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Preparation of ultrathin PZT films by a chemical solution deposition method from a polymeric citrate precursor

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Abstract

Ultrathin PZT film was prepared using a chemical solution deposition method from polymeric citrate precursors. The PZT solution was spin-coated on an amorphous silica layer formed on a Si(1 0 0) substrate. The films were thermally treated from the substrate side with a low heating rate (1°/min) up to 700 °C and finally annealed for 10 h. Ultrathin PZT films without microstructural instability were prepared in spite of high temperature and long annealing time. AFM and HRTEM investigations revealed the formation of a well-developed dense microstructure consisting of spherical crystallites (4–7 nm). Low roughness (2.2 nm) of a ~26 nm thick layer was obtained for a two-layered PZT film. The grazing incidence X-ray diffraction (GIXRD) measurements confirmed the polycrystalline structure of ultrathin PZT films. Also, GIXRD and electron energy dispersive X-ray (EDS) analysis showed that compositional variations were smaller than expected, in spite of the long annealing time.

Keywords: Precursors-organic; Films; Electron microscopy; PZT

1. Introduction

Lead zirconate titanate (PZT) is a ferroelectric material, offering a wide range of useful physical properties, especially when it is in the form of a thin film. Among all the compositions of PZT, $Pb(Zr_{0.52}Ti_{0.48})O_3$ is close to the morphotropic phase boundary, making it one of the most promising optoelectronic materials for the production of different optical devices.[1,2] Moreover, due to its exceptional ferroelectric behavior related to spontaneous electrical polarization below the Curie temperature and large remanent polarization at relatively small coercive fields, another branch of applications appears in microelectronics especially for devices such as dynamic random access memories and non-volatile random access memories.[3,4]

Some applications, for example in ferroelectric non-volatile memories, require a low film thickness below 100 nm for a better working quality.[5] Also, for that purpose it is essential to achieve highly oriented or epitaxial films. Generally, physical methods (metal–organic chemical vapor deposition or pulsed laser deposition) have shown considerable success in the growth of high quality ultrathin oxide films. But these methods are expensive and unfavorable when large substrate surfaces need to be deposited. In contrast, chemical methods appear to be more suitable for easier fabrication of larger areas, simpler composition control and better thin film homogeneity as well as for lowering the synthesis temperature. Unfortunately, some problems, such as microstructural instability, could appear as a result of high temperature or long annealing time when chemical methods are used for ultrathin film preparation. In other words, it was found that oxide thin films with thickness below the critical value break up and form nanoislands after high temperature processing.[6,7] This type of microstructural instability might have a negative influence on ferroelectric properties and needs to be avoided in the preparation of ultrathin films.

The main focus of the present work was to prepare ultrathin PZT film on amorphous SiO_2, using polymeric citrate precursors, and investigate its compositional and microstructural stability after thermal processing at a high temperature and for a long annealing time. For this purpose, slow thermal treatment, named *gradient thermal annealing* (GTA) was used. Our previous investigation suggested that this method is useful for obtaining highly oriented LNO/Si(1 0 0) and PZT/Si(1 0 0) ultrathin films.[8,9] To examine the microstructure, thickness and orientation of as-synthesized PZT films grown on amorphous

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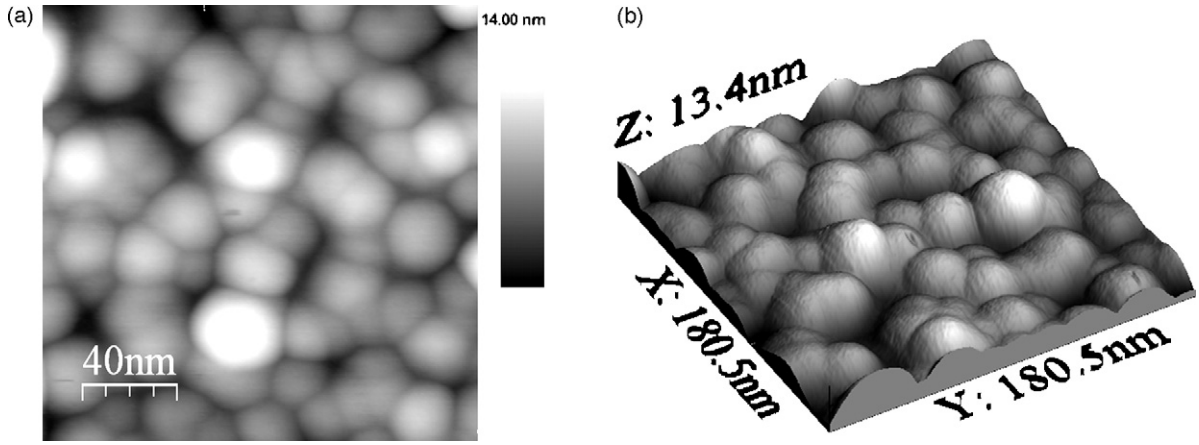

Fig. 1. 2D (a) and 3D (b) AFM micrographs of a one-layered ultrathin PZT film.

silica, detailed analyses were performed using Atomic Force Microscopy (AFM) and High Resolution Transmission Electron Microscopy (HRTEM), while GIXRD pattern and EDS analyses were employed to additionally confirm the film orientation and composition. The results shown in this work can be beneficial for further investigations of ultrathin PZT films.

2. Experimental method

The PZT precursor solution was prepared by a modified Pechini method using lead acetate trihydrate, titanium isopropoxide and zirconium dioxide, all p.a. as the starting materials. Separately synthesized titanium and zirconium citrates were mixed in the molar ratio Ti:Zr = 0.48:0.52 to form the composition, which lies near the morphotropic phase boundary. A detailed description of each step in the preparation of the mentioned citrates can be found in our previous study.[9] Lead acetate trihydrate was dissolved in water and a stoichiometric amount was added to the Ti–Zr citrate solution, while aqueous ammonia was used to adjust the pH value to 7, to avoid the precipitation of lead citrate. The final PZT solution, with the ratio of *metal ions:citric acid:ethylene glycol* = 1:4:16 was stirred and heated at 80–90 °C to promote the polyesterification reaction and increase the viscosity to 40 cP.

Using the spin-coating technique the solution was deposited onto an amorphous SiO_2 layer formed on a Si(1 0 0) substrate. The spin speed was 5000 rpm with the holding time of 20 s. Each of the deposited layers was slowly treated on a hot plate up to 700 °C with a heating rate of 1°/min and further annealed for 10 h on that temperature.

The microstructure of as-synthesized ultrathin films was analysed by AFM (VEECO Multimode Quadrex SPM). Characteristic parameters, such as the R_a (average roughness), Rms (root mean square roughness) and average grain size were extracted from micrographs.

High resolution transmission micrographs (HRTEM) of a polished cross-section of a two-layered PZT ultrathin film were acquired on a 200 keV TEM (JEM-2100, JEOL). The thin film thickness and its orientation were obtained from HRTEM micrographs.

Because of low thickness of the films GIXRD measurements were performed on a Bruker D8-Advance diffractometer using CuK_α radiation.

3. Results and discussion

Fig. 1 shows the AFM micrographs of one-layered PZT thin film deposited on Si(1 0 0) substrate and annealed at 700 °C for 10 h after very slow heating (1°/C) on a hot plate. Apparently, the slow heating rate provides enough time for diffusion processes taking place during decomposition of the organic material, which results in the formation of a well-developed, dense and continuous film, without any cracks or pores. Furthermore, thermal treatment from the substrate side promotes nucleation at the substrate surface and its propagation through the film as a result of the induced temperature gradient. Namely, the difference in the temperature between the substrate and the film surface plays a major role in controlling the films orientation.[8] Using this approach, highly oriented LNO films, with a function of bottom electrode for further deposition of ferroelectric PZT layers and films, have been successfully obtained on a Si(1 0 0) single crystal substrate.[8,9] Note also that such growth could not be expected on the substrate used in our experiment (SiO_2/Si), as it may be in the cases where films are grown on single crystals with a selected crystallographic orientation and lattice parameters. Indeed, on an AFM micrograph of a PZT film grown on amorphous silica (see Fig. 1) possible preferential growth could not be noticed as in the case of PZT/Si(1 0 0).[9] Obtained films are dense and continual, very smooth, with Rms roughness up to 2.2 nm and relatively small grains in the form of clusters composed of smaller spherical grains (~20 nm), easily recognized by careful analysis of Fig. 1. Characteristic parameters, namely average grain size, R_a and Rms roughness are presented in Table 1.

Table 1
Roughness and grain size of one and two-layered ultrathin PZT films.

Substrate	Layers	R_a (nm)	Rms (nm)	Average grain size (nm)
Si(1 0 0)	1	1.6	2.0	20
	2	1.9	2.2	19

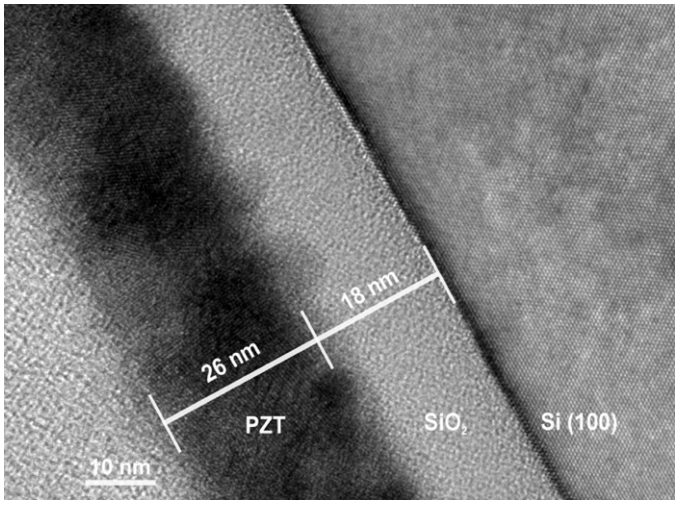

Fig. 2. Cross-section transmission electron micrograph of a two-layered PZT film grown on the silica layer.

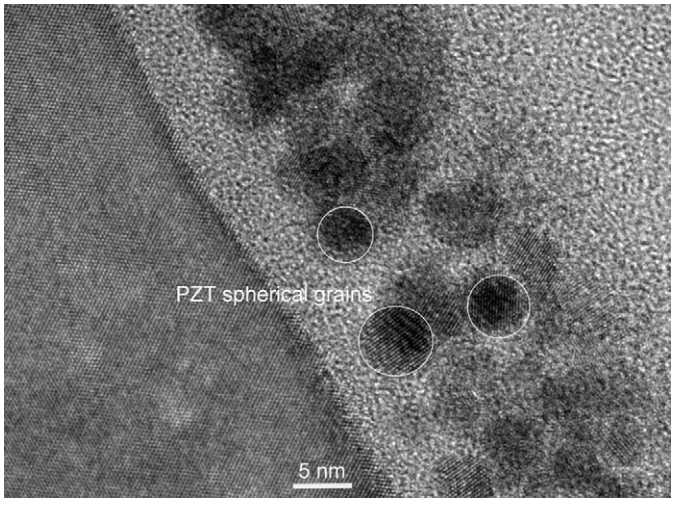

Fig. 3. Cross-section transmission electron micrograph of the thinner part of the PZT film.

Information on the thickness of PZT and silica layers could be extracted from the HRTEM image, shown in Fig. 2. A thick silica layer of ∼18 nm formed on the Si(1 0 0) substrate surface as a result of the thermal oxidation process is clearly visible. Also, a flat and well-defined interface between the silica layer and the PZT film, that is important for further growing of smooth PZT films with a well-developed structure, can be observed. The thickness of the PZT layers measured from the HRTEM micrograph is ∼26 nm. Obviously, PZT films with fairly low thickness can be synthesized using the CSD method from polymeric precursor solutions with the proposed thermal method—GTA. Some authors have indicated that microstructural instability can occur during high temperature treatment when very thin single crystal films are fabricated by the CSD method.[6,7,10] This instability caused a discontinuous thin film microstructure. For example, it was found that $PbTiO_3$ thin films broke up into isolated islands if they were thinner than 80 nm.[7] Similar behavior was reported for ultrathin PZT films.[6,10] Opposite to these reports, our experiments have shown that it is possible to achieve continuous microstructures of ultrathin PZT films during high temperature treatment with the film thickness below the critical value.

On the other hand, it seems that the silica layer has a negative influence on the formation of highly oriented films. While it is possible to see from Fig. 2 oriented grains in some segments of the PZT film, such features are only intermittently present throughout the film, which indicates that the crystallization process might be too fast and/or that the influence of the bottom SiO_2 layer is too strong for more organized columnar growth of the nuclei in such a thin film.

To confirm our assumptions that crystallization starts with nucleation of randomly oriented crystallites in the PZT film, the thinner part of the sample was analysed by HRTEM. A HRTEM micrograph is shown in Fig. 3. In the thinner part of the TEM sample it is possible to observe small 4–7 nm sized PZT crystallites that homogeneously nucleated within the film. The crystallites show no preferential orientation towards the substrate and are randomly oriented in the film, even though some of them have a similar orientation.

Finally, the GIXRD pattern of PZT films prepared on the amorphous silica layer (see Fig. 4) was measured to confirm the film orientation and composition. For this purpose four-layered films were used to obtain higher intensities of the GIXRD pattern. This analysis proved that the obtained PZT films are polycrystalline and contain no undesirable secondary pyrochlore phase.

Additional information about the composition of the ultrathin PZT films could be extracted from EDS analysis. For this purpose EDS analysis of a two-layered PZT film was performed near the amorphous silica layer (see Fig. 5). It was found that the Zr/Ti ratio is similar to the value in the PZT precursor solution. In contrast, the Pb/(Zr + Ti) ratio is less than one (0.8), even though the lead-deficient pyrochlore phase was not detected by GIXRD. Obviously, the prepared PZT films are lead deficient, but also the obtained composition is close to the common composition of PZT films deposited without excess Pb.[11] Some

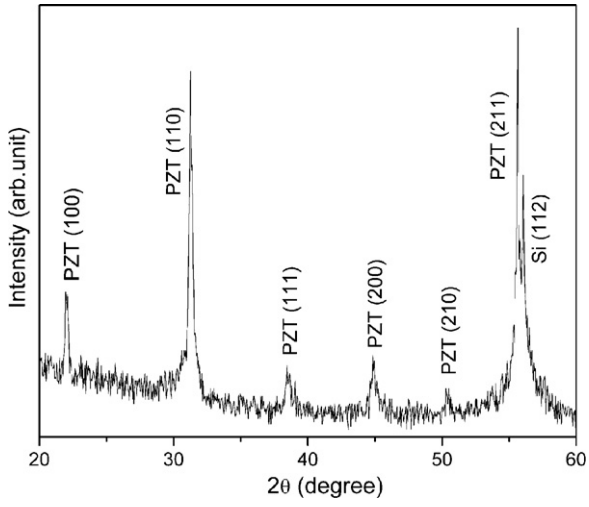

Fig. 4. GIXRD diffractogram at the incidence angle of 3° for a four-layered PZT film grown on the SiO_2/Si(1 0 0) substrate.

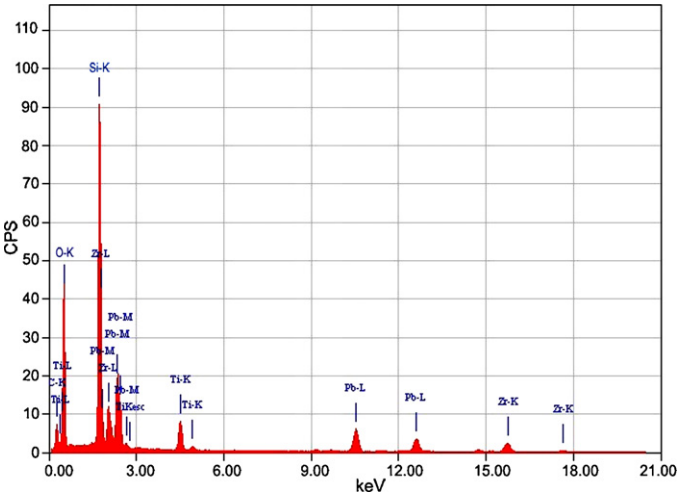

Fig. 5. EDS analysis of a two-layered PZT film near the amorphous silica layer.

published results indicated that the excess of lead content up to 20% had only a small effect on the fatigue and ferroelectric properties of PZT films prepared by the CSD method.[12] Lead losses and the resulting deviation from the nominal composition ($Pb(Zr_{0.52}Ti_{0.48})O_3$) were smaller than expected, if one assumes long annealing times. This can be explained by the thermal gradient inside the film, which results in a cooler film surface. The cooler film surface is responsible for inhibition of PbO evaporation.

In accordance with the results presented in this work, it is possible to conclude that the proposed heating method played a major role in the formation of ultrathin PZT films without microstructural instability. Foremost, the role of the silica layer must be highlighted, i.e. its double action in the formation of ultrathin PZT films: (i) by enabling the formation of an ultrathin PZT film with low surface roughness and (ii) disabling the formation of epitaxial PZT ultrathin films in spite of the applied thermal treatment.

4. Conclusions

Continuous ultrathin PZT films with a composition near the morphotropic phase boundary and thickness of 26 nm (two-layered PZT film) were successfully prepared by the CSD method on an amorphous silica layer. The slow thermal treatment and long annealing time provide enough time for the diffusion processes taking place during decomposition of the organic material and film crystallization and growth, resulting in the formation of a well-developed, dense and continuous film microstructure with a low surface roughness. From HRTEM and GIXRD measurements presented in this work, it was possible to conclude that the 18 nm thick amorphous silica layer disabled any oriented growth despite the adequate thermal treatment. Also, the obtained films were found to be lead deficient (calculated Pb/(Zr + Ti) ratio was ≈0.8), indicating the necessity of further optimization of the precursor solution composition and processing parameters.

Acknowledgments

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