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Growth mechanism and characteristics of $Pb(Zr_{0.52}Ti_{0.48})O_3$ films prepared with alternate deposition of $PbZrO_3$ and $PbTiO_3$ layers

JINGSONG LIU, SHUREN ZHANG, WENNAN YOU, JUNLIAN ZHOU
School of Microelectronics and Solid-State Electronics, University of Electronic Science and Technology of China, Chengdu, People's Republic of China
E-mail: SRZHANG@uestc.edu.cn

Lead zirconate titanate (PZT) thin films, especially the $Pb(Zr_{0.52}Ti_{0.48})O_3$ film near the morphotrophic boundary (MPB), have been extensively studied for a variety of applications involving nonvolatile ferroelectric random access memories (FRAM). However, the high temperatures in fabrication processing become the choke point for development of ferroelectric memories. To reduce the processing temperatures, understanding the growth mechanism of perovskite PZT films will be of vital importance. Although there are many studies reported to reduce the processing temperature, a few mechanisms have been concerned [1, 2]. Recently, Takashi Iijima *et al.* reported they prepared $Pb(Zr_{0.5}Ti_{0.5})O_3$ films by the following routes: the repeated operations involved the spin coating of $PbZrO_3$ (PZ)/$PbTiO_3$ (PT) solutions and pyrolysis of them at 400 °C, then a diffusion process was carried out at 500 °C for as long as 14 days and the final PZT film was obtained after firing at 700 °C [3]. In this letter, we report on a modified sol-gel technique to prepare $Pb(Zr_{0.52}Ti_{0.48})O_3$ films, in which PT and PZ layers were individually heated at 600 °C and then PZT films were formed without post-annealing. At the same time, the growth mechanism of the as-deposited film is discussed.

The PZ and PT precursor solutions with a concentration ratio of 52/48 were prepared from lead (II) acetate trihydrate, zirconium (IV) *n*-propoxide and tetrabutyl titanate (IV). Methanol and tetrahydrofuran were used as the solvent. The first layer deposited on the $Pt/Ti/SiO_2/Si$ substrates was PT layer, which was spin-coated at 6000 rpm and then heated from room temperature to 600 °C in 6 h. The second layer deposited on the PT layer with the same routes was PZ layer. The volume of precursor solutions for each layer was 30 microliter controlled by micropipet. The alternate deposition of the two layers was repeated until the total thickness of 400 nm was reached. The final film did not experience thermal treatments anymore.

Fig. 1 shows the X-ray diffraction (XRD) pattern of the as-deposited PZT film. Highly (110) orientation of a single perovskite phase was observed and no pyrochlore phase was detected. The $Pb(Zr_{0.52}Ti_{0.48})O_3$ perovskite-type phase of the as-deposited film was identified by the indexed planes in Fig. 1 according to the proclamation of Kakegawa. K [4]. Such analytical results suggest that the $Pb(Zr_{0.52}Ti_{0.48})O_3$ film can be prepared by the modified sol-gel technique mentioned above. The $Pb(Zr_{0.52}Ti_{0.48})O_3$ film may be formed through the solid phase reactions as following: $0.52PbZrO_3 + 0.48PbTiO_3 \rightarrow Pb(Zr_{0.52}Ti_{0.48})O_3$, which is initiated at the temperature as low as 600 °C. The PZ/PT molar-ratio was decided by the volumes and concentrations of PZ/PT precursor solutions.

Fig. 2 displays the surface micrographs of certain layers observed by atom force microscopy (AFM) just after the deposition of those layers. Fig. 2a shows that of the first layer, that is, only the PT layer. Discrete islands consisting of numerous columnar grains in the size of about 15 nm are observed. It is obvious that the columnar grains are the PT crystallites. Fig. 2b shows the surface micrograph of the second layer, which actually is the PZT layer synthesized from PT and PZ. Comparing with the first layer, the surface micrograph of the second layer exhibits general continuous islands containing a few of columnar bigger grains. Considering the high crystallization temperature of the PZ (about 1000 °C) and the PZT (about 700 °C), the low crystallization temperature of 600 °C in our work suggests that the PT layer deposited at first presents the perovskite nuclei for the crystallization of PZT by the formation of PT crystallites, which results in the decrease of crystallization potential barriers of PZT. Fig. 2c shows the surface micrograph of the final film. Instead of islands and columnar grains, large and densely stacked grains were observed from Fig. 2c. Surveying the whole course, an island-column hybrid growth mechanism can be derived from the variations of the surface micrographs.

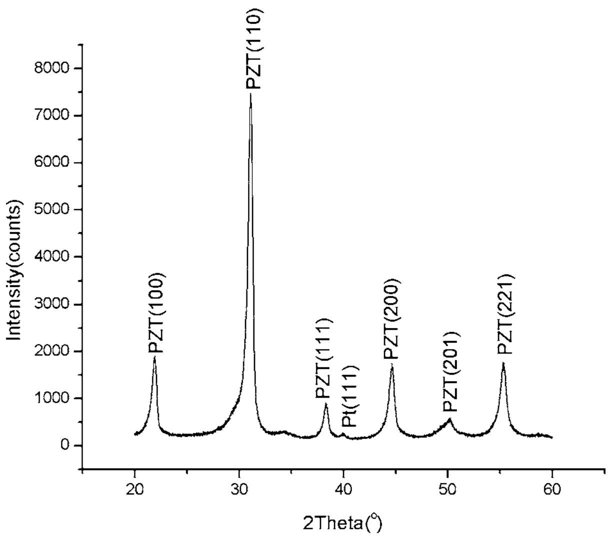

Figure 1 XRD pattern of the as-deposited PZT film.

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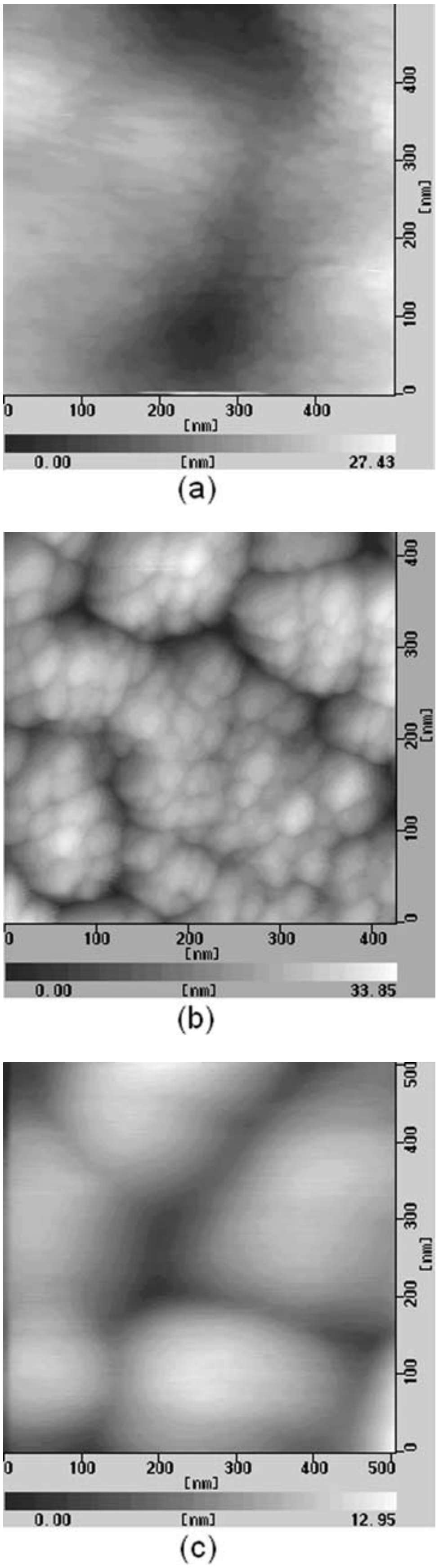

Figure 2 AFM surface micrographs of (a) the first layer, (b) the second layer and (c) the final film.

Depth profiles of constituent elements in the PZT films were performed by X-ray photoelectron spectroscopy (XPS). Typical results are shown in Fig. 3. The enrichment of lead and the deficiency of oxygen, zirconium, and titanium at the surface were observed. Dana *et al*. explain this behavior as the evaporation of Pb—O compounds and the formation of Ti—O and Zr—O compounds [5]. Except for the enrichment of lead, carbon was detected at the surface of the films, which exists in the form of hydrocarbons absorbed by the surface of the films. On the other hand, the peak areas of Pb, Zr, Ti and O elements become uniform in the bulk film as a function of depth. At the same time, the carbon peak disappeared in the bulk film. The composition of Pb, Zr, Ti and O elements in the bulk films is approximately stoichiometric and the Zr/Ti ratio is calculated to be 1.12 (near to 53/47).

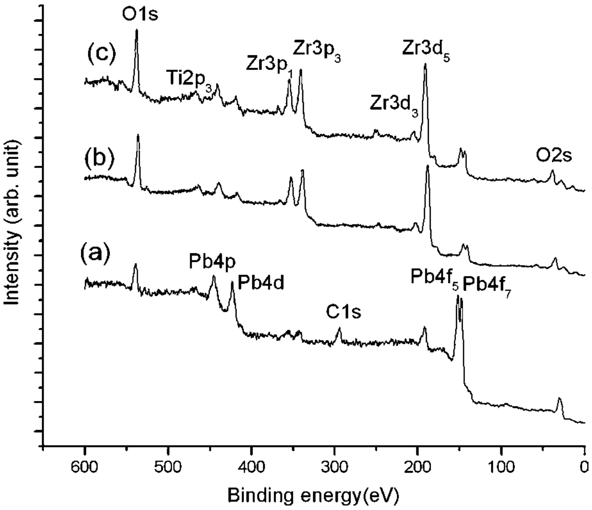

Figure 3 XPS spectra of the as-deposited PZT film: (a) without bombardment and (b) bombarded by Ar^+ for 10 min and (c) for 20 min.

Finally, ferroelectric properties of the PZT films were measured using RT66A ferroelectrics test system driven by the attached CHARGE program after the Au top electrodes had been deposited by ion plating. Typical hysteresis loop of the PZT films was shown in Fig. 4. An unclosed loop was observed, arising from the different top and bottom electrodes materials with the different bound charge density. The measured values for the remanent polarization ($2P_r$) and coercive field are 24 $\mu C/cm^2$ and 52 KV/cm, respectively. The

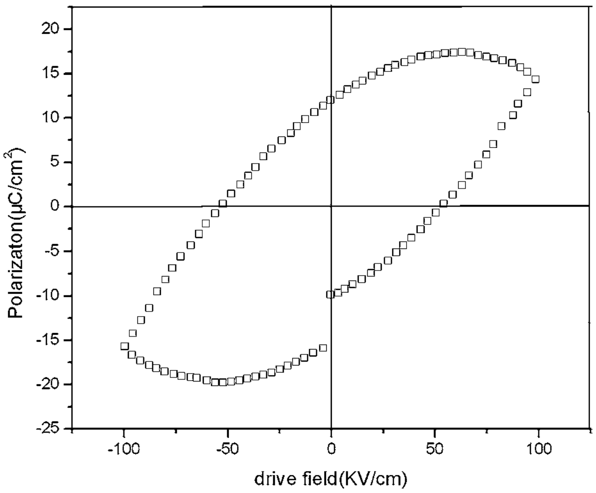

Figure 4 Hysteresis loop of the Au/PZT/Pt/Ti capacitor fabricated on the SiO_2/Si substrates.

leakage current density of the PZT films read out from the CHARGE program at an applied field of 100 KV/cm was 86 nA/cm^2.

In summary, we proposed a new sol-gel technique for preparing PZT films, in which the PZT films with a given Zr/Ti ratio can be prepared by alternate deposition of PZ and PT layers following with solid phase reactions between them. The PZT films were crystallized at 600 °C without post-annealing. An island-column hybrid growth mechanism was suggested for the PZT films prepared by this technique. The chemical composition in the bulk film is uniform as a function of depth. Judging from the measurement of ferroelectric properties, we now conceive that the use of alternate deposition of PZ and PT layers in the fabrication of PZT capacitors gives a promising application for the future FRAM.

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