Preparation and Characterization of PZT Piezoelectric Thick Film Generation Materials Enhanced by PZT Nanoparticles

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Abstract: The use of piezoelectric materials to capitalize on the ambient vibrations surrounding a system is one method that has seen a dramatic rise in use for power harvesting. Lead zirconate titanate, one of the most popular piezoelectric materials, has larger piezoelectric response than piezoelectric materials, such as ZnO and AlN. Ferroelectric films are suitable for vibration energy harvesting. Dense and crack-free (100) oriented PZT piezoelectric thick film is prepared on $Pt/Cr/SiO_2/Si$ substrate by sol-gel using PZT nanoparticles as reinforcing phase. The thick film possesses single-phase perovskite structure and perfectly (100) oriented. The influences of crystalline and amorphous PZT nanoparticles on the (100) oriented degree and the influences of the molar concentration ratio of amorphous PZT nanoparticles and PZT sol on surface morphology of PZT piezoelectric thick film are investigated. Experimental results show that, amorphous PZT nanoparticles are more helpful than the crystalline nanoparticles for the PZT thick film preferred orientation growth along the (100) direction. The 3 μm-thick PZT thick film enhanced by amorphous PZT nanoparticles annealed at 700 ℃ for 5 min has the strongest (100) orientation degree, being 82.3%, and the surface is dense, smooth and crack-free.

Key words: (100) orientation; PZT generation material; PZT nanoparticles

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0 Introduction

The development of the technology requires smaller and lighter electronic devices, a compatible power source remains a major concern for such devices, and also conventional batteries used for such devices are too larger to be utiluzed in them. Since piezoelectric power generation device has the advantages of simple structure, no heat, no electromagnetic interference, easy to manufacture and realization of miniaturization and integration, etc., the piezoelectric energy is one of the promising ways to power for smaller and lighter electronic devices. In the past two decades, researchers have made great efforts from different academic fields to understand how to harvest vibration/motion energy from ambient using piezoelectric energy harvesters[1-8]. In the piezoelectric materials, PZT is a kind of widely used inorganic non-metallic functional materials with excellent piezoelectric, pyroelectric and ferroelectric properties[9]. Many microfabrication processes of PZT thin or thick film for energy harvesters have been reported[10,11].

Different nucleation mechanism of PZT film causes the film different crystal planes oriented growth after crystallized. The properties of PZT film is closely related to its crystalline quality and micro-structure. Ferroelectric, dielectric and piezoelectric properties of the perovskite structure PZT film are influenced by the film preferred orientation[12-14]. In order to meet the requirements of a variety of devices, preparing grain oriented piezoelectric film is required. For micro electromechanical system (MEMS) power generation devices, the (100) oriented PZT film with larger piezoelectric coefficient is reguired; For ferroelectric

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random access memories, (111) oriented PZT film with large residual polarization intensity and strong polarization inversion capability in the external electric field are reguired[13,15-17]. Existing PZT thick film, mostly grows along the (110) direction, (110) oriented PZT thick film has good ferroelectric performances, but the piezoelectric properties are not ideal. In order to meet the requirements of the piezoelectric properties of PZT thick film for MEMS power generation devices, it is necessary to prepare the (100) oriented PZT piezoelectric thick film. The density of the piezoelectric film plays an important role in overall performance of the devices[18]. When subjected to mechanical loads in service, piezoelectric materials can fail prematurely due to defects, holes, etc, which arising during their manufacture process[19,20]. Therefore, preparing crack-free, as well as dense thick films is still a challenging task.

In this paper, dense, smooth and crack-free (100) oriented piezoelectric PZT thick films on Pt/Cr/SiO_2/Si substrate are prepared and used lead titanate(PT) transition layer and PZT nanoparticles reinforcing phase via sol-gel method, and the thick films can be applied in MEMS generators.

1 Experiment

Preparation PT sol and PZT sol have been described in elsewhere[21]. Pt /Cr /SiO_2/Si is used as substrate. Clear PT sol is spun on the substrate and then pyrolyzed at 350 ℃ for 5 min and annealed at 700 ℃ for 1 min obtained (100) oriented PT crystalline phase film to form a PT transition layer, which enhances the adhesion to the substrate and offers a template for PZT thick film. Then clear PZT sol incorporating polyvinyl pyrrolidone (PVP) and PZT sol suspension are spun alternately and pyrolyzed at 450 ℃ for 30 min and annealed at 700 ℃ for 5—15 min. Above process is repeated until the desired thickness is deposited, then the (100) oriented PZT thick film is formed.

2 Results and Discussion

Fig. 1 shows the XRD pattern of PT transition layer. The (100) oriented diffractive peaks of perovskite phase are observed obviously. On Pt/Cr/SiO_2/Si substrate, the interface of Pt and $PbTiO_3$ film form PtPb compounds easily, which benefits the crystallization of PT film[22]. Further more, in general PT film grows along (100) direction[23], and the interface thermal stress between PT film and substrate caused by rapid heating in the rapid thermal annealing process also helps PT film oriented growth. Fig. 2 shows the SEM image of PT transition layer. The surface of the PT film is dense and crack-free, which offers a good basis for PZT film oriented growing.

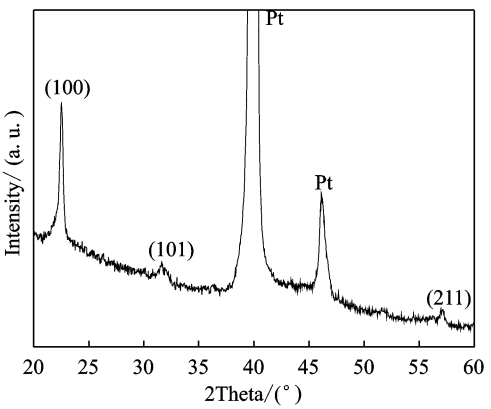

Fig. 1 XRD patterns of PT transition layer

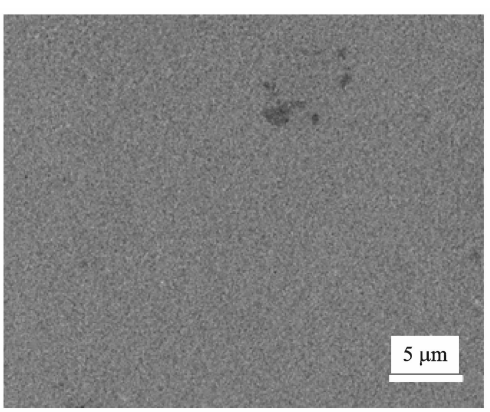

Fig. 2 SEM image of PT transition layer

The orientation degree of film can be expressed by the ratio of crystal plane group diffractive peak intensity to summation of all the crystal plane diffractive peak intensity[24]. Fig. 3 shows the XRD patterns of 4 μm-thick (100) oriented

PZT thick film enhanced by crystallized PZT nanoparticle with different annealing time. Table 1 shows their peak intensity ratios. It is clearly seen that all the thick films appear to be well crystallized and has the perovskite phase, and the diffractive peaks of perovskite phase are observed obviously and appear to be (100) oriented. This is because (100) oriented PT transition layer provides template for the growth of PZT thick film. In addition, in the PVP-containing system, PVP remains in the film after pyrolysis, and acts as a seed for the nucleation of PZT crystals during annealing. And the film grows along the direction with the lowest surface energy, which is found to be the (100) direction in the PZT system[25].

There is little difference between (100) orientation degrees of PZT thick film enhanced by crystallized PZT nanoparticle with different annealing time. Thick film with annealing time of 5 min has the largest (100) orientation degree of 62.4% compared with that with annealing time of 10 and 15 min. Crystallized PZT nanoparticles are (110) oriented. Which may affect (100) oriented growth of PZT thick film.

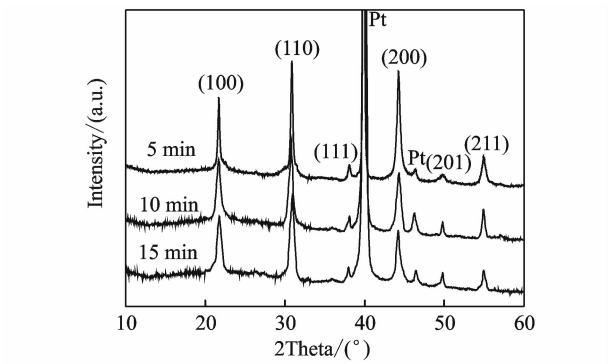

Fig. 3 XRD patterns of (100) oriented PZT piezoelectric thick film enhanced by crystallized PZT nanoparticle with different annealing time

Table 1 Peak intensity ratios of (100) oriented PZT piezoelectric thick film enhanced by crystallized PZT nanoparticle with different annealing time

Annealing time/min	I(100)	I(110)	I(200)	[(I(100)+I(200))/(I(100)+I(110)+I(200))]/%
5	6 952	9 493	8 801	62.4
10	6 650	7 989	5 745	60.8
15	6 232	7 598	5 269	60.2%

Fig. 4 shows the XRD patterns of 4 μm-thick (100) oriented PZT thick film enhanced by amorphous PZT nanoparticles with different annealing time. Table 2 shows their peak intensity ratios. It is clearly seen that all the thick films appear to be well crystallized and has the perovskite phase, and the diffractive peaks of perovskite phase are observed obviously and appear to be (100) oriented. The thick film with annealing time of 5 min has the largest (100) orientation degree of 80.5% compared with that with annealing time of 10 and 15 min. During the annealing process, due to the constraint of the substrate, a certain macroscopic thermal stress exists in the film, and the macroscopic thermal stress is always moving in a certain direction. The faster the heat treatment, the greater the macroscopic thermal stress generates, and it will make the grains have a growing trend along a certain direction, which is conducive to the formation of preferential orientation.

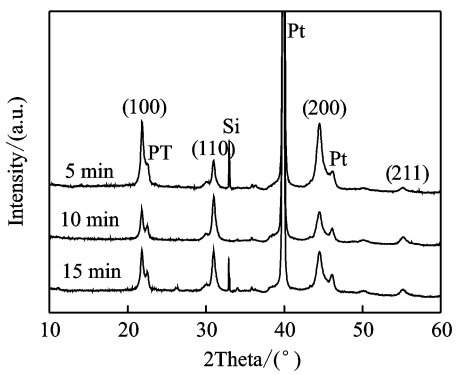

Fig. 4 XRD patterns of (100) oriented PZT piezoelectric thick film enhanced by amorphous PZT nanoparticles with different annealing time

Table 2 Peak intensity ratios of (100) oriented PZT piezoelectric thick film enhanced by amorphous PZT nanoparticles with different annealing time

Annealing time/min	I(100)	I(110)	I(200)	[(I(100)+I(200))/(I(100)+I(110)+I(200))]/%
5	13 023	6 263	12 760	80.5
10	6 842	9 051	6 341	59.2
15	8 932	8 613	8 636	67.1

The surface SEM photographs of PZT piezoelectric thick film enhanced by amorphous PZT nanoparticles with different PZT nanoparticle adding

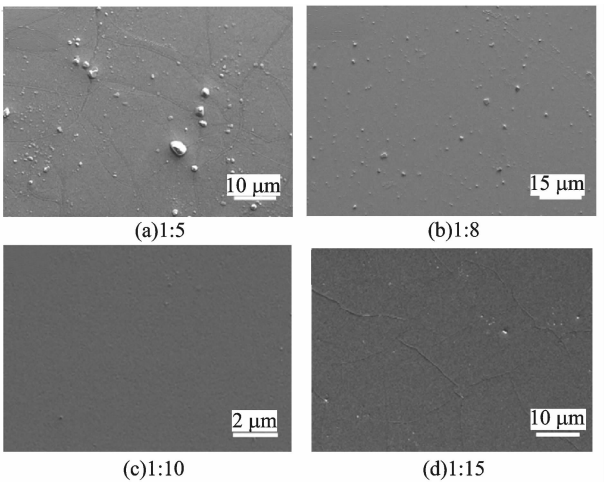

Fig. 5 Surface SEM photographs of PZT piezoelectric thick film enhanced by amorphous PZT nanoparticles with different PZT nanoparticle adding amount

Table 3 (100) orientation degrees of (100) oriented PZT piezoelectric thick film enhanced by amorphous PZT nanoparticles with different adding amount

Amorphous PZT nanoparticles adding amount	1∶5	1∶8	1∶10	1∶15
Orientation degree/%	69.1	78.9	82.3	82.6

amount are shown in Fig. 5. In PZT slurry, the molar concentration ratios of amorphous PZT nanoparticles to PZT sol are 1∶5, 1∶8, 1∶10 and 1∶15. The samples are annealed at 700 ℃ for 5 min and the thickness are about 3 μm. Table 3 shows their peak intensity ratios. The surface of the samples with molar concentration ratios of 1∶5 and 1∶8 are not smooth. The surface of the samples with molar concentration ratios of 1∶10 and 1∶15 are smooth, but the surface of the samples with molar concentration ratio of 1∶15 is crack. This is because that , the PZT nanoparticles distribute unevenly and is easily reunion accumulation while adding excess amount in PZT slurry. Then, the same upper layers of spin-coated PZT clarify sol cannot fully cover the PZT nanoparticles, and the surface is coarse. When adding too little PZT nanoparticles in PZT slurry, PZT nanoparticles cannot enhance the PZT thick film, and the surface is crack. The surface of the thick film with molar concentration ratio of 1∶10 is dense, smooth and crack-free.

The (100) orientation degree of the thick film with different molar concentration ratio of PZT amorphous nanoparticles and PZT sol decreases with the increase of molar concentration ratio. The thick film with molar concentration ratio of 1∶10 has the (100) orientation degree of 82.3%.

3 Conclusions

The (100) oriented PZT piezoelectric thick film generation material has been successfully fabricated on Pt/Cr/SiO_2/Si substrate used PT as transition layer and PZT nanoparticles as reinforcing phase. Amorphous PZT nanoparticles are more conducive to (100) oriented growth of PZT piezoelectric thick film than crystallized PZT nanoparticles do. The surface of PZT thick film adding excess PZT nanoparticles as reinforcing phase is coarse, and the surface of PZT thick film adding too little PZT nanoparticles is crack. The surface of the thick film with molar concentration ratio of 1∶10 is dense, smooth and crack-free, and has the (100) orientation degree of 82.3%. The thick films can be applied in MEMS generators.

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