# High Detectivity Infrared Detectors Using Porous PZT Pyroelectric Thick Films

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# Abstract

The fabrication, electric properties and application of porous  $PbZr_{0.3}Ti_{0.7}O_3$  (PZT) thick films are reported. The films were deposited on Pt coated Si substrates by electrophoresis deposition (EPD) using PZT nanoparticles and (001) single crystalline nanorods. Comparing with dense PZT films, the figure merit  $F_v$  and  $F_D$  of porous PZT films were  $3.51 \times 10^{-5} m^2 C^{-1}$ ,  $6.75 \times 10^{-5} Pa^{-1/2}$ , improved by 58 and 57.5 %, respectively. The detectivity of porous PZT film infrared detectors was  $1.0 \times 10^9$  cm Hz<sup>1/2</sup>W<sup>-1</sup> at 40-100 Hz, which was much larger than commercial infrared detectors.

## 1. Introduction

PZT thick films have been considered as one of the most promising candidates for integrated piezoelectric devices and pyroelectric infrared sensors. In recent years, research efforts have been made on porous pyroelectric PZT films. The porosity of PZT films benefited low dielectric constant, low heat capacity and low thermal conductivity, and resulted in figures of merit better than the corresponding values either for ceramic PZT or other pyroelectric materials (including TGS and LiTaO<sub>3</sub>)<sup>[1-3]</sup>.

In this paper, the infrared detectors using porous pyroelectric PZT thick film fabricated by adding (001) single crystalline nanorods have been studied.

# 2. Experiments

The thick films fabrication mainly consisted of two steps: Firstly, PZT nanopowder and nanorod were synthesized by hydrothermal reaction. The atomic ratio of Pb/Zr/Ti was 10/3/7. 1.5 M potassium hydroxide (KOH) was added as mineralizer. Additionally, surfactant polyvinyl alcohol (PVA) and polyacrylic acid (PAA) were added to the solution to obtain PZT nanorod. The hydrothermal suspension was transferred into a steel autoclave with Teflon line which was heated 175°C for 12 h. The cooled hydrothermal product was washed with distilled water and then dried at 85 °C for 24 h. Secondly, suspension including sintering aid was prepared and the films were fabricated by EPD. Suspension with 2 % g ml-1 PZT nanopowders, and ethanol solution was magnetic stirred and ultrasonic dispersed. This fabricated film contains only PZT nanopowders were denoted as PZT<sub>P</sub> in the following paragraph. Corresponding, the film which contained nanorod was denoted PZT<sub>R</sub>. A direct voltage was applied to drive the charged nanoparticles onto the Pt coated silicon substrate. The deposition time was 3 min and thickness was about 30 um. The samples were sintered at 800°C for 1 h.

The nanostructures of nanopowder and nanorod were

characterized by TEM (JEM2012-HT). The cross sectional structures of the samples were observed by scanning electron microscope (SEM, Inspect F, Holland). The Pc was tested at dynamic testing platform. The relative dielectric constant and loss of the composites were measured by an impedance analyzer (Agilent-4284A).

The detail fabrication process and photoelectric measurement of PZT thick film infrared sensor was described in our previous work<sup>[4]</sup>.

## 3. Results and Discussion



Fig.1 SEM image of single crystal PZT nanorod synthesized by hydrothermal reaction, inset: HRTEM and SAED images of nanorod.

The morphologies and crystal structures of the hydrothermal synthesized PZT nanorod were characterized by SEM and TEM, as shown in Fig. 1.The PZT nanorod had cuboid morphology with diameter about 100-200 nm, and showed preferred [001] growth orientation which was confirmed by the inset HRTEM image. Single crystalline structure of nanorod was demonstrated by the presented SAED dots.



Fig.2 SEM images of samples (a) cross-section view of as deposited films, (b) cross-section view of sintered films, and (c) top view of sintered films.

The cross sectional SEM images of the as-deposited and sintered (800°C /1 h)  $PZT_R$  were presented in Fig. 2. According to Fig. 2a, both nanorods and nanoparticles were contained in PZTR and there were many pores at the downside of the nanorods. After sintering, the particles of the both films became more round in appearance and significant necking between particles, and large pores existed in PZTR could be observed in Fig. 2 b and c. Due to the skeleton structure of nanorods, many large pores could still be observed in sintered PZTR, demonstrating that porous PZT thick film had been fabricated by this method. The forming mechanism of the large pores in  $PZT_R$  was schematically explained in reference<sup>[5]</sup>. Table 1 Electrical properties comparison of PZT thick films fabricated with and without nanorods

	$Pc(C/cm^2K)$	ε <sub>r</sub>	tanð	$F_{D}(Pa^{-1/2})$	$F_v(m^2/C)$
PZT <sub>P</sub>	5.73×10 <sup>-8</sup>	117	0.015	4.29×10 <sup>-5</sup>	$2.22 \times 10^{-2}$
PZT <sub>R</sub>	$4.82 \times 10^{-8}$	62	0.014	6.75×10 <sup>-5</sup>	3.51×10 <sup>-2</sup>

Generally, two significant figures of merit  $F_v$  (figures of merit for voltage) and  $F_D$  (figure of merit for detectivity) are frequently used to characterize a material for infrared detectors. The figures  $F_v$  and  $F_D$  are given in the following formulas:

$$F_{v} = \frac{P_{c}}{C\varepsilon_{0}\varepsilon_{r}} \tag{1}$$

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

Where  $P_c$  is pyroelectric coefficient, C is the volume specific heat,  $\varepsilon_0$  is the dielectric constant of free space,  $\varepsilon_r$  is the relative dielectric constant, and tan $\delta$  is the dielectric loss. The specific volume heat capacity C was assumed to be  $2.5 \times 10^6 \text{Jm}^3 \text{K}^{-1}$ , despite it should be lower considering about the high porosity structure. The data of both PZT<sub>P</sub> and PZT<sub>R</sub> were given in table 1.

It was found that the relative dielectric constant ( $\epsilon_r$ ) of of PZT<sub>R</sub> was lowed by approximate 47%. Compared with PZT<sub>P</sub>, the maximum F<sub>V</sub> and F<sub>D</sub> of PZT<sub>R</sub> were  $3.51 \times 10^{-5} \text{m}^2 \text{C}^{-1}$ ,  $6.75 \times 10^{-5} \text{Pa}^{-1/2}$ , improved by 58 and 57.5 %, respectively. These results demonstrated that a new way to deposit PZT porous thick film with low dielectric constant and high figures of merit was established.



Fig.3 optical photos of PZT porous thick film infrared detector (a) top view, (b) back view.

The images of PZT porous thick film infrared detector was shown in Fig. 3. The sensitive element area is about 3  $\times$  3 mm<sup>2</sup>, which was supported by 30 um thickness Si beam. The sensitive element was good thermal isolated, and has little thermal capacitance. Both features were benefiting to excellent photoelectric response of infrared detectors.

When an incident radiation made the change of sensitive element temperature, a response voltage  $(V_S)$  was measured between the top and bottom electrodes. Voltage response ratio  $(R_V)$  reflected the transformation capability of radiation to voltage signal which was expressed as:

$$R_{\nu} = \frac{V_s}{P} \tag{3}$$

Where, P is incident radiation power.

The noise equivalent power (NEP) is given as a ratio of total noise voltage ( $V_n$ ) and voltage responsivity, meaning the incident radiation power needed to make  $V_s$  equals to  $V_n$ :

$$VEP = \frac{P}{V_s/V_n} \tag{4}$$

The key performance of a pyroelectric detector was assessed by specific detectivity  $D^*$  which was defined as:

$$D^* = \frac{\sqrt{A_D \Delta f}}{P} \bullet \frac{V_s}{V_n}$$
(5)

Where  $A_D$  is the sensing area and  $\Delta f$  is the system bandwidth (which is 1 Hz in our measurement).



Fig.4 key parameters of PZT porous thick films measured as a function of chopping frequency (a)  $V_s$  and  $R_v$ , (b)  $V_n$  and NEP, (c)  $D^*$ .

According to Fig.4, the maximum  $R_V$  up to 200 V/W occurred at 5.3 Hz. The  $R_V$  decreased gradually when the frequency (f) was smaller than 100 Hz. At the frequency lower than 100 Hz, the noise decreased exponentially, indicating the dominating noise of 1/f noise source. The constant noise voltage revealed the Johnson noise at frequency larger than 100 Hz. The calculated NEP was about  $6 \times 10^{-9}$ W between 5 - 40 Hz and  $5 \times 10^{-10}$ W at f >120 Hz, respectively. The D<sup>\*</sup> was  $1.0 \times 10^{9}$  cm Hz<sup>1/2</sup>W<sup>-1</sup> at 40-100 Hz, which is 1 order magnitude higher than that of PM622 infrared detector made by Nicera Sensor Company ( $9.3 \times 10^7$  cmHz<sup>1/2</sup>W<sup>-1</sup>), and is large enough for commercial applications.

# 4. Conclusions

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Porous structure was formed in the as-deposited and sintered PZT thick film by adding (001) single crystalline nanorods. Due to low dielectric constant, excellent figures of merit  $F_V$  and  $F_D$  were obtained despite inferior pyroelectric coefficient. A  $3 \times 3 \text{ mm}^2$  PZT thick film pyroelectric detector with back to back silicon cups structure was developed in which the thick film was shaped in the front silicon cup. The D<sup>\*</sup> was  $1.0 \times 10^9$  cm Hz<sup>1/2</sup>W<sup>-1</sup> at 40-100 Hz, which is large enough for commercial applications

#### References

- C. P. Shaw, R. W. Whatmore, J. R. Alcock, Journal of the American Ceramic Society, 2007, 90 (1), 137–142.
- [2] A. Seifert, P. Muralt, and N. Setter, Appl. Phys. Lett., 1998, 72, 2409-2411.
- [3] S.P. Beeby, N. Ross, N. M., Electron. Lett., 1999, 35, 2060–2061.
- [4] Q. X. Peng, C.G. Wu, W.B. Luo, C. Chen, G.Q. Cai, X.Y. Sun, Infrared Physics & Technology, 2013, 61, 313 - 318.
- [5] Q. X. Peng, W. B. Luo, J. Meng, W. Y. Fu, X. Qing, X. Y. Sun, Y. Shuai, C. G. Wu, W. L. Zhang, J Mater Sci: Mater Electron, 2014, 25(1), 297-302.