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The Preparation and Rapid Thermal Annealing of PZT thin Film

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In this paper, the PZT thin film with the perovskite structure are prepared with two different sputtering methods:(1) By sputtering on the substrate with high temperature(550°C); (2) By sputtering on the substrate with low temperature(400°C) then the as-grown film through rapid thermal annealing at 650°C within 10 seconds. By using x-ray diffraction technique, the influence of the substrate temperature and rapid annealing on the structure of PZT thin film are described. It is found that the low temperature sputtering method with rapid annealing is a good method to prepare the PZT thin film.

1.INTRODUCTION

Ferroelectric thin films, particularly the Lead Zirconate Titanate (PZT) thin films have good dielectric and ferroelectric properties and have been used in many devices, including electro-optic switches, infrared detectors, surface-acoustic-wave devices and nonvolatile memories[1-4]. In recent years, many methods, such as RF sputtering, MOCVD, sol-gel,and electron beam evaporation[5-8] have been developed in preparation of PZT thin films. In most cases, in order to form the perovskite PZT thin film, the substrate temperature is usually higher than 500°C and is not compatible with silicon technique. So these common methods are not suitable for the preparation of ferroelectric thin films being used in non-volatile memories.

In our experiment, in order to find out the proper sputtering technique , two different preparation methods have been employed to fabricate PZT thin film for the use of non-volatile memories, which include sputtering on the substrate with high temperature, sputtering on the substrate with low temperature and then annealing by rapid thermal annealing method (RTA). And the related results are also discussed in details.

2.EXPERIMENT

The PZT thin film is prepared by RF sputtering method, the target which is 50 mm in diameter and 5mm in thickness is doped PZT (53/47) ceramics plate .The substrate used is silicon crystal coated with oxide silicon layer formed by thermal growth, Pt layer as bottom electrode is deposited by RF sputtering method on the substrate. The substrate temperature can be adjusted between room temperature to 600°C.

During experiment, the sputtering chamber is evacuated to a base pressure of 10^{-5} torr and then the mixture gas of Ar and O_2 is filled into until the chamber pressure was $6\text{-}8X10^{-3}$ torr. The ratio of Ar to O_2 is 70:30. The deposition rate is about 100 μm/hr.

3.RESULTS

3.1.Sputtering at high temperature

In this method, the PZT thin films are fabricated at different substrate temperature, ranging from 400°C to 550°C.

Fig.1(a) shows the x-ray diffraction pattern of thin film prepared at 400°C. It is found that only the pyrochlore type PZT thin film is formed. By increasing the temperature up to 500°C, we can find that the pyrochlore and perovskite type PZT co-exist [shown in fig.1(b)]. When the temperature is further increased to 550°C, only perovskite type PZT thin film exists [shown in fig.1(c)]. As shown in Fig.2, the grain size of thin film is about 0.1 μm. These experiment results demonstrate that the formation of the perovskite-type PZT thin film require high substrate temperature with sputtering method.

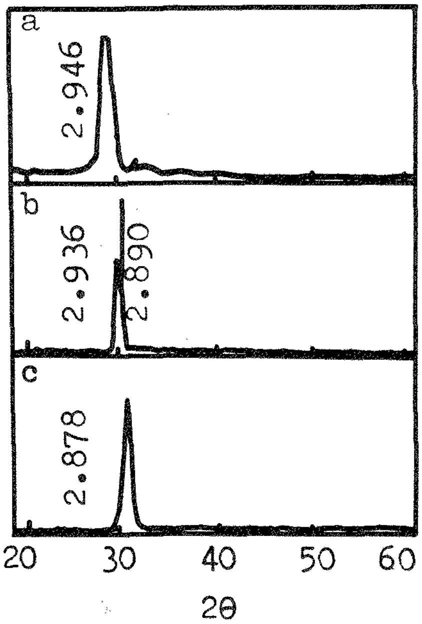

Fig.1 XRD pattern of PZT thin film sputtered at (a) 400°C (b) 500°C (c) 550°C

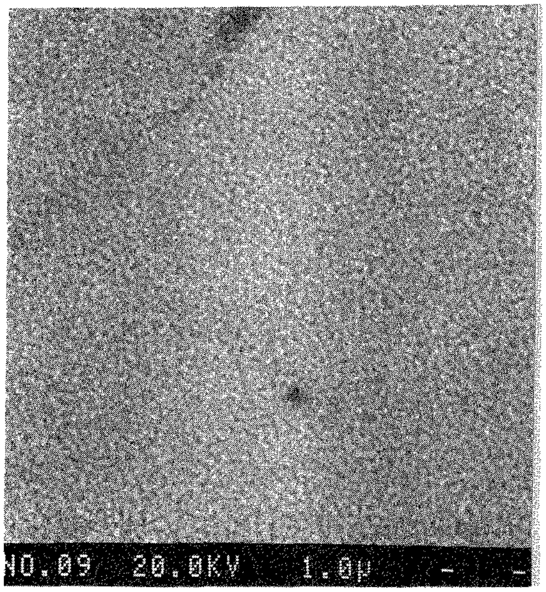

Fig.2 The SEM picture of the surface of PZT thin film sputtered at 550°C

With the increase of the substrate temperature up to 550°C, the perovskite-type PZT thin film can be obtained, but as the silicon integrated technique requires that the formation temperature should be controlled below 500°C, so it is not the appropriate technique and is not compatible with silicon integrated technique.

In order to overcome this disadvantage, the following technique are adopted to form PZT thin film of perovskite structure, that is, the PZT thin film is first fabricated by sputtering at low temperature (less than 500°C) and then annealed through RTA process.

3.2. Sputtering at low temperature and then annealing by RTA.

In this method, the PZT thin film is fabricated at 400°C, then, the rapid thermal annealing is used to anneal the as-grown film. The RTA is carried out in a special furnace, in which, the heat produced by tungsten halogen lamps is concentrated on the quartz tube by reflected films, where the sample is placed. The annealing temperature is 650°C and the time lasted is about 10 seconds. The experiment result shows that the structure of thin film was obviously changed from pyrochlore type structure [shown in fig.3(a)] to pure perovskite type structure [shown in Fig.3(b)] through RTA process.

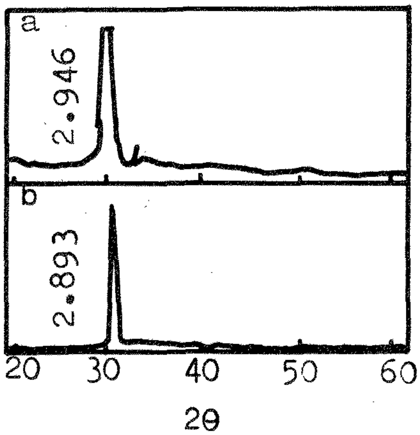

Fig.3 XRD pattern of PZT thin film (a) before RTA (b) after RTA

4.DISCUSSION

According to the theory of film growth, at the primary stage incident atoms randomly disperse on the substrate to form a lot of crystal nucleus. New atoms deposited the substrate diffuse to the site of nucleus by surface jump, and the nucleus grow larger by step growth.The higher the substrate temperature, the easier atoms diffuse. With the deposition process, the separate crystal nucleus gradually grow to continuous film. So the formation of $Pb(Zr,Ti)O_3$ thin film includes three steps. ie., the deposition of the incident atoms on the substrate, the diffusion of atoms and the reaction of the atoms to form PZT by solid-state reaction on the substrate.

When the sputtering at low temperature, the substrate temperature is so low that the deposited atoms are cooled rapidly. The incident atoms are difficult to diffuse and react each other, so no perovskite-type PZT thin film is formed. With the increase of substrate temperature up to 500°C, the atoms can diffuse and the solid-state reaction can take place. The perovskite-type PZT and pyrochlore-type PZT (as intermediate phase) can co-exist in the PZT thin film. When the substrate temperature is increased to 550°C, the solid-state reaction can proceed completely and the pure perovskite-type PZT thin film is formed.

As the energy of PZT thin film in pyrochlore state is higher than that of in perovskite state, the phase transition may take place under suitable annealing condition. With the RTA process, the PZT thin film structure is changed from pyrochlore type structure to perovskite type in very short time. This technique avoids the influence of the high temperature for long time on the sample.

5.CONCLUSION

With the experiments and results mentioned above, we can conclude that the formation of the perovskite-type PZT thin film requires high substrate temperature (550°C) if only with sputtering method alone. By sputtering at low substrate temperature and then annealed by RTA process, the pyrochlore structure of PZT thin film obtained at 400°C can change to perovskite structure.

Sputtering at low substrate temperature and then annealing by RTA method may be a suitable method as it is compatible with silicon technique for preparing PZT thin film.

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