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Microcantilevers Fabrication Process of Silicon-based (Pb, La)(Zr, Ti)O3 Antiferroelectric Thick Films for Microactuator Applications

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Abstract. (Pb, La) (Zr, Ti)O_3 (PLZT) antiferroelectric thick films were deposited on Pt (111)/ Ti/SiO_2/Si (100) substrates via sol-gel process. X-ray diffraction (XRD) analysis indicated that the films derived on Pt (111)/ Ti/SiO_2/Si (100) substrates showed strong (111) preferred orientation. The Bulk and Surface silicon of micromachining process were employed in the silicon-based antiferroelectric thick film microcantilever fabrication, such as wet chemical etching for PLZT, inductive couple plasmas (ICP)for silicon etching, platinum etching and so on. Challenges such as Pt/Ti bottom electrode and morphology of PLZT thick film were solved, the integration of functional antiferroelectric materials and MEMS technology, provide a new way of thinking for the design and manufacture of micro-actuators.

Intorduction

Antiferroelectric(AFE) materials have received extensive increasing attention due to their potential applications in the integrated devices, such as large displacement micro-actuators and high-strain micro-transducers.[1]. The AFE phase can be induced into ferroelectric (FE) phase under the external sufficient electric field. For the unit cell of the FE phase is larger than that of AFE phase, so the volume of the material changes together with the phase transition [2, 3]. W.Y Pan et al [4, 5] reported that the strain of (Pb,La)(Zr,Ti,Sn)O_3 antiferroelectric ceramics can reach 0.85%. For (Pb,La)(Zr,Ti,Sn)O_3 bulk-type AFE ceramics, the switching time of phase transition is about 2us, of which is less than 300ns for the AFE thick film [6].

Compared with other methods, such as metal organic chemical vapor deposition (MOCVD)[7] techniques, electron beam deposition(EBD)[8]and so on, sol-gel[9] process is one of the most popular technique to fabricate Pb-based antiferroelectric thick films on platinum electrodes because of its simple process, lower price, accurate chemical control and large area production.

In this paper, a microcantilever structure is adopted as the driving component. The micro-patterning of PLZT antiferroelectric thick film and the top/bottom electrodes played a key part during the process of preparation, the micro-patterning technology include chemical etching, reactive ion etching, and lift-off technology etc. In this study, the wet chemical etching was introduced for PLZT, inductive couple plasmas (ICP) for silicon etching and sputtering process for electrodes. Series of these processes have successfully realized micro-patterning of the sensitive cell. The difficulties of electrodes etching were solved, which laid a good foundation for further study of silicon-based antiferroelectric thick film micro-actuators.

Experimental procedure and analysis

The flow chart, shown in figure.1, depicted the sol-gel deposition process for PLZT antiferroelectric films. At first, acetate trihydrate $Pb(CH_3COO)_2 \cdot 3H_2O$ with 10% excess in order to compensate Pb loss during annealing and prevent the formation of the pyrochloren phase, lanthanum acetate hydrate $La(CH_3COO)_3 \cdot H_2O$ and acetate acid CH_3COOH were mixed in a ratio according to the predetermined number, the mixed solution was distilling at 110°C for one hour to remove water, after

cooling the above solution to room temperature, zirconium propoxide $Zr(OC_3H_7)_4$ and titanium isopropoxide $Ti[OCH(CH_3)_2]_4$ were added and stirred for 30min. At the same time, distilled water was added in order to stabilize the solution.

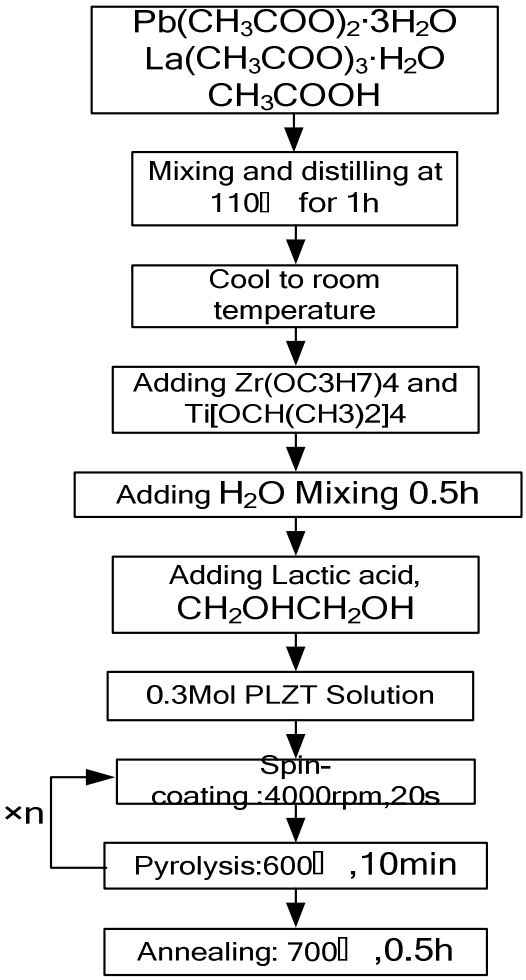

Fig. 1 Flow diagram of sol-gel processing for PLZT films

Lactic acid was added into the solution as the function of catalyzer and chelation in the proportion of one mole of lactic acid to one mole of lead. To improve the properties of the films, ethylene glycol was mixed into the solution as a kind of polymerizing agent in the proportion of one mole of ethylene glycol to one mole of lead. Finally, the solution was adjust to 0.3mol/L using acetic acid and CH_2OHCH_2OH, the addition of CH_2OHCH_2OH lowered the surface tension of the solution and could improve the wettability. PLZT thin films were grown on Pt (111)/Ti/SiO_2/Si (100) substrates by spin-coating method. Each PLZT thin film was spin-coated at 4000rpm for 30s and pyrolyzed at 600 ^oC for 10 min. The spin-coating and heat treatment were repeated several times to obtain desired thickness. A capping layer consisting 0.4mol/L PbO precursor solution ,which was prepared from lead acetate trihydrate, was added before the films went through a final anneal at 700 ^oC for half an hour. This capping layer served the purpose of preventing excessive Pb loss.The final thickness of the thin films was about 3.3um. Gold pads (of which surface is 1um) were coated on the film surface as top electrodes by dc sputtering.

X-ray diffraction (Bruker Germany) and atomic force microscope (AFM) were employed to characterize the phase structure and surface morphology of the films respectively. X-ray diffraction patterns (XRD) of PLZT antiferroelectroc thick films deposited on Pt (111)/Ti/SiO_2/Si (100) substrates were shown in Figure. 2. The XRD patterns were recorded with a step of $0.02^o min^{-1}$ within the 2θ range from 20^o to 60^o. It can be seen from figure.2, the PLZT thick films annealed at 700 ^oC showed more highly (111)-preferred orientation and displayed a pure perovskite structure.In order to obtain a numerical estimation of the (111) orientation of the PLZT thin films, the orientation factor was calculated according to the following equation:

Orientation factor = I (111)/[I(100)+I(110)+I(111)] (1)

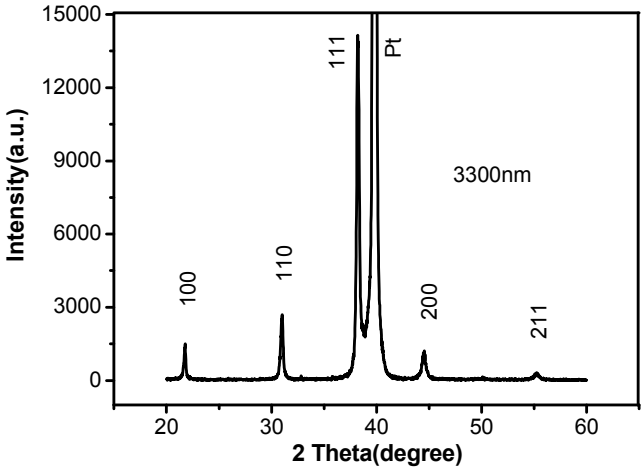

Fig.2 XRD patterns of PLZT antiferroelectric thick films annealed at 700 °C

The obtained PLZT antiferroelectric thick film (with thickness of 3.3um) deposited on 3inches Pt (111)/Ti/SiO_2/Si (100) substrates was shown in figure.3. Figure.4 depicted the surface microstructure of PLZT antiferroelectric thick films by using (atomic force microscope，CSPM-5500). As can be seen from the figure that PLZT films prepared by using CH_3COOH as precursor showed dense microstructure with low surface roughness (the roughness of this PLZT films is 3.65nm).

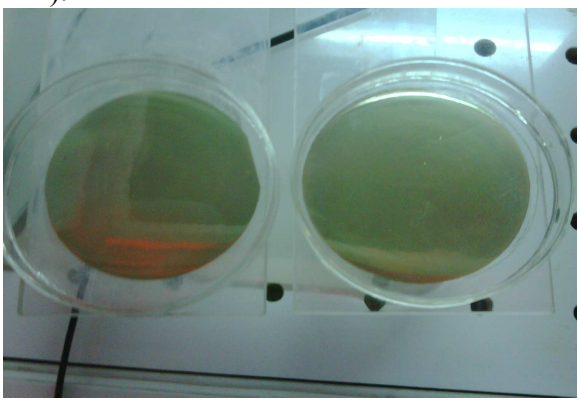

Fig.3 PLZT antiferroelectric thick films deposited on Pt (111)/Ti/SiO_2/Si (100) substrates

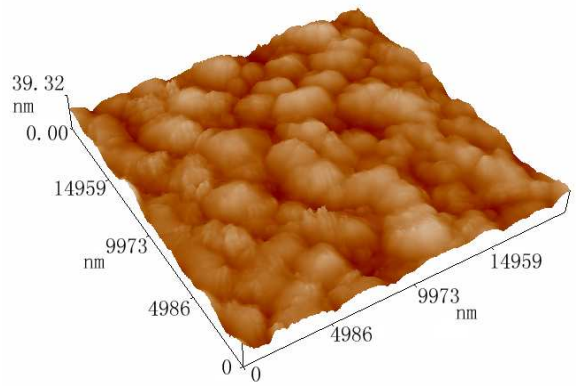

Fig.4 AFM surface morphology of PLZT antiferroelectric thick films

Fabrication of microcanlilevers

Compared with plasama etching and reactive ion etching，wet chemical etching of PLZT films has become one of the most popular technology because it is the economical and fast graphical process. The etching process can be described as follows: The wafer was spin-coated with a 2um-thick layer of positive photoresist(Az4330). Then the photoresist was patterned by the lithography process. Next, the PLZT antiferroelectric thick films were etched, the ratio of etching solutions is BHF：HCL：NH4CL：H2O=1：2：4：4. (The lead-reach film may be formed due to the different etching rate of different element, so HNO_3 (50%) was used to remove the lead-reach film). At last, the photoresist was removed from the surface of the wafer. Figure.5 displayed the CCD array camera of wet chemical etching for PLZT antiferroelectric thick films.

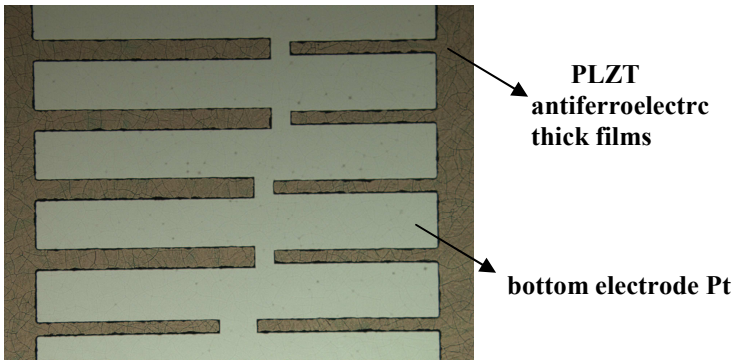

Fig.5 CCD array camera of wet chemical etching for PLZT antiferroelectric thick films

Since there is no effective wet etching solution for Pt/Ti electrode, Ar reactive ion etching was exploited to solve this problem. Conditions were: Ar gas flow at standard conditions 60 mL / min, pressure 2038Pa, power 575 W, repeat several times, Pt/Ti electrode beside the cantilevers was etching out. The sputtering process for top electrode(Au) were ordinary lithography process, the positive photoresist (Az4330) was spinning-coated at 3000rpm with thickness of 2um, after drying at 90℃ for 1h, then explosure(time:20s, power:15mJ/s), development(time:40s), post bake at 100℃ for 30min, and then Au was sputtered on PLZT substrate(shown as figure.6). In order to avoid short circuit, the distance between top electrode(Au) and PLZT antiferroelecreic thick films is about 3-5um,which can be seen from Figure. 7.

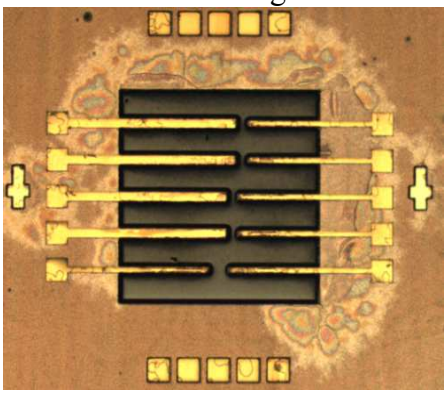

Fig.6 CCD array camera of sputtering process for the top electrode(Au)

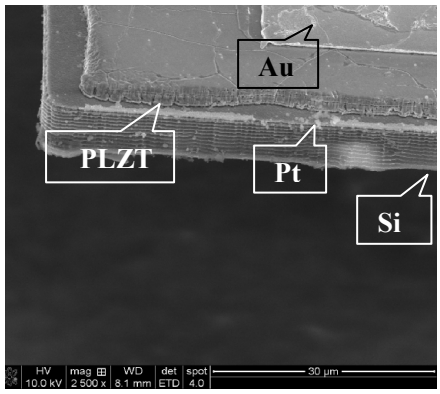

Fig.7 SEM images of side Si-based PLZT antiferroelectric microcantilevers

Inductively coupled plasma (ICP) system has been widely used for anisotropic silicon etching because it offers high aspect ratio with a vertical side wall. In this study, the cantilver beams were completely covered by photoresist, and were released intactly with a high etch rate about 9.1 μm per minute. To completely release the cantilever beam, the anisotropic dry etching must go through the 225-μm-thick sacrificial silicon from the backside of the wafer. Finally, the isotropic etching processing was applied by the ICP system to release cantilever from front-sided (Figure.8).

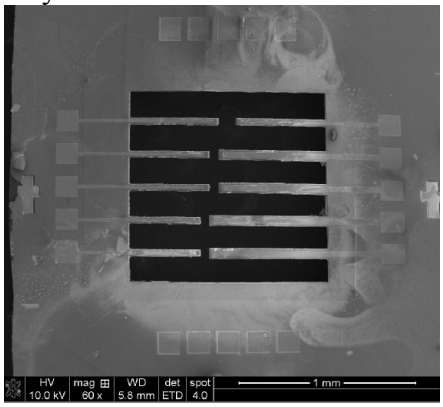

Fig.8 SEM images of released PLZT antiferroelectric microcantilevers

Conclusion

PLZT antiferroelectric thick films were fabricated on Pt (111)/ Ti/SiO_2/Si (100) substrates via sol-gel process at annealing temperature of 700 ^oC. The film displayed a pure perovskite structure with the strongest peaks of (111). The surface morphology of PLZT thick films showed compact microstructure with roughness of 3.65nm. The Bulk and Surface silicon of micromachining process was introduced in the silicon-based antiferroelectric thick film microcantilever fabrication, like wet chemical etching for PLZT thick films, lithography and Inductively coupled plasma for silicon, and sputtering processs for electrodes. The combination of new functional PLZT antiferroelectric materials and MEMS technology make great significance in the field of microactuators applications.

Acknowledgements

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