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Ion beam etching of PZT thin films: Influence of grain size on the damages induced

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Abstract

Ion beam etching (IBE) of sputtered Pb($Zr_{0.54}$,$Ti_{0.46}$)O_3 has been performed using pure Ar gas. We have studied the damages induced by the etching process on the microstructural and electrical properties. In a previous study, we had demonstrated the influence of etching parameters on the extent of the degradations. We evaluate now the influence of the microstructure (grain size) of the PZT thin film. Indeed, we can obtain sputtered PZT thin films with small ($<$1.5 μm) and large ($\gg$1.5 μm) grain size. In the first part, we compare the properties of these two types of PZT thin films before etching. In the second part, we compare the results obtained after etching. The properties (particularly the roughness and the ferroelectric properties) of PZT films with large grain size appear to be more damaged after IBE.

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1. Introduction

Lead titano-zirconate (PZT) ferroelectric thin films have developed a great interest for their applications in memory devices, and more recently in microelectromechanical systems (MEMs) because of their interesting piezoelectric properties. The patterning has become an essential element for PZT integration in devices. However this integration stage can induce many defects, as well microstructural as electrical. So it is very important today to understand more precisely the mechanisms of degradations. Several techniques have been developed for patterning: wet chemical etching,[1] ion beam etching (IBE),[2] reactive ion etching (RIE),[3,4] electron cyclotron resonance (ECR) etching,[5] and inductively coupled plasma (ICP) etching.[6] The technique used in this study is the IBE (pure Ar beam). Indeed, the different etching parameters can be adjusted independently and it allows to evaluate more easily the influence of each one. Moreover, in the frame of PZT integration, this technique, essentially based on the physical bombardment, is efficient to etch structures composed of different materials such as a Pt/PZT/Pt capacitor. The influence of the etching parameters (current density, acceleration voltage) on the extent of the degradations has already been studied.[7] We have observed that not only the etching conditions but also the PZT microstructure could influence the results. So we have distinguished the two following cases: the etching of PZT thin films having a grain size of several micrometers, and the etching of films having a grain size lower than one micrometer. In this study, we compare the structural, microstructural and electrical properties of these PZT thin films before and after etching.

2. Experimental procedure

Pb($Zr_{0.54}$,$Ti_{0.46}$)O_3 (PZT) thin films were deposited on Si/SiO_2/Ti/Pt substrates by rf magnetron sputtering. Pt and Ti layers of 100 and 20 nm thick, respectively, were deposited on SiO_2/Si substrates by DC sputtering. The PZT sputtering conditions are summarized on Table 1. The PZT films were annealed by conventional annealing at 625 °C for 30 min to form the perovskite phase.

Ion beam etching of PZT was investigated by using Veeco Microetch 3″. This system was equipped with a Kaufman type source and is described in the reference.[7] Argon ions

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Table 1
Sputtering parameters

Target composition	$PbO + 0.54\ ZrO_2 + 0.46\ TiO_2$
Gas	Argon
Pressure (mTorr)	30
Power density (W/cm^2)	2.34
Temperature	Unheated

were extracted by acceleration potential (typically between 0.6 and 1 kV). The current density can be adjusted by varying the magnetic field, pressure, arc power and cathode emission. A filament allows the positive charge of the ion beam to be neutralized. The sample holder is water-cooled.

X-ray diffractogramms allow the crystallographic orientation to be controlled. The topography of unetched and etched PZT was characterized by atomic force microscopy (AFM). Images in the contact mode AFM were carried out using a Park Scientific Instruments Autoprobe CP.

Pt top electrodes were sputtered through a shadow mask on etched PZT to determine electrical properties evolution. They were then compared to the unetched samples to evaluate the extent of IBE effect. Capacity, tan δ, and $C(V)$ were performed using an impedance analyser HP4192A at a frequency of 10 kHz and an alternative voltage $V_{ac} = 100$ mV. The ferroelectric loops $P(E)$ were measured using a standardized Radiant RT6000 system. The average coercive field E_a is defined as $(|E_c^+| + |E_c^-|)/2$.

3. Microstructural and electrical properties of PZT thin films

After crystallization annealing, the PZT thin films can present different grain sizes: the grain diameter is ranging from 0.3 µm to a size greater than 5 µm. These thin films have the same thickness (1.3 µm), and we have not changed the growth or crystallization parameters. So, this result is surprising. Moreover, different preferential crystallographic orientations are linked to these various grain sizes. The PZT thin films having the smaller grain size (<1.5 µm) are (1 1 1) preferentially oriented, whereas the thin films having a grain size $\gg 1.5$ µm are (1 1 0) preferentially oriented.

We have chosen to present in this study the structural and electrical properties of these two types of PZT thin films.

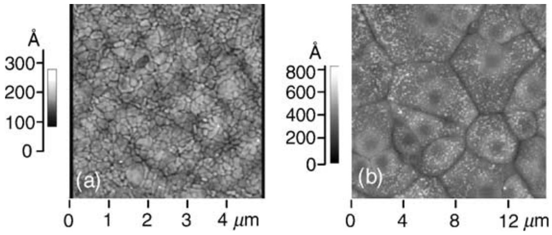

Fig. 1. AFM micrographs of PZT thin films with (a) a small grain size (<1.5 µm) and (b) a large grain size (>1.5 µm).

3.1. Structural and microstructural properties

Fig. 1 compares the surface morphology of two samples. Fig. 1a (5 µm × 5 µm) illustrates the topography of a sample with grains having an average diameter inferior to 1 µm. The roughness r_{ms} (root mean square) is about 10–20 Å. The diffractogramm of this sample is reported in Fig. 2a: we observe the (1 1 1) preferential orientation.

At the opposite, Fig. 1b (15 µm × 15 µm) shows the topography of a PZT film having large grains. The roughness is now around 40–50 Å. The (1 1 0) preferential orientation is demonstrated in Fig. 2b. We are precise that in the two cases, the Pt bottom electrode is (1 1 1) preferentially oriented (Fig. 2a and b). The difference measured concerning the roughness is in part due to the fact that the grain boundaries of large grains are slightly hollowed out before etching.

The origin of these various orientations has already been discussed in literature. It is currently reported that the crystallographic orientation can be changed by a modification of the deposition temperature, the annealing temperature or the lead content.[8,9] Some authors have observed a slight evolution of the grain size with the change of orientation, but the grain size remains lower than 1 µm.[11] In no case they have observed a so large increase of the grain size.

3.2. Electrical properties

The influence of the orientation[10,11] and of the grain size[12] on the electrical properties has already been studied. But in these works, the modification of orientation and grain size are linked for the most part to a change of a parameter during the growth process. In our study, the dielectric and ferroelectric properties of the two types of PZT thin films have been

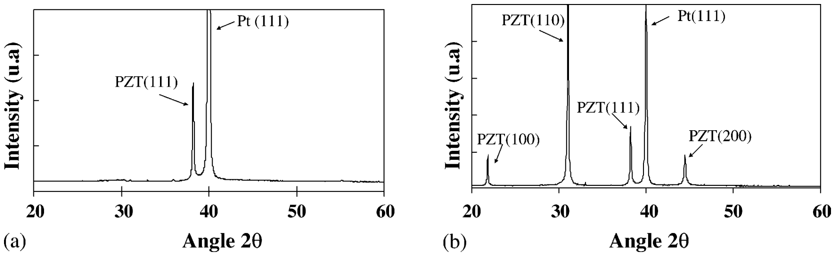

Fig. 2. X-ray diffractogramms of PZT thin films with (a) a small grain size (<1.5 µm) and (b) a large grain size (>1.5 µm).

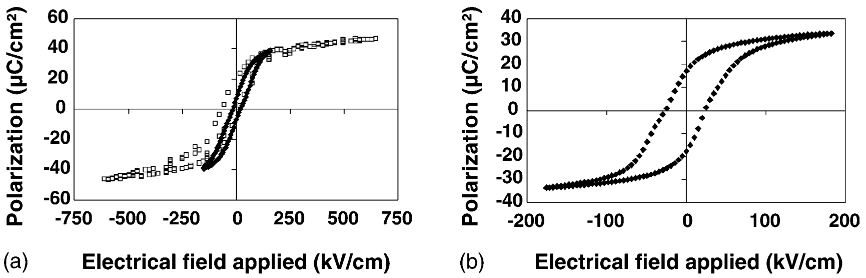

Fig. 3. *P*(*E*) hysteresis loop measured on PZT thin films with (a) a small grain size (<1.5 μm) and (b) a large grain size (>1.5 μm).

compared. We have observed that the permittivity of a film having a small grain size is higher: the value measured is superior to 1100, whereas it reaches only 850 for PZT films having a large grain size. This result can be explained by two ways: an increase of the domain density when the grain size decreases as it is the case for BaTiO$_3$ ceramics,[13] and a modification of the nature or the mobility of the domains. Fig. 3 presents the hysteresis loops *P*(*E*) performed on each sample. We observe that the shape is very different for the two PZT films. When we apply an electrical field superior to 150 kV/cm, the hysteresis loop is well saturated for large grains PZT film (Fig. 3a). For the sample having a smaller grain size, the loop appears to be tilted, not saturated and the remnant polarization is very low. If we apply a sufficient electrical field on this film (about 400 kV/cm), we observe now the saturation of the loop (Fig. 3b). The remnant polarization is now about 18 μC/cm^2, i.e. in the same order as for large grain PZT film. So, the PZT thin films having a small grain size present good ferroelectric properties if the external field applied is enough high. This result seems to confirm that the nature of the domains is probably not the same, or that the dynamic of the domains is modified, maybe in connection with a change of the strains due to the increase of the domain density.

4. Influence of ion beam etching on PZT properties

We compare in this part the properties of the types of PZT thin film measured after ion beam etching. The etching parameters are summarized in Table 2. The etch rate is the same, whatever the PZT microstructure (about 40 nm/min). We have already demonstrated that these etching conditions induced large degradations of the microstructural and electrical properties of PZT thin films with a large grain size.[7] Particularly, we have observed an increase of the surface roughness, a large decrease of the permittivity and a widening of the ferroelectric loop.

Table 2
Etching parameters

Acceleration voltage (V)	800
Current density (mA/cm^2)	1
Pressure (mTorr)	0.2
Gas	Argon
Temperature (°C)	>100

4.1. Structural and microstructural properties

The crystallographic orientation keeps unchanged after etching. It is not the case for the microstructure, as we can see it in Fig. 4. Fig. 4a and b present the surface after etching for PZT with small and large grains respectively. For PZT films having a large grain size, the increase of the $r_{\rm ms}$ (300 Å) is explained by the preferential etching of lead (PbO inclusions are present in the grains and lead excess can be located at the grain boundaries). Moreover, the microstructure of the layer is also responsible: indeed, the presence of “cavity” between two grains induces an ion rebounding at this location, and so a local increase of the etch rate. This results in the preferential etching at the grain boundaries. For the other film (Fig. 4a), the increase of the $r_{\rm ms}$ is smaller (90–100 Å). We do not observe the phenomenon of preferential etching. This result is due to the microstructure of the PZT film: the grain boundaries have no relief before etching. The second reason may be a difference of composition (particularly a lead excess less important).

4.2. Electrical properties

The PZT thickness after etching is 0.7–0.8 μm.

We observe a large decrease of the permittivity after etching. The decrease is quiet the same, whatever the grain size. The permittivity value is 650 and 500, respectively for PZT film having small and large grain size. The decrease can be explained by different hypothesis: formation of microstructural and electrical defects (accumulation of charges at the

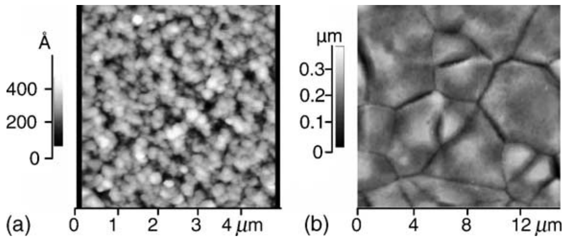

Fig. 4. AFM micrographs performed after IBE of PZT thin films with (a) a small grain size (<1.5 μm) and (b) a large grain size (>1.5 μm).

Table 3
Comparison of the degradations measured on PZT thin films with small and large grain size

	Small grain size	Large grain size
Pmax (%)	−12	−29
Pr_a (%)	−10	−14
E_a (%)	+84	+159

domain walls and grain boundaries) in the surface atomic layers. They can be at the origin of the formation of a surface layer that does not have the same properties as the PZT film, and that may be not ferroelectric. Moreover, they can induce a domain wall pining: this reduces the domain wall mobility, and thus contributes to lower the extrinsic contribution to the permittivity. It is also well-known that the decrease of the PZT thickness is responsible for the permittivity decrease.[14] At the same time, the average coercive field increases. But in our case, the evolution of the thickness is too low to justify the result observed.

If we compare now the ferroelectric properties, we observe that the degradations are not the same for PZT thin films with small or large grain size. Indeed, in the two cases, we observe a decrease of the remnant and maximum polarizations, whereas the average coercive field E_a increases. But, the extent of the degradations is more important for thin films having a large grain size. The results are summarized in Table 3. For a greatest clearness in the presentation of our results, we have given them in percentage of decrease (−) or percentage of increase (+) as compared to the unetched PZT.

As we have already observed, the topography of the two samples is very different after etching. For PZT thin films with large grain size, we can suppose that the widening of the grain boundaries favors the accumulation of defects at this location and so the domain pining. The domain structure, as well as the strains, can also be modified close to the grain boundaries. We think that these hypothesis can explain that the extent of etching damages is more important for PZT with large grain size.

5. Conclusion

In this study, we have shown that the electrical properties of PZT thin films grown in the same conditions, but having various grain size and crystallographic orientation, are very different. The permittivity of PZT with small grain size (<1.5 μm) and (1 1 1) preferential orientation is higher than the permittivity of PZT with large grain size and (1 1 0) preferential orientation. Moreover, the ferroelectric loop is very difficult to saturate. We think that a change of the domain density, or the domain nature, can explain this result.

We have demonstrated that, after ion beam etching, the microstructural and electrical properties of PZT thin film with large grains are more damaged. The grain boundaries zones are in part responsible for this result. Indeed, a preferential etching occurs at this location, and this favors the accumulation of defects during etching, and so the domain wall pining.

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