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Ferroelectric properties of $Pb(Zr,Ti)O_3$ thin films prepared by low-temperature MOCVD using $PbTiO_3$ seeds

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Abstract

Low-temperature metalorganic chemical vapor deposition (MOCVD) of $Pb(Zr,Ti)O_3$ (PZT) thin films, as low as 370 °C, was successfully achieved. Influence of the crystalline nature of $PbTiO_3$ seeds on crystalline and ferroelectric properties of PZT thin films were investigated. The orientation of PZT thin films and its degree were strongly influenced by those of $PbTiO_3$ seeds. $PbTiO_3$ seeds were very useful to decrease growth temperature of PZT films. The PZT film was successfully obtained at 370 °C only when $PbTiO_3$ seeds were used, exhibiting remanent polarization ($2P_r$) of 4.2 μC/cm^2 and coercive field ($2E_c$) of 63 kV/cm.

Keywords: Ferroelectric properties; Films; MOCVD; Perovskites; PZT

1. Introduction

In the past several years, a number of researches and developments into the practical utility of ferroelectric random access memories (FeRAMs) have been reported. For memory application, development of optimum ferroelectric thin film fabrication techniques which are compatible with the latest LSI manufacturing is very important, because integration of ferroelectric thin film with silicon-based LSIs is indispensable. In particular, development of low-temperature thin film fabrication techniques is one of the most important key issues. Low-temperature growth of ferroelectric thin films can prevent the degradation of the ferroelectrics/metal/semiconductor interfaces or ferroelectrics/insulator/semiconductor interfaces caused by thermal damage and mutual diffusion.

Among the many ferroelectric thin film fabrication techniques, metalorganic chemical vapor deposition (MOCVD) is one of most promising techniques, because it can achieve low-temperature deposition of ferroelectric thin films, large-area deposition on 6–8 inch wafers and conformal deposition on three-dimensional surfaces.

Several low-temperature MOCVD methods for $Pb(Zr,Ti)O_3$ (PZT) and $(Ba, Sr)TiO_3$ (BST) have been already reported, such as (1) the seed layer method,[1–4] (2) plasma- or photo-enhanced method,[5–8] (3) gas modulation method[9,10] and (4) appropriate source materials combination method.[11,12] Among these methods, we have adopted methods of (1) and (4) for preparing PZT thin films at low growth temperatures.

In our earlier works, the effects of the growth condition of $PbTiO_3$ seeds, in particular the effects of seed thickness on crystalline and ferroelectric properties of PZT thin films were investigated and PZT films were successfully grown at 395 °C.[13]

In this report, we investigate the effects of crystallinity of $PbTiO_3$ seeds on crystalline and ferroelectric properties of PZT thin films. Difference in ferroelectric properties of PZT films with and without seeds and minimum growth temperature of PZT thin films are also discussed.

2. Experimental procedure

In our study, PZT films were grown on $PbTiO_3$ seeds. Both PZT and $PbTiO_3$ seeds were prepared by MOCVD using $(C_2H_5)_3PbOCH_2C(CH_3)_3$, $Ti(O\text{-}iC_3H_7)_4$ and $Zr(O\text{-}tC_4H_9)_4$ as precursors and O_2 as an oxidant. PZT films and $PbTiO_3$ seeds were deposited at temperatures from 340 to 450 °C and from 380 to 450 °C,

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respectively. Substrate used was $Pt/SiO_2/Si$. Thicknesses of PZT and $PbTiO_3$ seeds were 250 and 5–6 nm, respectively.

The crystalline structure was examined using the X-ray diffraction method (Phillips: X'Pert MRD). The surface morphology was observed using atomic force microscopy (AFM) (Seiko Inst. Inc.: SPI-3800N). Electrical properties were measured using a Sawyer-Tower circuit (f = 10 kHz), an electrometer (Keithley: 6517), a pulse generator (NF: 1946) and a digitizing oscilloscope (HP:54602B).

3. Results and discussion

The effect of the crystalline nature of $PbTiO_3$ seeds on crystalline structure of PZT thin films was examined. Fig. 1 shows X-ray diffraction patterns of PZT films grown at 390 °C on $PbTiO_3$ seeds with various growth temperatures. Crystalline properties of PZT films were strongly influenced by the crystallinity of $PbTiO_3$ seeds. X-ray diffraction peak intensities, in particular PZT(100) peak, increased as deposition temperature of $PbTiO_3$ seeds increased, as shown in Fig. 1.

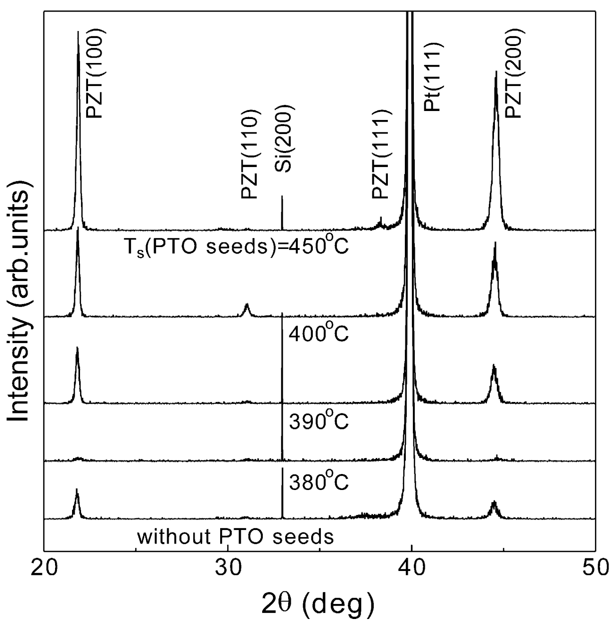

Fig. 1. X-ray diffraction patterns of PZT thin films grown at 390 °C. $PbTiO_3$ seeds were deposited at 380–450 °C.

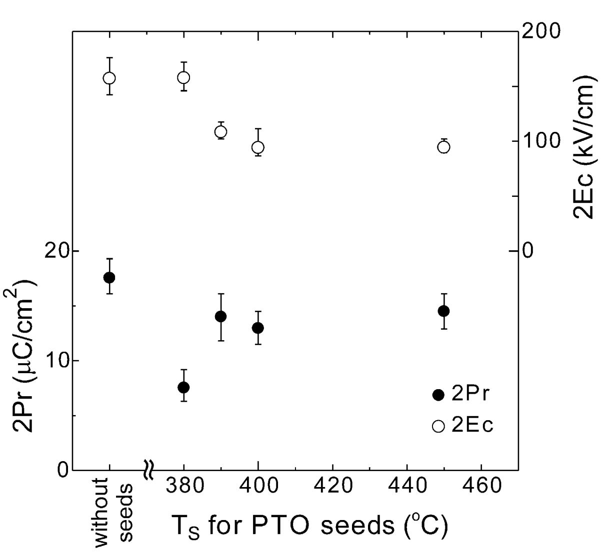

Fig. 2. Dependence of $2P_r$ and $2E_c$ of PZT thin films on the deposition temperature of $PbTiO_3$ seeds.

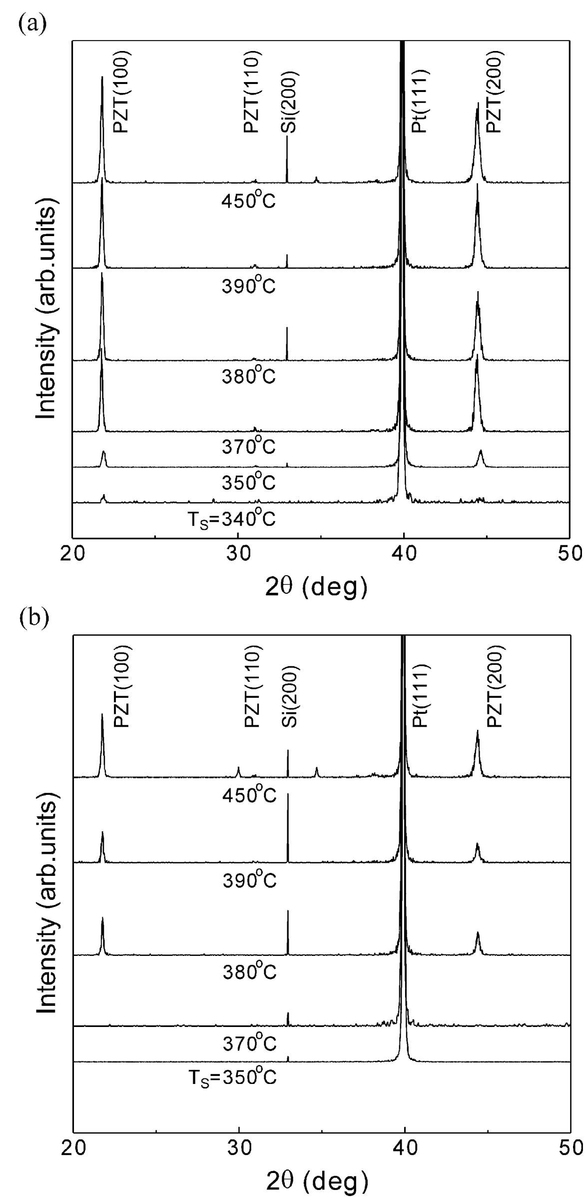

Fig. 3. X-ray diffraction patterns of PZT thin films grown at various temperatures (a) with $PbTiO_3$ seeds and (b) without $PbTiO_3$ seeds.

$PbTiO_3$(100)-peak intensity also increased as deposition temperature of $PbTiO_3$ seeds increased.[14] When $PbTiO_3$ seeds were deposited at 380 °C, they were amorphous and PZT films on the seeds were not sufficiently crystallized. These results mean that crystallinity and orientation of PZT films were effected by those of $PbTiO_3$ seeds. The PZT film without seeds had a perovskite structure, though crystallinity was poor, even when deposition temperature was 390 °C. Ferroelectric properties of PZT films coincide with the results obtained by X-ray diffraction measurements. Remanent polarization increased and coercive field decreased as deposition temperature of seeds increased, as can be seen in Fig. 2. The PZT film without seeds showed high remanent polarization ($2P_r$) and coercive field ($2E_c$) values due to its poor crystallinity and high leakage current densities.[14]

The effect of growth temperature on crystalline and ferroelectric properties of PZT films was also investigated. X-ray diffraction patters of PZT films grown at various temperatures are shown in Fig. 3. In this figure, $PbTiO_3$ seeds were deposited at 450 °C. X-ray diffraction intensity increased as growth temperature increased for PZT with and without $PbTiO_3$ seeds. As shown in Fig. 3(a), when seeds were used, the weak PZT(100) peak was observed for the PZT film grown even at 340 °C. On the other hand, when seeds were not used, no distinct perovskite peaks were observed for PZT grown at temperatures lower than 380 °C, as shown in Fig. 3(b). This result means that $PbTiO_3$ seeds played an important role of initial growth of PZT and seeds were very effective in reducing the growth temperature.

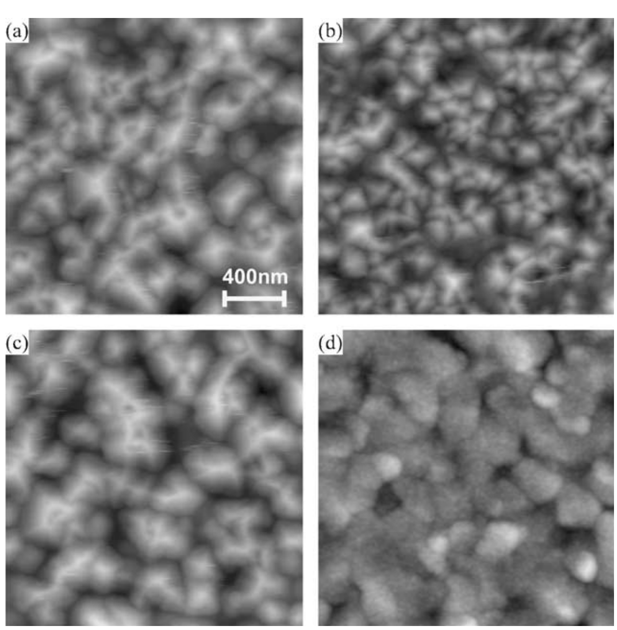

Fig. 4. AFM images of surfaces of PZT thin films grown at (a) 390 °C with $PbTiO_3$ seeds, (b) 390 °C without seeds, (c) 370 °C with seeds and (d) 370 °C without seeds.

Surface morphologies of PZT thin films grown at 390 and 370 °C with and without $PbTiO_3$ seeds are shown in Fig. 4. For PZT films with and without seeds, crystalline grains were observed and grain size of PZT film with seeds was larger than that of PZT without seeds, as can be seen in Fig. 4(a) and (b). When PZT films were grown at 370 °C, surface morphology of PZT film with seeds were quite different from PZT without seeds, as shown in Fig. 4(c) and (d). Crystalline grains were observed for PZT with seeds as shown in Fig. 4(c). Grains in Fig. 4(d) were those of Pt substrate.

Ferroelectric properties of PZT with and without $PbTiO_3$ seeds were shown in Fig. 5. With and without using seeds, PZT films grown at 390 °C showed D–E hysteresis loops, as shown in Fig. 5(a). When PZT films were grown at 370 °C, drastic difference in D–E

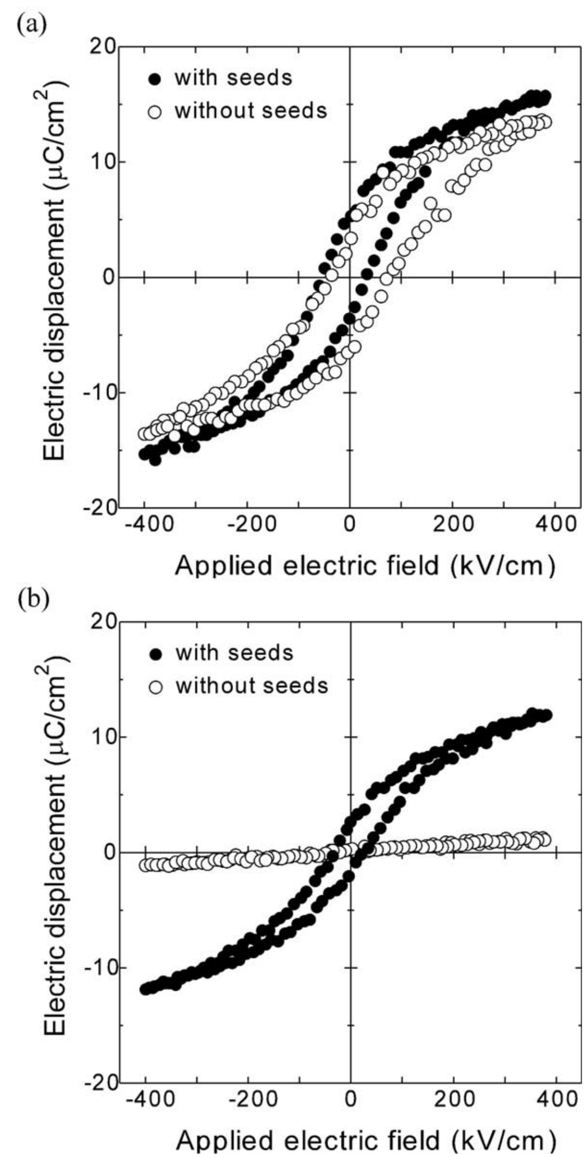

Fig. 5. D–E hysteresis loops of PZT thin films grown at (a) 390 °C with and without seeds, and (b) 370 °C with and without seeds.

hysteresis loops for PZT films with and without $PbTiO_3$ seeds was observed, as shown in Fig. 5(b). The PZT film with seeds grown even at 370 °C showed polarization hysteresis loop, exhibiting remanent polarization ($2P_r$) of 4.2 μC/cm^2 and coercive field ($2E_c$) of 63 kV/cm. On the other hand, the PZT film without seeds did not show ferroelectric hysteresis loop. This result corresponds with that of X-ray diffraction measurements. Generally, PZT films without seeds showed larger leakage current densities than PZT films with seeds.[14]

4. Conclusions

We investigated the effects of $PbTiO_3$ seeds and their crystalline nature on crystalline structure, growth temperature, surface morphology and ferroelectric properties of PZT thin films. PZT films with high-temperature-deposited $PbTiO_3$ seeds showed crystalline and ferroelectric properties superior to those of PZT films with low-temperature-deposited seeds. $PbTiO_3$ seeds were useful in decreasing growth temperature of PZT thin films and PZT films with seeds grown even at 370 °C showed ferroelectric hysteresis loops, exhibiting remanent polarization ($2P_r$) of 4.2 μC/cm^2 and coercive field ($2E_c$) of 63 kV/cm.

Acknowledgements

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