentage. The $P_c$ of the PZT thick film without PGO additive can not be given because the film was still scattered powder state after sintering process. The $P_c$ of 1.5wt% PGO added PZT was $0.48\times10^{-8}$ C/(cm$^2$K) and increased to $1.73\times10^{-8}$ C/(cm$^2$K) at 3wt%. Then, it decreased gradually to $0.58\times10^{-8}$ C/(cm$^2$K) at 9wt%. Thus, the PGO percentage was fixed at 3wt% in the following to study the effect PGO on PZT thick film.

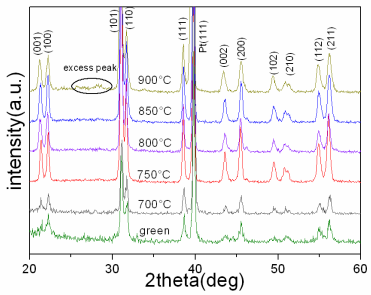


Fig.3 XRD patterns of the green film and the PZT thick films sintered at temperature ranging from 700°C to 900°C

3wt% PGO-added PZT films were sintered at temperature ranging from 700°C to 900°C for 1h. For comparison, the XRD patterns of the green film were also presented. Fig.3 is the XRD patterns of the samples. All the peaks of PZT films sintered below 900°C showed standard PZT phase (JCPDS-ICDD2002, 500346). However, weak excess-diffraction peaks were observed between 25°-28° when the $T_s$ increased up to 900°C, which might be attributed to the lead silicate (JCPDS-ICDD2002, 720062).

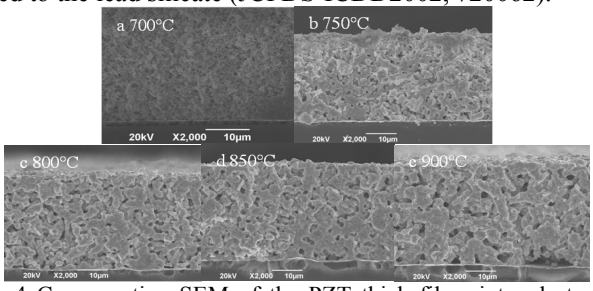


Fig.4 Cross section SEM of the PZT thick film sintered at: (a) 700°C, (b) 750°C, (c) 800°C, (d) 850°C, (e) 900°C

Fig.4 is cross-sectional SEM morphologies of the sintered PZT thick films corresponding to the specimens in Fig.3. It could be clearly seen that the particle size increased from hundreds nanometer to micrometer level due to neck growth and aggregate formation as the $T_s$ increased from 750°C to 900°C. Combined with the changes of peak width in XRD result, the re-crystallization should happen at the grain boundary after sintered at $T_s$ higher than 750°C. This demonstrated that the lowest $T_s$ was 750°C.

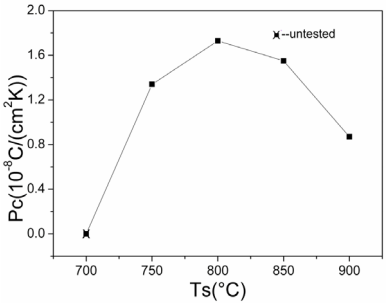


Fig.5 Pc of the PZT films sintered at 700-900°C

The $F_D$ is evaluated using the following formula:

$$F_D = \frac{P_c}{C(\varepsilon_r \varepsilon_0 \tan\delta)^{1/2}} \qquad (1)$$

Where $C$ is the heat capacity of the capacity structure, $\varepsilon_0$ is the permittivity of the free space, $\varepsilon_r$ is the permittivity of pyroelectric material and tan$\delta$ the dielectric loss. In this paper, 3wt% PGO-added PZT thick films had tanδ about 0.015 and $\varepsilon_r$ about 330 which were tested by Agilent 4284 (1 kHz, 100mV). By the formula (1), the $F_D$ of these prepared PZT thick films sintered at 800°C is about $1.7\times10^{-5}$Pa$^{-0.5}$.

## 4. Conclusions

The effects of PGO sintering aid on $T_s$ and pyroelectric properties of PZT thick film were investigated. It was found that the $T_s$ could be decreased to 750°C. Proper PGO percentage could improve the pyroelectric properties of PZT thick film, whereas overdose would serve an opposite role. When sintered at 800°C, the 3wt% PGO-added PZT films exhibited the highest $P_c$, whilst advisable $F_D$ figure of merit and low dielectric loss. These results show that PGO-added PZT thick film fabricated by EPD on silicon substrate has potential in MEMS device for pyroelectric application.

## References

[1] R.A. Dorey, R.W. Whatmore, J. Electroceram. 12, 19-32 (2004) .
[2] K. Sone, S. Sekiguchi, H. Naganuma, T. Miyazaki, T. Nakajima, J. Appl. Phys. 111, 124101-5 (2012).
[3] P. Glynne-Jones, S.P. Beeby, P. Dargie, T. Papakostas, N.M. White, Meas. Sci. Technol. 11, 526-531 (2000).
[4] H. Iwasaki, S. Miyazawa, H. Koizumi, K. Sugii, N. Niizeki, J. Appl. Phys. 43, 4907-4915 (1972)
[4] Ch.G. Wu, W.L. Zhang, Y.R. Li, X.Zh. Liu, J. Zhu, Jpn. J. Appl. Phys. 45, 2674-2677 (2006).