EXAFS study of PZT ferroelectric thin films of different crystallinities

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Abstract: Lead zirconate titanate (PbZrₓTi₁₋ₓO₃, PZT) thin films were deposited on Pt/TiOₓ/SiO₂/Si substrate by RF-magnetron sputtering with a Pb₁₋ₓZrₓTiO₃ target at room temperature. The Zr K-edge of PZT thin films of different crystallinities were studied by extended x-ray absorption fine structure (EXAFS) spectrum. Scans were made in fluorescence mode to monitor the structural differences between the amorphous thin films and the crystalline thin films. It was found that the local structure of the amorphous thin films was quite different from that of the crystalline thin films from the analyses of the EXAFS spectra. In the amorphous PZT thin films only one oxygen coordination shell can be found. By contrast, in the crystalline PZT thin films, the EXAFS spectrum was fitted with three shells and Zr-Pb bond was found. The oxygen coordination numbers of the amorphous and crystalline PZT thin films were same. The Zr-O bond distance of the amorphous samples were bigger than the crystalline samples. Thus, the influences of the phase transformation on the ferroelectric properties of PZT thin films were interpreted from the angle of the local chemical structures.

1. Introduction

Lead zirconate titanate (PbZrₓTi₁₋ₓO₃, PZT) thin films have been of great interest for many years because of the excellent properties and promising applications in non-volatile ferroelectric memories, micro-electro mechanical system (MEMS), and piezoelectric ultrasonic motors [1,2]. Many deposition methods were used to fabricate PZT thin films, such as evaporation [3], RF-magnetron sputtering [4], sol-gel process [5], chemical vapor deposition (CVD) [6], metal organic decomposition (MOD) [7], pulsed laser deposition (PLD) [8] and so on.

Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy is a highly sensitive technique with elemental specificity. As such, EXAFS is an extremely powerful technique to determine the chemical structure of materials, even with a very low abundance or concentration irrespective to the state of the samples [9,10]. By means of theoretical computations, the analysis of the EXAFS spectrum allows the determination of the coordination number, the bond distance, the “Debye-Waller”-like factor, and the nature of neighboring atoms surrounding the excited atoms. So far,
EXAFS has been used in the research fields of environmental chemistry, medical science and so forth [11]. However, the use of EXAFS received little attention for the research of ferroelectric thin films.

In the present study, RF-magnetron sputtering was used to deposit the PZT thin films on Pt/TiO$_x$/SiO$_2$/Si substrates [12]. The structures and ferroelectric properties of the PZT thin films of different crystallinities were discussed. Zr K-edge EXAFS spectra of PZT thin films of different crystallinities were collected and the local structure parameters of zirconium atoms were obtained. The relationship between the local structure and ferroelectric properties was discussed.

2. Experimental

The Pb$_{1.2}$ (Zr$_{0.3}$Ti$_{0.7}$) O$_3$ target was used because of the lead lose during the sputtering deposition process. PZT thin films of about 200nm were deposited on the Pt/TiO$_x$/SiO$_2$/Si substrates. Before each deposition, the chamber was evacuated to a base pressure lower than $8 \times 10^{-4}$ Pa. The as-deposited PZT films were amorphous while the PZT films become crystallized upon 3min annealing in pure oxygen at 700°C. Pt top electrodes were deposited by sputtering. The crystal structure of the PZT thin films was examined by X-ray diffraction (XRD, MSALXD-3) using Cu K$_\alpha$ radiation and graphite monochromator. The surface structure of thin films was characterized using atomic force microscopy (SPM 5500, Agilent). The hysteresis properties were examined at 5V and 100 kHz by an aixACCT TF analyzer 2000 system.

EXAFS spectra at Zr K-edge of PZT thin films were collected in fluorescence mode at the 1W1B beam line in Beijing Synchrotron Radiation Facility (BSRF). The storage ring was operated at 2.5GeV and 200mA. All the experiments were carried out at room temperature.

Fluorescence EXAFS spectra were summed, calibrated and background subtracted using the Athena program which is implanted in IFEFFIT [13]. Best fits were achieved using Artemis program, also a part of IFEFFIT. The Fourier transformations (FT) of $k^3\chi(k)$ from K space into R space were performed in the 3-9Å$^{-1}$ range using a Hanning window. The R-range used for fitting was between 1.0 and 4.0 Å. The bond distance, coordination numbers, nature of neighboring atoms surrounding the excited atoms were obtained.

3. Results and discussion

3.1. X-Ray Diffraction and AFM

XRD spectra of the amorphous and crystalline PZT thin films are shown in Figure 1. In the figure, PZT (100), (101)/(110), (111) diffraction peaks showed in the crystalline PZT thin films, while no PZT diffraction peak appeared in the amorphous samples. It means that the perovskite structure was formed without any observable secondary phases in the crystalline PZT films which showed a preferential orientation of (111) and are better crystallized than the amorphous films. And the XRD results indicated that the crystalline films exhibit a tetragonal structure.

AFM pictures of the amorphous and crystalline PZT thin films as shown in Figure 2 provide a visualization of the change of surface microstructure. The film morphology changes from smooth with no grain structure (amorphous) to an fine-grained structure (crystalline). The roughness of the annealed sample is 12.9 nm while the amorphous one is 8.47 nm. It is obvious that after crystallized, the roughness of the samples is increased.
Figure 1 XRD spectra of amorphous and crystalline PZT thin films

Figure 2 AFM images of the amorphous (a) and crystalline (b) PZT thin films
3.2 P-V properties
The P-V hysteresis loops of the PZT thin films are shown in Figure 3. It can be seen that the typical P-v hysteresis loop of the PZT thin films showed in the crystalline films. The amorphous films did not have ferroelectric properties. The result is consistent with XRD spectra.

![Figure 3 P-V hysteresis loops of the amorphous and crystalline PZT thin films](image)

3.3 EXAFS Analyses
The EXAFS measurements in fluorescence mode of Zr K-edge (17998.0eV) of the PZT thin films samples were performed at the 1W1B beam line in BSRF.

![Figure 4 Experimental and calculated k^3χ(k) functions (a, c) and their Fourier transformation (b, d) of the PZT thin films (Zr K-edge)](image)
Figure 4 shows the experimental and calculated $k^3 \chi (k)$ functions and Fourier transform curves obtained from the Zr K-edge EXAFS spectra. As can be seen, the first peaks of the Fourier transform curves of amorphous and crystalline PZT thin films between 1 and 2.2Å present a high intensity and mainly formed by contributions from single path Zr-O. The coordination number N and the nearest Zr-O bond length R were evaluated via best fit of $k^3 \chi (k)$, calculated by inverse Fourier transform. According to the calculation, the Zr-O distances of the crystalline samples are shorter than in the amorphous samples. However, the oxygen coordination numbers are nearly the same. Local structure parameters of PZT from Zr K-edge EXAFS spectra are shown in Table 1.

In addition, other intense peaks between 2.2 and 4Å are also observed in the Fourier transform curve of the Zr K-edge EXAFS spectra of the crystalline samples. It does not shown in the Fourier transform curve of the amorphous samples (Fig.4(b) and (d)). In the amorphous PZT thin films only one oxygen coordination shell can be found in the EXAFS spectra at the Zr K-edge. According to calculations, these peaks are mainly formed by contributions from single scattering path Zr-Pb and from some multiple scattering paths. It means that significant differences of the local structure exist between the amorphous and crystalline PZT thin films.

| Table 1. Local structure parameters of PZT thin films from Zr K-edge EXAFS spectra. |
|---|---|---|
|   | R (Å) | N | σ^2 (Å) |
| crystalline | Zr-O | 2.09±0.03 | 6 | 0.00686 |
|    | Zr-Pb | 3.12±0.05 | 4 | 0.00625 |
|    | Zr-Pb | 3.85±0.06 | 4 | 0.00286 |
| amorphous | Zr-O | 2.14±0.02 | 6.1±0.2 | 0.00958 |

4. Conclusions
We measured Zr K-edge EXAFS spectra for amorphous and crystalline PZT thin films. The structure differences were discussed from the viewpoint of local structure. According to the results, the Zr-O distances of the crystalline samples are shorter than in the amorphous samples whereas the oxygen coordination numbers are nearly the same. Other intense peaks between 2.2 and 4Å are only observed in the Fourier transform curve of the crystalline samples.

According to the comparisons between the EXAFS spectra at the Zr K-edge, the local structure of PZT thin films of different crystallinities are obviously different. The analysis of our EXAFS spectra can be consistently interpreted with the result of XRD, and demonstrated that the ferroelectric property change of PZT films are closely related to the structure changes.

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