Determination of the Orientations and Microstructures of Pb(Zr,Ti)O Films Fabricated on Different Substrate Structures

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Piezoelectric (PZT) films with different orientations and microstructures were fabricated on different substrate structures in one chip. To investigate the substrate structural effect of Pb(Zr₀·₅₂Ti₀·₄₈) films, different substrate structures of a Pt membrane and Pt on a Si substrate (called platinized Si) were fabricated after Si back-side etching. The PZT films were fabricated on the prepared substrates by RF magnetron sputtering with a single oxide target. After the annealing of a PZT film, different microstructures and orientations were observed from different parts of the sample. The PZT film on the Pt membrane has (001) orientation and grains of ~1 µm size. On the other hand, the PZT film on platinized Si has (111) orientation and grains of ~3 µm size.

1. Introduction

Ferroelectric thin films have attracted considerable attention owing to their multifunctional applications to micro-electromechanical systems (MEMS) devices, which require the high dielectric, piezoelectric, and electrooptic properties of ferroelectric materials.(1–5) Among the ferroelectric materials, Pb(Zr,Ti)O (PZT) is one of the best candidates for these applications owing to its high ferroelectric and piezoelectric properties.(6) In particular, its superior piezoelectricity meets the requirement for various sensors, e.g., tactile and biomass-detecting sensors.

According to theoretical calculations,(7,8) the piezoelectric properties of the (001)-oriented rhombohedral PZT films are better than those of the (111)-oriented or randomly oriented films. On the other hand, the (111)-oriented films have higher ferroelectric properties than the others. For a specific device purpose, PZT films with...

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different preferred orientations are required. For example, dynamic random access memory (DRAM) devices need a high ferroelectric value, which can be obtained from highly (111)-oriented PZT films, and MEMS actuators need a large displacement, which can be obtained from highly (001)-oriented PZT films. This means that the sensibility of the sensors can be enhanced by the (001) orientation control of PZT films. Many researchers have introduced various methods of controlling the orientation of PZT films for their own device purpose.\(^{[9-14]}\) In this study, PZT films were fabricated under different substrate conditions to investigate their microstructures and orientations.

2. Experimental Details

The schematic diagrams of two different structures of PZT films are shown in Fig. 1. Areas A and B show a PZT film on a Pt membrane structure and a PZT film on a platinized Si substrate, respectively. First, a Pt/Ti layer was fabricated on a 2 cm\(^2\) Si chip. To fabricate two different substrate structures, a Pt membrane structure was fabricated after the back-side Si etching of the platinized Si substrate. A circle of 1 cm diameter was etched in the middle of the Si substrate by deep reactive ion etching from the back side, and then the PZT film was deposited on a Pt/Ti membrane by RF magnetron sputtering and annealed. For fabricating the Pt/Ti bottom electrode, polycrystalline Pt and Ti metal disks (75 mm in diameter and 5 mm in thickness) were prepared as the sputtering targets. First, the sputtering chamber was pumped until 10\(^{-4}\) Pa, and then Ar gas was introduced at 0.5 Pa for sputtering. An RF power of 300 W was applied to the targets and the deposition rates of Pt and Ti films were approximately 20 and 10 nm/min, respectively. For PZT film sputtering, a polycrystalline Pb\((Zr_{0.52}Ti_{0.48})O_3\) ceramic disk (75 mm in diameter and 5 mm in thickness) was prepared as the sputtering target. For deposition, the sputtering chamber was pumped to 10\(^{-4}\) Pa and then an Ar gas

![Fig. 1. Schematic diagram showing the PZT membrane structure and PZT film on platinized Si substrate in one sample.](image-url)
pressure of 0.5 Pa was introduced. Sputtering was conducted at an RF power of 100 W and the deposition rate of the PZT film was approximately 1 µm/h. The samples were annealed using rapid thermal annealing equipment at 650°C for 10 min with a heating rate of approximately 100 °C/s under O₂ atmosphere.

The microstructures of the PZT film surfaces were observed by atomic force microscopy (AFM) (SPM-9500J2, Shimadzu, Japan). X-ray diffraction (JDX-3530, Jeol, Japan) was performed to investigate the film orientation. Pt top electrodes (1 mm in diameter and 300 nm in thickness) were sputtered on the PZT films with a metal mask for the determination of ferroelectric properties. The P-E hysteresis curve was measured with a Q-V Amp. setup (Model 6252, Toyo Corporation, Japan).

3. Results and Discussion

The crystalline structures of PZT films on the Pt membrane and Pt on the Si substrate were evaluated by X-ray diffraction analysis. The XRD patterns of the PZT films on the different structures are shown in Fig. 2. In the case of the PZT film on a platinized Si substrate with a Pt film of (111) orientation, the PZT film has a (111)-preferred orientation after rapid thermal annealing. This is a reasonable result because the orientation of the PZT film is affected by the orientation of the (111)-Pt bottom electrode with a PbPtₓ(111) intermediate phase, which leads to the lattice matching between PZT and Pt (111). However, the PZT film on the Pt membrane structure has a (001)-preferred orientation and even the Pt bottom electrode has a (111) orientation, under the same sputtering and annealing conditions, such as those of the PZT film on a platinized Si. This different PZT film orientation on the Pt membrane shows some existing factors for determining the PZT orientation on the membrane structure. In particular, the lattice

![Fig. 2. X-ray diffraction patterns of the PZT membrane structure and PZT film on platinized Si substrate.](image)
parameter change of the Pt bottom layer due to the absence of the Si substrate can affect the orientation of the PZT film during crystalline growth.\(^{(17)}\) When materials are deposited on the substrate, the films have stress owing to differences in lattice parameters between the films and the substrate. Therefore, the films with curvature were found frequently after releasing the films from the substrate owing to the release of the stress from the films. For the same reason, there can be a change in lattice parameter between the Pt membrane and Pt on the Si substrate. Therefore, the lattice mismatch between the PZT film and the Pt membrane hinders the (111)-oriented growth of the film.\(^{(17)}\)

According to the thermal dynamics point of view, the PZT film has a low energy when it grows up to the (001) orientation. Grain structures of PZT films from different structures are shown in Fig. 3. Figure 3 shows the atomic force microscopy (AFM) images of the PZT films on the Pt membrane and Pt on the platinized Si substrate. The surface morphology of the films shows that the films have homogeneous and fine grain structures without any crack in both cases. The grain size and roughness are ~1 µm and 9.3 nm, respectively, for the PZT film on the Pt membrane. The grain size and roughness are ~3 µm and 14.2 nm, respectively for the PZT film on the platinized Si substrate. There is no marked difference in roughness between PZT films with and without a Si substrate. However, the grain size of the film on the Si substrate is 3 times larger than that of the PZT film on the Pt membrane. This phenomenon can be explained on the basis of the annealing condition difference between them owing to the absence of the Si substrate. Because the decreasing heat capacity of the membrane structure results in the absence of the substrate, the heating rate could increase during the annealing process. As shown in ref. 18, the small grains of the PZT membrane structure are created because the heating rate of the PZT membrane film is higher than that of the normal PZT film with a fixed Si substrate. The film with small volume has a smaller heat capacity than that with large volume.\(^{(19)}\)

The ferroelectric hysteresis curves of the 1-µm-thick PZT film on a Pt membrane and that on a platinized Si substrate are shown in Fig. 4. A comparison of the remnant polarization (Pr) values between the PZT films with and without a Si substrate shows that there is no marked difference between the Pr values of 25 and 22 µC/cm\(^2\). Normally, it is well known that PZT films with a (111)-preferred orientation have higher ferroelectric properties than those with a (001) or random orientation. However, there is no marked difference between them owing to the merit of the PZT membrane structure. Good ferroelectric properties could be expected with the removal of the Si substrate. Without the clamping effect from the substrate, excellent electrical and piezoelectric properties could be maintained.\(^{(20–22)}\)

4. Conclusions

To investigate the microstructure and orientation of Pb\((Zr_{0.52}Ti_{0.48})\) films as a function of substrate structure, PZT films were fabricated and annealed on two different structures in the same sample. PZT films on a Pt membrane and a platinized Si substrate have a well developed perovskite structure; however, they have different preferred orientations and grain sizes. These different crystalline structures and surface morphologies are expected owing to the different lattice parameters and/or annealing conditions during
Fig. 3. AFM images of PZT films: (a) PZT membrane structure and (b) PZT film on platinized Si substrate.

Fig. 4. Polarization hysteresis loops of 1-µm-thick PZT membrane structure and PZT film on platinized Si substrate.
the crystallization step. The PZT films can be allowed to enhance the sensibility of the piezoelectric sensors by controlling the orientation of the film.

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