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A systematic study on the growth of PZNT films by LPE method

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Liquid phase epitaxy (LPE) was used to grow $(1-x)\mathrm{Pb(Zn_{1/3}Nb_{2/3})O_3}-x\mathrm{PbTiO_3}$ (PZNT) films on different substrates. The morphology and epitaxial relationship of PZNT films with these substrates were investigated by optical microscopy and XRD. It was found that PZNT grains on planes of (001) MgO, (001) $\mathrm{LaAlO_3}$ (LAO) and two specific planes of $\mathrm{SrTiO_3}$ (STO), i.e. (110) or (111), distribute randomly and show no evident epitaxial relationship with these substrates. However PZNT films on (001) STO substrates exhibit very encouraging in-plane epitaxial relation: $[100](001)_{\mathrm{PZNT}}$ // $[100](001)_{\mathrm{STO}}$, which was observed directly by OM, SEM and further confirmed by X-ray diffraction. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Relaxor ferroelectric $(1-x)\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}-x\mathrm{PbTiO_3}$ (PMNT) and $(1-x)\mathrm{Pb(Zn_{1/3}Nb_{2/3})O_3}-x\mathrm{PbTiO_3}$ (PZNT) have attracted much attention recently due to their outstanding performances, e.g. an extraordinary large piezoelectric strain (>0.6%), piezoelectric constant (d_{33} >2500 pC/N), and a very high electro -mechanical coupling factor (k_{33} >90%) [1–9]. However, pure perovskite PMN and PZN are difficult to achieve because of their relatively poor stability. Compared with PMN, perovskite phase PZN has a more excellent piezoelectric property, nevertheless a worse stability due to a smaller tolerance factor and electronegative difference of zinc ion ($\mathrm{Zn^{2+}}$) than those of magnesium ion ($\mathrm{Mg^{2+}}$) [10]. Pyrochlore phase appears inevitably when we expect to fabricate PZN single crystals or PZN films. By introducing a propriety of lead titanate (PT) or lead zirconate titanate (PZT) as stabilizer, a variety of synthesis techniques have been used to fabricate PZN single crystals and thin films [6–9, 11, 12].

The PZNT film grown by the liquid phase epitaxy (LPE) method may be an alternative to the single crystal and thin film for its applications as actuators, capacitors and sensors. Compared with the single crystal growth, the growth time for the LPE process is rather short. Therefore, the chemical compositions and physical properties of the as-grown PZNT films may be more homogeneous. Compared with these thin film synthesis techniques, it is relatively easier to acquire several microns thickness layer with quasi single crystallinity. Additionally, an approximate equilibrium state is usually introduced for the LPE process so the growth process may be more steadily. Other phases may not be induced because of a rather narrow range temperature adopted.

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By using sol-gel, perovskite PMNT films on the (001) $LaNiO_3$ (LNO) substrates and PZN-PZT films on the (111) self-textured $Pt/Ti/SiO_2/Si$ substrates have been developed successfully by Shyu and Fan, respectively [9, 13]. In our previous work, we reported the preliminary results concerning the LPE growth of PZNT films on (001) STO substrates [5]. In this paper, we will make a systematic study on different phases and their epitaxial relationships with substrates by optical microscopy (OM), scanning electron microscopy (SEM) and X-ray diffraction for the liquid phase epitaxially grown PZNT films. In order to seek the most suitable substrate, (001) oriented MgO, LAO and different oriented STO substrates will be used for the liquid phase epitaxy growth of PZNT in this work. The epitaxial relationships between the as-grown films and substrates are to be investigated.

2. Experimental

The powders of PbO, ZnO, TiO_2 and Nb_2O_5 according to the chemical stoichiometric proportion of $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ were used for the formation of the perovskite PZNT. The mixtures were firstly sintered at 900°C for 4 h in an alumina crucible. Then they were mixed with PbO in the ratio of PZNT:PbO = 1:1 in mole percentage and pressed into pellets of approximate 20 mm in diameter after a sufficient blend. Subsequently, these pellets were put into the crucible as starting substance for the LPE growth experiments of the PZNT films on different substrates, such as MgO, LAO and STO. These substrates had been optically polished with their surface roughness less than 15 Å and orientation tolerance less than 0.5 degrees. The temperature was controlled by a thermocouple located at the bottom of the crucible and measured accurately by a thermocouple near the surface of the liquid before dipping. The detailed LPE process basically consisted of: (1) heating to 1150°C within 2 h in air and dwelling for several hours until achieving a complete melt; (2) cooling down to the temperature of 1075°C at a rate of 3∼5°C/min; (3) vertically or laterally dipping these substrates into the solution for 15 s with an approximately pulling rate of 2 mm/s for the LPE growth of PZNT91/9; (4) suddenly withdrawing about 10 mm above the liquid surface and rotating to throw away the flux on the film.

The morphologies and different phases of these LPE growth samples were observed by using an OLYMPUS BX51 M Optical Microscopy (OM). The orientation relations between the PZNT films and different substrates were analyzed by OM and a D8 Advance BRUKER-AXS (Cu, K_α) X-ray diffractometers. Further investigations on these morphologies and semi-quantitative microanalysis on the compositions of different phases, e.g. PZNT perovskite phase, pyrochlore phase and PbO whiskers, were performed by employing a PHILIPS515 scanning electron microscopy (SEM) with an energy dispersive analysis of X-rays (EDAX) detecting unit.

3. Results

3.1. PZNT growth on (001) MgO substrates

Fig. 1a shows the preliminary optical microscope observation results of PZNT growth at 1075°C from the melt solution on the (001) MgO substrates. The square-shaped grains of several microns in size are perovskite phase PZNT crystals. They distributed randomly on the surface of the substrates. It can be concluded that spontaneous nucleation of these grains occurred instantaneously when the MgO substrate was dipped into the melt. No markedly change happens when we vary the temperature in a wide range from 1050°C to 1080°C and the melt composition with PbO mole ratio from 40% to 60%. Fewer and smaller sized grains will be observed on the MgO substrate when we raise the temperature higher than 1080°C. Meanwhile,

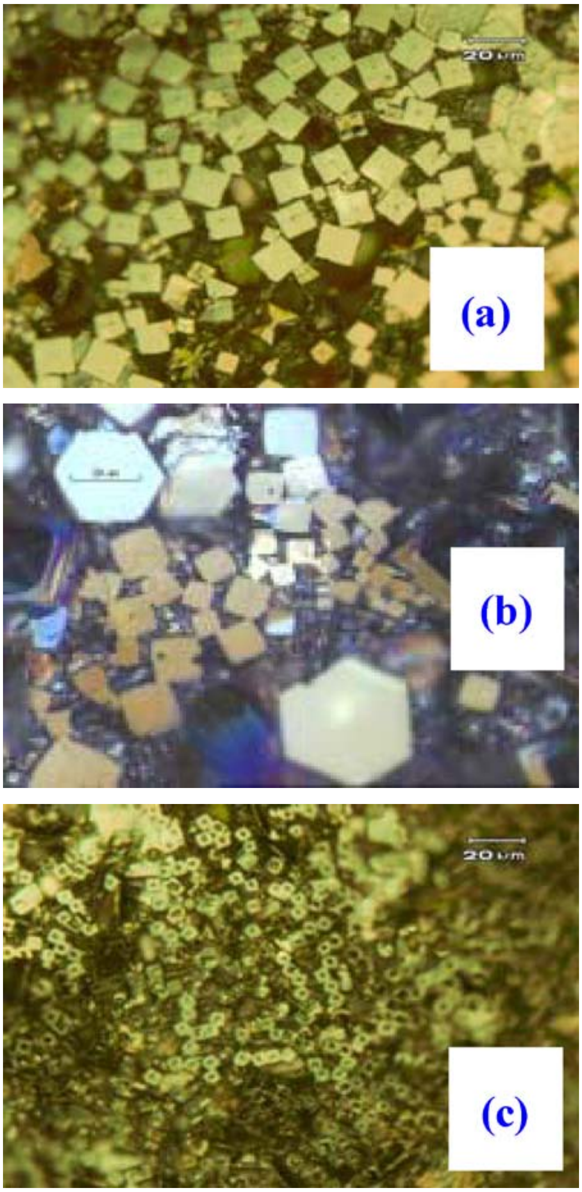

Figure 1 Optical microscope images showing morphologies of PZNT growth on (001) MgO (a), (001) $LaAlO_3$ substrate (b) and STO substrate (c).

few pyrochlore and a mass of flux can be seen on its surface.

3.2. PZNT growth on (001) $LaAlO_3$ substrates

Fig. 1b is an optical image displaying the results of PZNT grown on the (001) $LaAlO_3$ substrate. The growth conditions are similar to those of LPE growth on MgO substrates described above. The square-shaped grains spontaneously nucleated randomly on its surface when the LAO substrate was in contact with the melt. The flux covers a majority of the substrate surface, which is similar to the Fig. 1a. Nevertheless, a large amount of pyramid-shaped pyrochlore phase appears on the surface, which is different from that when using MgO as substrate. This may be partially accounted for the introducing of MgO, which can stabilize the perovskite phase PZNT. It was reported that the appropriate addition of MgO or ZnO will benefit to the formation of perovskite phase PZNT [12, 14]. When the MgO substrate is applied for the LPE growth of PZNT, corrosion of the substrate was found by using an optical microscope. This maybe caused by the melting back and partial dissolution of MgO into the surrounding melt. It will act as the same role as the addition of MgO and restrain the pyrochlore phase from being formed. The melting back of LAO may also inevitably occur when it was dipped into the melt because the elements of the substrates completely differ from those of the melt. However, the stabilizing effect on the perovskite phase does not happen in this case.

3.3. PZNT growth on (110) or (111) $SrTiO_3$ substrates

Fig. 1c shows the morphology of PZNT by LPE growth on (110) STO substrate observed by an optical microscope, which is almost the same to that on the (111) STO substrate. Perovskite phase PZNT with island shape distributes almost randomly and the flux accompanies those PZNT grains on the surface of the (110) STO substrate. The pyramid shaped pyrochlore can hardly be seen. This can also be interpreted by the melting back phenomenon and the stabilizing effect of STO on the perovskite structure, which is suggested by Wakiya *et al*. [10]. According to his work, 9–10% additives of $SrTiO_3$ in mole ratio into PZN can stabilize the perovskite structure.

3.4. PZNT growth on (001) $SrTiO_3$ substrates

Fig. 2a is an optical image showing the perovskite phase PZNT film with good alignment on the (001) STO substrate. The square-shaped perovskite phase PZNT islands stand out independently on the surface of the STO substrate. The thickness of the film dipped for 15 s is about 2∼3 microns, as can be seen from Fig. 2b. Fig. 3 is a SEM image displaying the morphology of PZNT film on the (001) STO substrate. Two different phases have been observed on its surface. One is perovskite PZNT, the other is the unwanted pyrochlore phase. It is found that the perovskite shows a good alignment on the (001) STO substrate, which implies an epitaxial growth of PZNT on its surface. However, most of PZNT grains nucleate heterogeneously on the (001) STO independently, the coalescence of PZNT grains during the growth process sporadically happens. It covers the majority of the STO surface. From Fig. 3, we can find that the pyrochlore also has an evident epitaxial relationship with the (001) STO substrate. This intermediate pyrochlore phase will not only introduce a second phase unexpected into the PZNT film, but also baffle the coalescence of the PZNT grains, and finally make a great contribution to resulting in the Volmer-Weber growth instead of Frank-van der Merwe growth mode. So it will be catastrophic to the growth for high quality PZNT film. Both phases were confirmed by the energy dispersive spectrum (EDS) analysis. As listed in Table I, one compound has an approximate composition to the nominal composition of PZNT, which is corresponding to the square-shaped grains in Fig. 3a. Completely different from this, the other compound is basically composed of lead and niobium with the atomic ratio corresponding to 6.8:2.5 approximately. It is suggested that an improvement should be made to suppress the effects caused by pyrochlore phase.

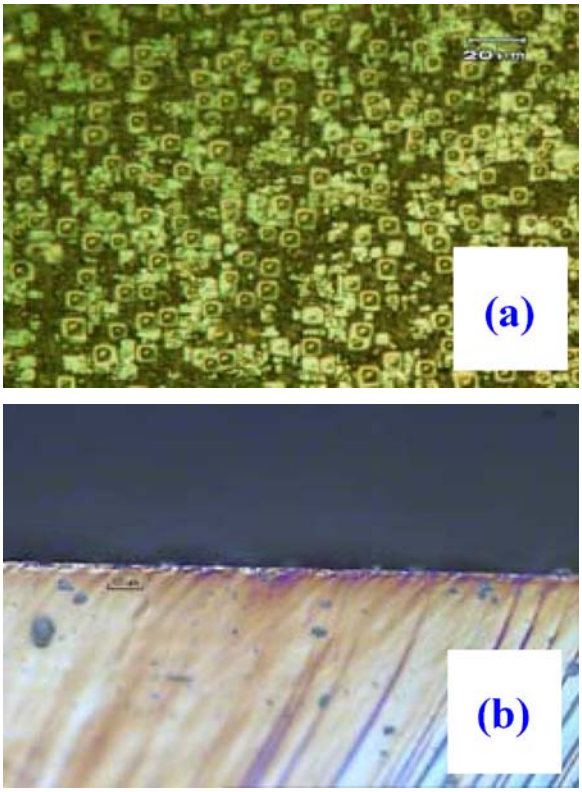

Figure 2 Optical microscope images showing morphology (a) and thickness (b) of PZNT film grown on the (001) STO substrate.

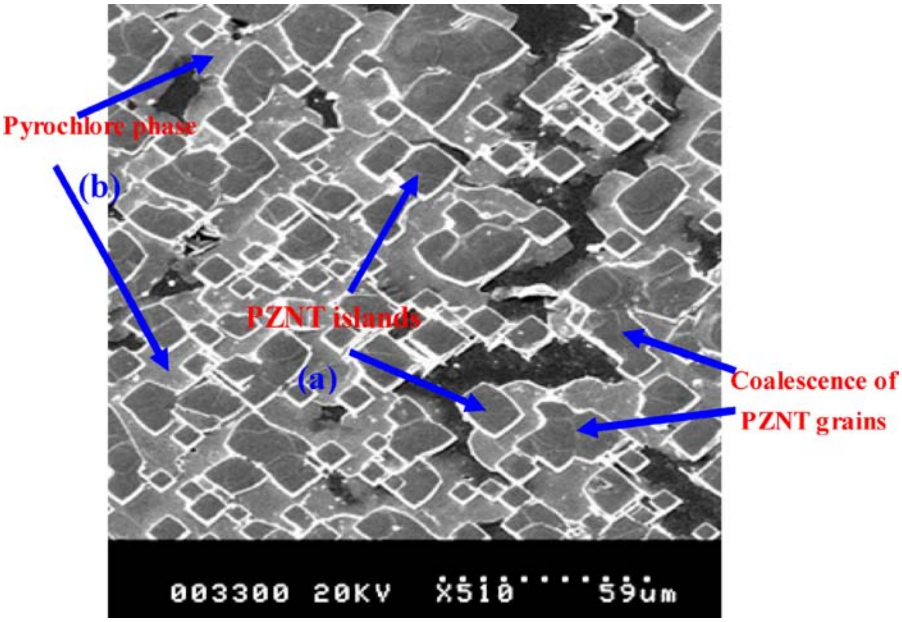

Figure 3 SEM image showing a general morphology of PZNT film on (001) STO substrate.

4. Discussion

In order to make clear the epitaxial relation between the PZNT film and (001) STO substrate, X-ray diffraction was carried out. Fig. 4a shows the 2θ X-ray (Cu, K_α) scanning of the PZNT film grown by the LPE method. Compared with the XRD pattern of the PZNT powders, only two strong peaks appear experimentally, namely, (002) peaks of the perovskite PZNT and STO, respectively. Additionally, a weak peak corresponding to the (002) peaks of PbO also occurs, which confirms that the PbO may have a special epitaxial relationship with the (001) oriented substrate. It can also be found that the XRD peak of PZNT $\{002\}$ is very close to the STO $\{002\}$ peak, which is consistent with the similar lattice constants between them [15, 16]. No other incidence direction of the PZNT is found in our experimental range, so it can be concluded eventually that the as-grown PZNT LPE film should have a regular epitaxial orientation with $(001)_{\mathrm{PZNT}}$ // $(001)_{\mathrm{STO}}$, namely PZNT grows epitaxially on the (001) STO substrate.

Further investigations on the orientation relationship between the grown PZNT film and (001) STO substrate have been performed by X-ray diffraction pole figures (Cr, Kα), which were obtained by Φ-scan method. The position of the detector is determined by 2θ. For [110] PZNT in Fig. 4b, the two-theta is corresponding to 47 degree and for [110] STO in Fig. 4c, the two-theta is corresponding to 49 degree. The sample's position is confirmed by ω, χ and Φ. In this experiment, Chi is fixed at 54.47 degree, while Omiga, i.e. half of the two-theta, is 23.5 degree (for PZNT) and 24.5 degree (for STO), respectively. When the Phi is changed from 0 degree to 360 degree, the data collection was carried out every 5 degree. After that, the pole figure can be calculated according to the 72 groups of data. No distinctive difference has been found between the two pole figures except for the small deviation along the [110]. It is evident that the PZNT film and the STO substrate have an epitaxial relationship of [100] $(001)_{\mathrm{PZNT}}$//[100] $(001)_{\mathrm{STO}}$ when we combine the results obtained by the two-theta scanning and pole figure X-ray diffractions. PZNT and STO have the same perovskite structure and similar lattice constant, so the interfacial free energy between them should be low, which may make it easy for the PZNT film to grow on the STO substrate with a certain epitaxial orientation.

To realize the epitaxial growth on a substrate, the total energy of the described system should be taken into account. Generally, the total energy difference can be expressed by:

$$\Delta G = \Delta G_v + \sigma_{s-n} + \sigma_{n-v} - \sigma_{s-v}$$

where ΔG_v is the bulk Gibbs free energy, σ_{s-n} is interfacial energy between the substrate and nucleus, σ_{s-v} is the surface free energy between the substrate and vapor, and σ_{n-v} is the surface free energy between the nucleus and vapor. For the initial nucleation stage of LPE growth on the substrate, σ_{s-n} makes great contribution to the total free energy of the nucleus. The substrate-nucleus

TABLE I Composition of different phases observed in LPE experiments being analyzed by EDS

	Perovskite PZNT (a)		Epitaxial pyrochlore (b)	
Phase	1	2	1	2
Composition (at%)				
Pb	48.59	49.29	68.43	68.19
Nb	28.44	30.83	25.36	25.75
Zn	17.94	13.88	2.61	2.97
Ti	5.04	6.00	3.49	3.20

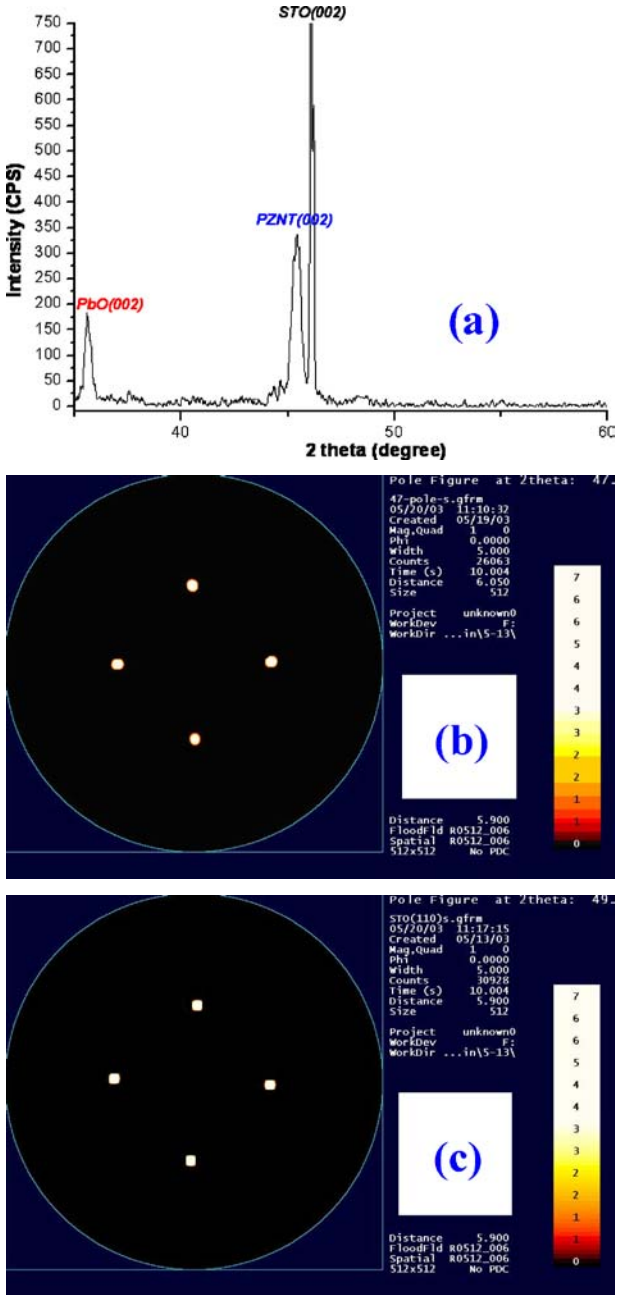

Figure 4 X-ray diffraction (2θ-scanning, K_α, Cu) (a), and X-ray (K_α, Cr) pole figure patterns showing the orientation relationship between the as-grown PZNT film (b) and (001) STO substrate (c).

interfacial energy may come mainly from the chemical bonding energy and the atomic column force between the substrate and the nucleus, which is greatly influenced by the substrate geometry and morphology. The flat and lower-energy face will be the preferred nucleation because of relatively lower σ_{s-n} consumed. While the nucleation happens on the rough substrate surface, the nucleus has to contact with some substrate faces with high free energy, which will largely increase the σ_{s-n} value [17]. In our study, the substrates are optically polished and well washed in ethanol, i.e. the interfacial energy part related to the substrate surface roughness is minimized. So the nucleation depends mainly on the bonding energy between the as-grown film and the substrate. During this stage, the bonding energy is greatly determined by the geometric lattice parameters, i.e. lattice mismatch. Table II shows the substrates used in these work, together with the lattice constants, thermal expansion coefficients, melting points of the substrates and PZNT. All the substrates can be classified into the same cubic crystal system to the film at a high temperature, however there is still different to some extent for MgO. It is just a simple cubic structure that could be interpreted as the filling of magnesium ions to the void of oxygen ions stacking. However, the growth mechanism of perovskite could be explained from the viewpoint of assembling of [BO6] octahedral growth unit into $(111)_{\text{cub}}$ interface because the lowest bonding energy is consumed on this interface [18, 19]. The periodicity of the atoms on a substrate surface is the template for the epitaxial growth of the film material [19]. When the substrate having different structure to the film, e.g. when MgO substrate, contacts with the PZNT melt, spontaneous nucleation rather than epitaxial nucleation usually happens, as can be seen from Fig. 1a. Even the substrate has the same structure to the film, direct epitaxial growth is still difficult because their periodicity is generally not identical, i.e. their lattice parameters are different. Langjahr *et al* have made a relatively systematic study on the effects of lattice mismatch accommodation in perovskite films on substrates [19]. The lattice mismatch may induce strain either compressive or tensile. The in-plane strain is given by

$$e_{//} = -\frac{d_f - d_s}{d_f} = -\varepsilon_s \frac{d_s}{d_f}$$

where $e_{//}$ is the strain in directions parallel to the interface, ε_s is the lattice mismatch strain, d_f and d_s represent the lattice parameters of the film and substrate, respectively. In the case where mismatch is very small, it can be considered as a nearly homogeneous epitaxial growth. The film grows directly layer-by-layer, i.e. it grows in the Frank-van der Merwe mode and some dislocation forms to release the strain. As a rule, a highly oriented film with quasi-single crystalline structure may be expected to grow in this case. When the mismatch become larger, the epitaxy growth in the mode of Frank-van der Merwe is impossible to happen, the heterogeneous epitaxy growth in a Volmer-Weber mode appears instead. As for the STO substrate, the lattice mismatch strain is approximate 0.036, with a certain extent deviation to the mismatch at a higher temperature. So it may be deduced that the Frank-van der Merwe epitaxial growth mode is hard for PZNT film on STO substrate. In the case where the mismatch is very large, spontaneous nucleation may take place instantaneously. In this case, the drive force for spontaneous nucleation is very close to that for heterogeneous nucleation, so when the supersaturation is higher enough, spontaneous nucleation will take place predomi-

TABLE II Parameters of MgO, LAO, STO and PZNT

Crystals	Crystal system (at growth Temperature)	Crystal structure	Lattice constant (Å)	Melting point (°C)	Thermal expansion ($\times 10^{-6}$/K)
MgO	Cubic	NaCl	4.216	2852	12.8
$SrTiO_3$	Cubic	Perovskite	3.905	2050	10.4
$LaAlO_3$	Pesu-cubic	Perovskite	3.821	2100	9.2
PZNT	Cubic	Perovskite	4.047 [15]	~1268 [20]	

nantly. For PZNT film on LAO substrate, ε_s is about 0.059, which is much larger than that on the STO substrate. Spontaneous nucleation happens and the PZNT polycrystals distribute randomly on LAO surface, as shown in Fig. 1b.

5. Conclusions

Liquid phase epitaxy growth of PZNT film on different substrates was studied. Randomly distribution of PZNT islands was found when MgO and $LaAlO_3$ were adopted as substrates. No epitaxial relation was detected on the STO (110) and (111) plane as well. However, it was found interestingly that the PZNT film and the STO substrate have an epitaxial relationship of [100] $(001)_{PZNT}$//[100] $(001)_{STO}$ by X-ray diffraction analysis. Effects of substrates on the growth have been discussed in view of their lattice mismatch. It can be concluded that spontaneous nucleation happens when MgO and $LaAlO_3$ were used as substrates due to a very large lattice mismatch introduced and heterogeneous nucleation usually happens when the (001) STO substrate with a mismatch strain of approximately 0.034 is applied. However, it is still difficult for these PZNT grains to coalesce with each other on this kind of substrate directly. A buffer layer or a film seed layer with smaller lattice mismatch is suggested to acquire a higher quality and complete PZNT film for applications.

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References

1. B. J. KIM, S. M. CHO, T. Y. KIM and H. M. JANG, *Phys. Rev. Lett.* **86** (2001) 3404.
2. B. NOHEDA, D. E. COX, G. SHIRANE, S. E. PARK, L. E. CROSS and Z. ZHONG, *Phys. Rev. Lett.* **86** (2001) 3891.
3. S. E. PARK and T. R. SHROUT, *J. Appl. Phys.* **82** (1997) 1804.
4. S. ZHANG, L. LEBRUN, D. Y. JEONG, C. A. RANDALL, Q. ZHANG and T. R. SHROUT, *J. Appl. Phys.* **93** (2003) 9257.
5. X. H. ZENG, X. YAO, Q. L. RAO, Y. L. ZHANG, J. HU and J. Y. XU, *J. Cryst. Growth.* **262** (2004) 251.
6. J. Y. XU, J. TONG, M. L. SHI, A. H. WU, S. J. FAN, *J. Cryst. Growth.* **253** (2003) 274.
7. B. J. FANG, H. Q. XU, T. H. HE, H. S. LUO and Z. W. YIN, *J. Cryst. Growth.* **244** (2002) 318.
8. W. CHEN and Z. G. YE, *J. Cryst. Growth.* **233** (2001) 503.
9. H. Q. FAN, S. H. LEE, C. B. YOON, G. T. PARK, J. J. CHOI and H. E. KIM, *J. Eur. Ceram. Soc.* **22** (2002) 1699.
10. N. WAKIYA, N. ISHIZAWA, K. SHINOZAKI and N. MIZUTANI, *Mater. Res. Bull.* **30** (1995) 1121.
11. K. HARADA, Y. HOSONO, Y. YAMASHITA and K. MIWA, *J. Cryst. Growth.* **229** (2001) 294.
12. K. HARADA, S. SHIMANUKI, T. KOBAYASHI, Y. YAMASHITA and S. SAITOH, *J. Am. Ceram. Soc.* **85** (2002) 145.
13. M. J. SHYU, T. J. HONG and T. B. WU, *Mater. Lett.* **23** (1995) 221.
14. W. F. SU, *Mater. Chem. Phys.* **62** (2000) 18.
15. Y. ABRAMOV *et al.*, *Acta Crystallogr. Sec. B: Structural Science.* **51** (1995) 942.
16. L. ZHANG, M. DONG and Z. G. YE, *Mater. Sci. Eng.* **B78** (2000) 96.
17. A. A. CHERNOV and H. J. SHEEL, **149** (1995) 187.
18. G. S. XU, H. S. LUO, W. Z. ZHONG, Z. W. YIN and K. LIU, *Acta Chimica Sinica.* **58** (2000) 172.
19. P. A. LANGJAHR, F. F. LANGE, T. WAGNER and M. RUHLE, *Acta Mater.* **46** (1998) 773.
20. Z. G. YE, M. DONG and Y. YAMASHITA, *J. Cryst. Growth.* **211** (2000) 247.

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