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Electrophoretic deposition of $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ thick film on Pt wire

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Abstract

$0.2PbNi_{1/3}Nb_{2/3}$–$0.8Pb(Zr,Ti)O_3$ (PNN–PZT) thick films were deposited on Pt wire with the diameter of 50 μm by electrophoretic deposition (EPD) method. The EPD deposition times on the microstructures of PNN–PZT thick films were investigated. By optimizing the EPD process, the Pt wire can be uniformly wrapped with the PNN–PZT powders. During the sintering process, the as-deposited PNN–PZT/Pt wires were buried in the mixed powders of $PbCO_3$ and ZrO_2, and then sintered in the optimal temperature to get a dense microstructure. The piezoelectric properties of the thick films were characterized by scanning force microscopy (SFM) method. The results show that the PNN–PZT thick films prepared by EPD method have good piezoelectricity.

Keywords: A. Films; B. Grain size; C. Piezoelectric properties; EPD

1. Introduction

Piezoelectric thick films have been widely used in the applications such as information technology, biotechnology and nano-measurement technology. The methods of producing thick films include screen printing, tape casting, electrophoretic deposition (EPD) and so on. Among them, screen printing and tape casting are two traditional methods, which are appropriate for mass production. However, screen printing and tape casting methods can only fabricate thick films on plane substrates [1–4], EPD is more flexible and can fabricate thick films on both plane substrates and curved substrates, so EPD method has attracted intense studies during the past decades.

Different substrates can be used in EPD processing, such as $Pt/Ti/SiO_2/Si$ and Pt/Al_2O_3. Comparing with $Pt/Ti/SiO_2/Si$, Pt/Al_2O_3 substrates take the advantages of lower cost and simpler process [5]. However, there are still some problems with Pt/Al_2O_3 substrates. The reaction between the films and the substrates was observed in many experiments. Su et al. [5] have reported that PZT films deposited on Pt coated alumina substrates had shown a strong interaction between the PZT films and alumina substrates. Kuscer and Kosec [6] improved the process, they used $PZT/Pt/Al_2O_3$ plates as the substrate to deposit PMN–PT. They found that PZT layer deposited between the Al_2O_3 substrate and the platinum electrode served as a barrier layer that prevented the diffusion of aluminium ions into the active PMN–PT layer as well as the diffusion of lead ions from the PMN–PT into the alumina. Su et al. [5] chose Pt wire as the substrate, and water as the solvent. Due to the limitation of deposition voltage, which should lower than the decomposition voltage of water, the thick film with an inferior packing density was obtained. Ng and Boccaccini [7] deposited PZT films on stainless steel fibres. Some large cracks were found after the thick films were sintered at the temperature of 800 °C for 30 min. It seems that it is difficult to obtain piezoelectric thick films on metal wires with high quality.

In this study, dense and crack-free PNN–PZT thick films were deposited on Pt wire by EPD method through optimizing the process, and the effect of different process on the quality of the films were investigated.

2. Experimental

The starting materials used were Pb_3O_4(97.27%), Nb_2O_5(99.93%), NiO(97.66%), TiO_2(99.28%), ZrO_2(98.93%). The powders were weighed according to the stoichiometry of

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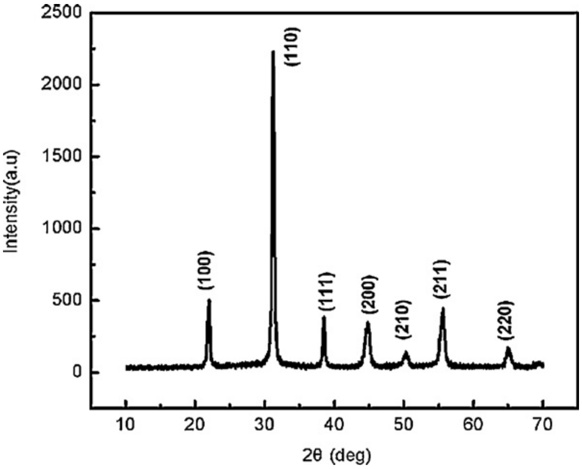

Fig. 1. X-ray diffraction (XRD) pattern of the PZT–PNN powders calcined at 850 °C for 2 h.

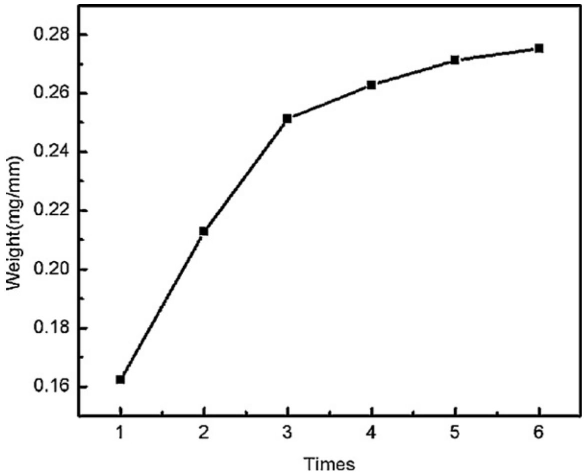

Fig. 2. Deposited mass vs. deposition times during EPD of PZT–PNN particles on Pt wire at 15 V.

$0.2PbNi_{1/3}Nb_{2/3}$–$0.8Pb(Zr,Ti)O_3$. Considering the volatility of PbO during calcination and sintering, 3% excess of PbO was added into the raw powders [8]. The powers was calcined at 850 °C for 2 h to get a perovskite crystalline structure, and then prepared by ball milling for 8 h to reduce the particle size. The crystal structure of the powders (after calcined at 850 °C for 2 h) was analyzed by X-ray diffraction (XRD) method with Cu Kα radiation (D/MAX-2550V, Rigaku, Tokyo, Japan). Fig. 1 shows the XRD pattern of the powders. It can be seen that the powders showed a single phase perovskite structure.

The Pt wire with the diameter of 50 μm was chosen as cathode, and a stainless tube was chosen as anode. The distance between the cathode and the anode was about 1.5 cm [9]. The PNN–PZT powders were dispersed in the ethanol solvent to get the suspension. The solid loading of the suspension was 5 g/100 ml. In order to make the suspension more stable, 2 wt% PEG was added. Furthermore, 1.11 wt% PVB was added to prevent the films from cracking. HNO_3 and $NH_3{\cdot}H_2O$ were used to adjust the pH of the solution, and the final pH was controlled between 4 and 5. The suspension was first sonication for 30 min, and then stirred for 3–6 h. The voltage was fixed to be 15 V. The suspension was deposited for different times (1–6 times), with each time lasting for only 1 min. The time interval between each EPD processing was controlled to be 10 min [9]. After EPD, the film was kept in an oven with the temperature of 80 °C for 12 h.

After dried for 12 h, the film was sintered at 1180 °C in an electric furnace for 30 min. In order to minimize the volatilization of PbO, the as-deposited PNN–PZT thick films were buried in PNN–PZT powders and in 1:1 molar mixture of $PbCO_3$ and ZrO_2 powders, respectively during the sintering process.

3. Results and discussion

3.1. Different deposition times

The quality of the thick films prepared by the EPD method depends strongly on the deposition times. It is easy for the thick films to peel off after dried in the oven, therefore they were sintered at 1180 °C for 30 min.

Fig. 2 indicates that the weight of PNN–PZT thick films increases with the increasing deposition times. The deposited mass increases rapidly in the initial three times, however, slightly increase of the deposited mass can be observed in the later three times. During EPD processing, the resistance increases rapidly with the thickness of the film, which results in the decrease of the current density. The decrease in the current density results in the decrease of the effective field between the electrodes, which is a cause of the decrease in deposition rate.

Fig. 3 shows the scanning electron microscope (SEM) photographs of the PNN–PZT thick films buried in PNN–PZT powders with different deposition times. It can be found that the PNN–PZT thick film deposited four times is the best, which has least pores and cracks. The reason is as follows: when the PNN–PZT thick film is deposited for the first time, there is not enough time for the powders in the solvent to wrap the Pt wire thoroughly, thus leaving many pores behind. With the increasing of the deposition times, the pores are filled by the powders gradually. After several EPD processes, most pores are filled, and the thick film becomes dense. However, new pores are formed in the further deposition, and the PNN–PZT thick film becomes poly-porous again.

3.2. The mixed powders of $PbCO_3$ and ZrO_2 used in burying sintering process

In our research 1:1 molar mixture of $PbCO_3$ and ZrO_2 was used to bury PNN–PZT wires. Fig. 4 shows the scanning electron microscope (SEM) photographs of the PNN–PZT thick films which are buried in PNN–PZT powders and in the mixture of $PbCO_3$ and ZrO_2 sintered at 1180 °C for 30 min. It is found that some small pores occur in the thick film buried in PNN–PZT powders, however, the thick film is completely free of microcrack and pore when buried in the mixed powders of $PbCO_3$ and ZrO_2. Particularly, there is a major increase of the grain sizes, most of which are over 10 um.

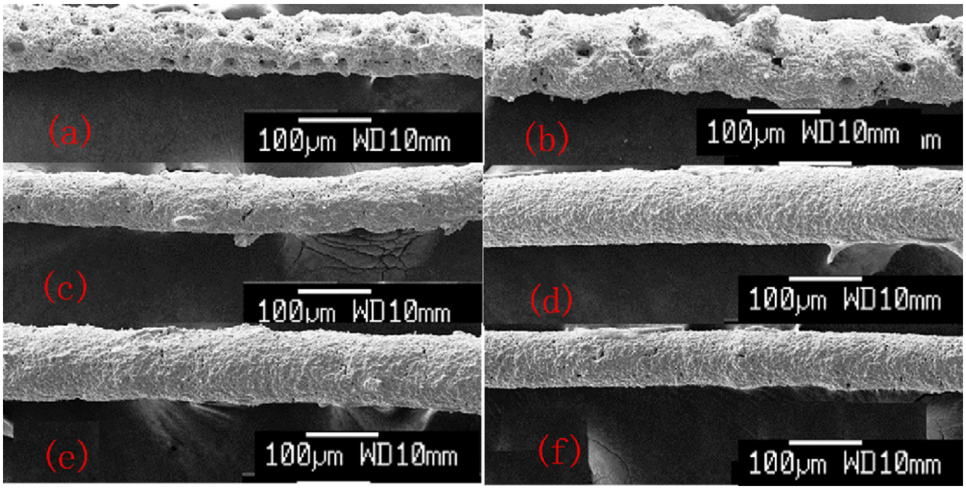

Fig. 3. Scanning electron microscope (SEM) photographs of the PNN–PZT films deposited for different times. (a) One time; (b) two times; (c) three times; (d) four times; (e) five times; (f) six times.

During the sintering process, the $PbCO_3$ decomposes to PbO and CO_2. PbO has a very low melting point (886 °C) and forms liquid phase in the films. The liquid phase can improve the sinter ability of the ceramics. Also some liquid PbO fills into the pores and then reacts with ZrO_2. As a result, the pores disappear, and the PNN–PZT thick films become dense.

From Fig. 4(c), it is observed that the film is fairly uniform in thickness with no crack or obvious pore. The film has a shape of the normative ring, and the radius is about 25 um. It is also found that the Pt wire broke away from the middle of the PNN–PZT thick film, which may be due to the role of the external force when the film was broken off.

Combing the SEM of the surface and the cross section of the PNN–PZT thick film, it is known that dense thick film can be made by burying in the mixture of $PbCO_3$ and ZrO_2 sintered at the temperature of 1180 °C for 30 min. By EDS analysis, the substrate of Pt wire is identified as pure Pt, so it can be concluded that PNN–PZT does not diffuse into the substrate.

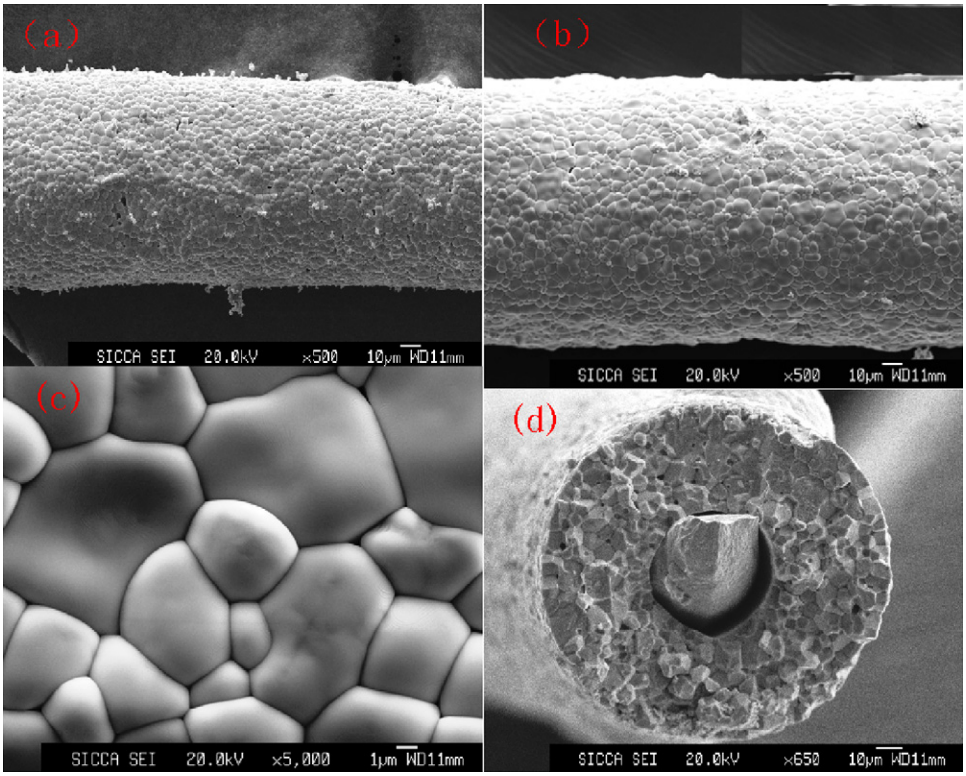

Fig. 4. SEM photographs of the surfaces and the cross section of the films buried in PNN–PZT powders and in the mixture of $PbCO_3$ and ZrO_2 powders sintered at 1180 °C for 30 min. (a) Buried in PNN–PZT powders; (b) buried in the mixture of $PbCO_3$ and ZrO_2; (c) buried in the mixture of $PbCO_3$ and ZrO_2; (d) cross section of the film buried in the mixture of $PbCO_3$ and ZrO_2.

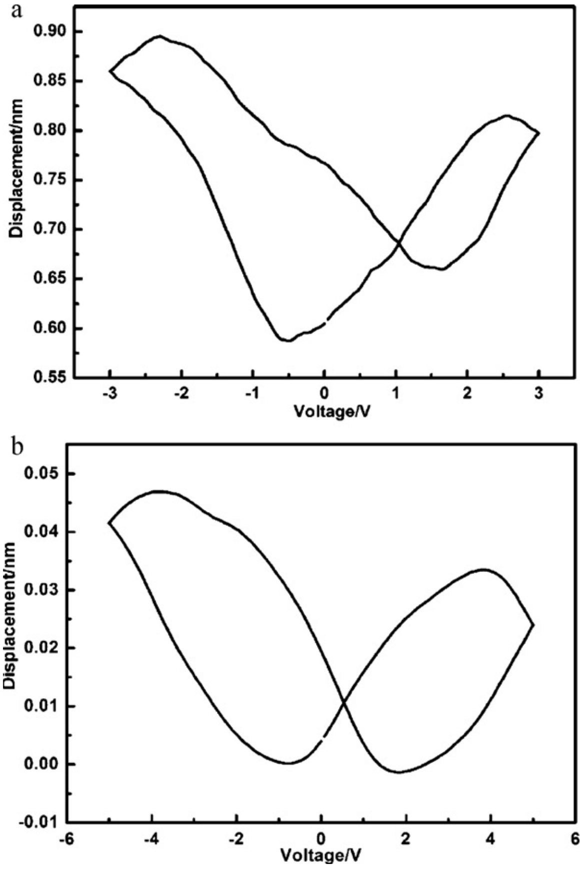

Fig. 5. The electric field induced displacement (E–D) of the film sintered at 1180 °C buried in PNN–PZT and in the mixture of $PbCO_3$ and ZrO_2. (a) In PNN–PZT powders; (b) in the mixture of $PbCO_3$ and ZrO_2.

3.3. Piezoelectric properties

Fig. 5 shows the electric field induced displacement (E–D) of the PNN–PZT thick films buried in PNN–PZT powders and in the mixture of $PbCO_3$ and ZrO_2 sintered at 1180 °C. From the E–D curves, the efficient piezoelectric constant can be roughly calculated to be about 90 pm/V for the PNN–PZT thick films buried in PNN–PZT powders, which is quite good piezoelectric coefficient for thick films, while the piezoelectric constant for the PNN–PZT thick films buried in the mixture of $PbCO_3$ and ZrO_2 is only 8 pm/V. Although dense PNN–PZT thick films were prepared by burying in the mixture of $PbCO_3$ and ZrO_2, the incorporation of $PbZrO_3$ into PNN–PZT film makes the chemical deviate from the designed formula, which causes the deterioration of the piezoelectric properties. It can also be noted that the E-D loops are asymmetric. It is attributed to the internal field caused by the defect dipoles. In lead-base piezoelectric ceramics, Pb has a high partial pressure, it can readily evaporate from their lattice sites and leave vacancies behind [10], in order to keep electrochemistry balance, oxygen vacancies will occur. Oxygen vacancies and lead vacancies will form defect dipoles during the sintering process, which will cause an internal electric field opposite to the outer electric field.

4. Conclusion

By optimizing the EPD process, the PNN–PZT powders can uniformly deposit on Pt wire. When the PNN–PZT thick films are buried in PNN–PZT powders during the sintering process, the efficient piezoelectric constant of 90 pm/V can be obtained, but some pores occur in the PNN–PZT thick films. Dense PNN–PZT thick films with no pore and crack can be fabricated when buried in the mixture of $PbCO_3$ and ZrO_2 during the sintering process, but the piezoelectric constant is small.

Acknowledgements

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