Japanese Journal of Applied Physics
Vol. 43, No. 8A, 2004, pp. 5409–5413
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Low-Temperature Deposition of $Pb(Zr,Ti)O_3$ Thin Films on Si Substrates Using $Ba(Mg_{1/3}Ta_{2/3})O_3$ as Buffer Layer

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(Received November 4, 2003; accepted May 7, 2004; published August 10, 2004)

Utilization of $Ba(Mg_{1/3}Ta_{2/3})O_3$ materials as buffer layers was found to achieve perovskite $Pb(Zr,Ti)O_3$ (PZT) thin film growth on silicon at very low substrate temperature (~350 °C) by *in situ* pulsed laser deposition (PLD). Formation of a continuous layer is of critical importance in order to use the $Ba(Mg_{1/3}Ta_{2/3})O_3$ materials as diffusion barriers for suppressing the PZT-to-Si interaction and, at the same time, as seeding layers for enhancing the crystallization kinetics of the PZT films. Perovskite and amorphous PZT thin films can be obtained by simply adjusting the ambient oxygen pressure or substrate temperature in the PLD process. The amorphous PZT films possess a markedly smaller optical refractive index than the perovskite ones ($n_{amorphous} = 2.02$ and $n_{perovskite} = 2.39$), such that the perovskite/amorphous PZT films are a good combination for core/cladding materials for planar optical waveguides. [DOI: 10.1143/JJAP.43.5409]

KEYWORDS: $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Pb(Zr,Ti)O_3$, Pulsed laser deposition, Optical properties

1. Introduction

Silicon dioxide materials possess excellent optical properties and have been widely used for planar optical waveguide applications, which have great potential for the miniaturization of planar light wave circuits (PLC) employed in fiber optical communication systems.[1–3] However, these materials are not tunable, which makes the design and fabrication of active components such as a digital optical switch and an electroptic modulator difficult. In recent years, ferroelectric $Pb(Zr,Ti)O_3$ (PZT) thin films deposited on single crystal substrates such as sapphire, MgO and $SrTiO_3$ have revealed excellent electroptic properties, and exhibited great potential for the fabrication of voltage tunable optical waveguides.[4–6] However, being able to grow PZT thin films on silicon-based substrates is extremely important for the purpose of integrating the active components with passive devices so as to miniaturize the planar waveguide circuits. The preparation of PZT thin films on Si substrates is not straight forward as the pyrochlore phase always forms preferentially during the heat treatment process even on sapphire single substrates.[7] Another problem frequently encountered is the mismatch in thermal expansion coefficients and interdiffusion between a PZT layer and Si substrate.[8,9] In order to overcome these problems, various kinds of buffer layers were used to suppress the interdiffusion between the PZT and Si substrate materials.[10–12] The characteristics of the PZT thin films were observed to strongly correlate with the nature and deposition parameters of the buffer layer.

In this study, we used $Ba(Mg_{1/3}Ta_{2/3})O_3$, BMT, as a buffer layer for synthesizing a perovskite PZT thin film on a silicon substrate at low substrate temperature by *in situ* pulsed laser deposition (PLD), since the BMT is dense and of perovskite structure, which can act as a diffusion barrier as well as a seeding layer. The effects of substrate temperature and oxygen pressure on the crystallinity and microstructure of the BMT and PZT thin films deposited by *in situ* PLD were investigated and the growth mechanisms of these films were discussed.

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2. Experiments

The bulk ceramic targets of the $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) and $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) materials were prepared by the conventional solid state reaction method. The perovskite PZT and BMT powders were pelletized and then sintered, respectively, at 1300°C and 1500°C for 4 h. A KrF excimer laser (248 nm) with a laser fluence of 2–3 J/cm^2 was used in the deposition of the films. The target to substrate distance was 7 cm. The BMT buffer layer was *in situ* grown on the Si substrate at 350°C for 15–60 s and the PZT films were subsequently deposited at 300°C to 400°C, with the oxygen pressure maintained at 0.1 to 0.2 mbar. An X-ray diffractometer (XRD, Rigaku DMX) was used for examining the phase constituents as well as crystallinity, whereas a scanning electron microscope (SEM, Jeol, JSM 6300) was used for examining the surface morphology of these thin films. The optical properties of the PZT films were measured by prism coupling method (Metricon Model 2010).

3. Results and Discussion

One advantage of the PLD process is that the stoichiometry of the target materials can be transformed exactly that of the thin films, provided that the energy density of the laser beams is sufficiently high. The characteristics of the thin films can thus be optimized easily by systematically adjusting the processing parameters, such as substrate temperature (T_s), ambient oxygen pressure (P_{O2}), and post annealing temperature (T_a). Figure 1(a) shows that, when *in situ* PLD is under 0.18 mbar P_{O2}, the crystalline PZT phase deposited on the BMT buffer layer starts to form at a substrate temperature as low as 350°C, whereas Fig. 1(b) reveals that, when PLD is at 350°C, the crystallinity of the *in situ* deposited films varies markedly with deposition oxygen pressure (P_{O2}). A pure perovskite phase was obtained only for the films deposited under $P_{O2} = 0.18$ mbar (curve II). An amorphous PZT phase was obtained for the films grown under high oxygen pressure ($P_{O2} = 0.20$ mbar, curve I) and a pyrochlore phase was induced, together with the perovskite PZT phase for the films deposited under low oxygen pressure ($P_{O2} = 0.15$ mbar, curve III). In the extreme case,

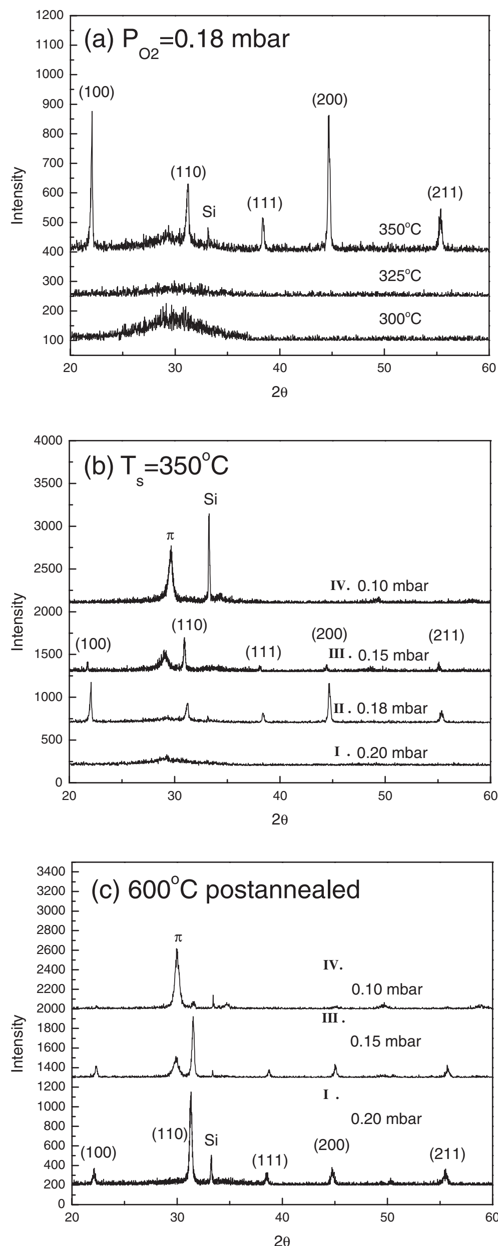


Fig. 1. XRD patterns for PZT thin films synthesized on BMT buffer layers by *in situ* PLD: (a) at 300–350°C substrate temperature ($P_{O2} = 0.18$ mbar) and (b) under 0.10–0.20 mbar oxygen pressure ($T_s = 350$°C); those for PZT films (b) postannealed at 600°C for 1 h.

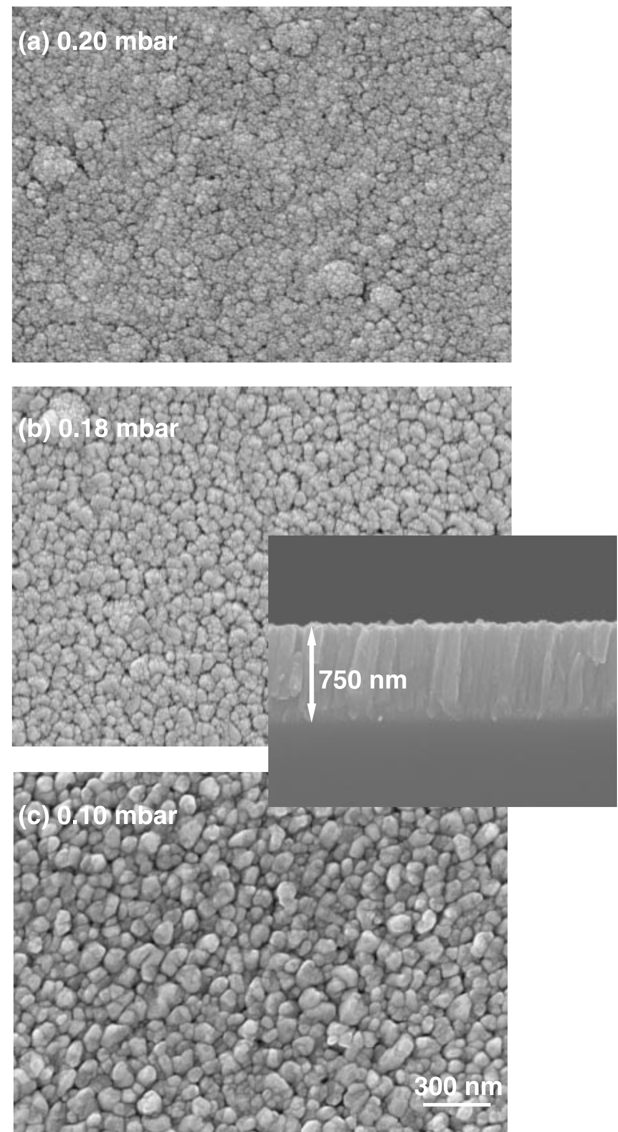


Fig. 2. SEM photographs of PZT thin films synthesized on BMT buffer layers by *in situ* PLD under ambient oxygen pressures (a) 0.20 mbar, (b) 0.18 mbar, and (c) 0.10 mbar (the inset in (b) shows the typical cross section of the PZT films deposited under the optimized condition).

only a secondary phase was observed when the oxygen pressure was too low ($P_{O2} = 0.1$ mbar, curve IV).

Figure 2 shows the microstructure of the films deposited under different P_{O2} levels. No granular structure is observed for the high-P_{O2} (0.20 mbar)-deposited PZT films, as they are amorphous [Fig. 2(a)]. The optimally synthesized PZT films, which were deposited under $P_{O2} = 0.18$ mbar, contain very fine grains [80–100 nm, Fig. 2(b)]. The cross-sectional micrograph shown in the inset in Fig. 2(b) reveals that these films contain densely packed columnar grains with very smooth surfaces. In contrast, deep grooving in grain boundaries, accompanied with large grain size, is observed for low-P_{O2} (0.10 mbar)-deposited films [Fig. 2(c)]. The grooving is possibly due to the etching effect induced by the bombardment of energetic species. These results indicate that pure perovskite PZT films can be synthesized on silicon substrates using BMT materials as buffer layers. The substrate temperature required (~350°C) in this process is significantly lower than that reported in the literature, which is of technological importance as such a low processing temperature is compatible with semiconductor device processes and opens up the potential for device applications such as embedded DRAM.

Presumably, the P_{O2} level influences the crystallinity of the PZT films via the modification of the kinetic energy of the laser-ejected species.[13,14] A high-P_{O2} level induces excess scattering of the laser-ejected species with environmental gas molecules, resulting in species with a very low kinetic energy and the laser-ejected species accumulate as amorphous if the thermal energy provided by the substrate is not sufficient to trigger crystallization. In contrast, a low-P_{O2} level results in laser-induced species with a sufficient kinetic energy, which can rearranged by themselves to crystallize. However, too low oxygen pressure (P_{O2}) produces too

energetic species, which induces bombardment damage on the previously grown crystalline films and results in the formation of the pyrochlore phase. The lower the P_{O2}, the higher the damage and the larger the content of the pyrochlore phase.

To examine the validity of the above-described mechanism for the P_{O2} effect on the growth behavior of the PZT/BMT/Si thin films, the films shown in Fig. 1(b) were postannealed at 600°C (1 h). Curve I in Fig. 1(c) shows that postannealing can effectively transform the $P_{O2} = 0.2$ mbar-deposited amorphous films into perovskite, implying that these films contain cations in an appropriate composition for PZT materials. The same heat treatment process cannot transform the 0.10 mbar-deposited films, which are pyrochlore, into the perovskite phase [curve IV, Fig. 1(c)], implying that permanent damage has been induced in these films. This is most probably the loss of Pb species induced by the bombardment of energetic species produced in a low oxygen pressure environment. Moreover, for the 0.15 mbar-deposited films, postannealing increases the proportion of the perovskite phase, but cannot completely eliminate the pyrochlore phase [curve III, Fig. 1(c)]. This once again implies that only the amorphous constituent of the films can be converted into the perovskite phase, whereas the pyrochlore constituent is stable against the heat treatment process. Restated, the oxygen pressure during deposition affects the characteristics of PZT films mainly through the modification of the kinetic energy of laser-ejected species.

The optical properties of the films deposited under different P_{O2} levels were measured by the prism coupling technique and the results are shown in Fig. 3. The refractive index is the highest ($n = 2.39$ at 632.8 nm) for perovskite films, which were deposited under the optimized condition ($P_{O2} = 0.18$ mbar, curve II), and is the lowest ($n = 2.02$) for the amorphous films, which were grown under $P_{O2} = 0.20$ mbar ambient oxygen pressure (curve I). The pyrochlore films deposited under $P_{O2} = 0.10$ mbar ambient oxygen pressure possess optical refractive index between two extremes ($n = 2.25$). The optical refractive index decreases as the measuring wavelength increases. The optical transmission loss (β) was estimated by the decaying rate of the prism-coupled ray, and is $(\beta)_{\text{c-PZT}} = 2.86$ dB/cm for crystalline PZT thin films and $(\beta)_{\text{a-PZT}} = 4.82$ dB/cm for amorphous PZT ones. The silent feature of these observation is that the amorphous PZT films can be used as cladding materials for a planar optical waveguide structure, which uses crystalline PZT films as core materials. Restated, the amorphous PZT/perovskite PZT can be a good combination for a planar optical waveguide material system. The low-refractive-index amorphous PZT films can be formed easily by reducing the mobility of laser-ejected species, which can be achieved by either lowering the substrate temperature or increasing the ambient oxygen pressure in the PLD process. Both approaches are compatible with the *in situ* PLD process for growing perovskite PZT thin films.

Table I. Lattice parameters of the buffer materials frequently used for growing PZT thin films on Si substrates[a)]

	a_0 (Å)	c_0 (Å)	ϵ (%)
PZT	4.036	4.146	—
BMT	4.08	—	1.5
$SrTiO_3$	3.905	—	3.0
CeO_2	5.411	—	30
MgO	4.211	—	4.3

a) ϵ: lattice mismatch $= \{(a_0)_{\text{buffer}} - (a_0)_{\text{PZT}}\}/(a_0)_{\text{PZT}} \times 100\%$

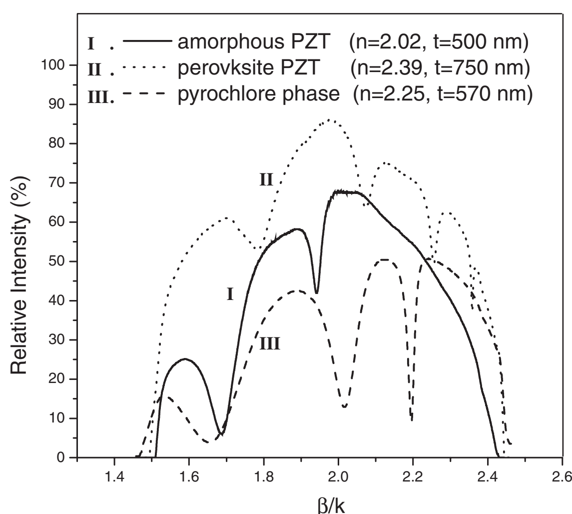
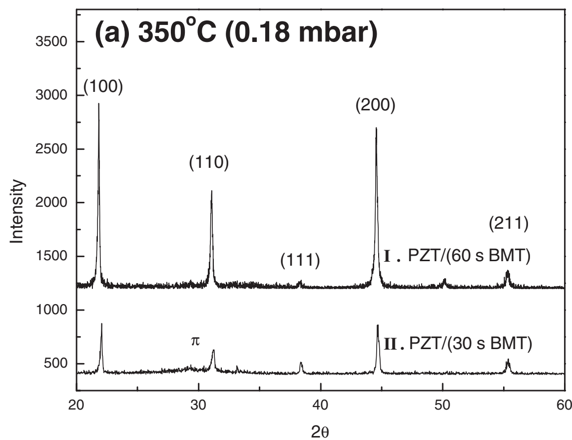


Fig. 3. Optical properties measured by the prism coupling technique of PZT thin films synthesized on BMT buffer layers by *in situ* PLD under I. $P_{O2} = 0.20$ mbar, II. $P_{O2} = 0.18$ mbar, and III. $P_{O2} = 0.10$ mbar ambient oxygen pressure.

BMT layers are excellent buffer materials, since they crystallize easily even on bare silicon substrates, forming a perovskite structured phase. Moreover, the BMT materials are of pseudocubic structure with the lattice parameter $(a_0)_{\text{BMT}} = 4.08$ Å, which is very close to the lattice parameters of PZT materials, $(a_0)_{\text{PZT}} = 4.036$ Å and $(c_0)_{\text{PZT}} = 4.146$ Å. The lattice mismatch between the BMT and PZT materials is about 1.5%, which is markedly smaller than those of the other buffer materials (Table I). Therefore, the BMT materials can not only serve as buffer layers for preventing the interdiffusion between the PZT and Si materials, but also act as seeding layers for promoting the nucleation of the crystalline phase. The perovskite PZT can thus be grown on silicon substrates at a substrate temperature as low as 350°C by *in situ* pulsed laser deposition. However, the characteristics of the BMT layer still need to be critically controlled for growing high-quality PZT thin films.

Figure 4(a) indicates that it needs at least 60 s deposition time to form a BMT layer for effectively crystallizing the PZT materials. The intensity of XRD peaks is markedly lower for the PZT films grown on a 30 s-deposited BMT buffer layer [curve II, Fig. 4(a)], implying the coexistence of the amorphous phase and the crystalline phase. In the extreme case, a very thin BMT layer completely losses the seeding effect for promoting the crystallization of PZT materials. Thus, only the pyrochlore phase is observable for the PZT films grown on a 15 s-deposited BMT buffer layer (not shown). For the purpose of understanding these phenomena, the morphology of 30 s-deposited BMT layer was further examined by SEM. Figure 4(b) shows that the BMT layer contains particulates about 20 nm in size rather



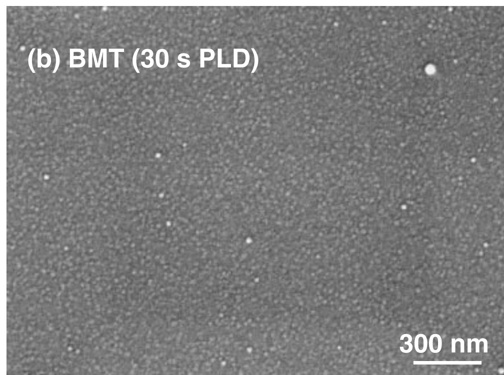


Fig. 4. (a) XRD patterns of PZT thin films synthesized on BMT buffer layers by *in situ* PLD for 30 or 60 s and (b) a SEM micrograph of a BMT layer synthesized by *in situ* PLD for only 30 s at 350°C substrate temperature.

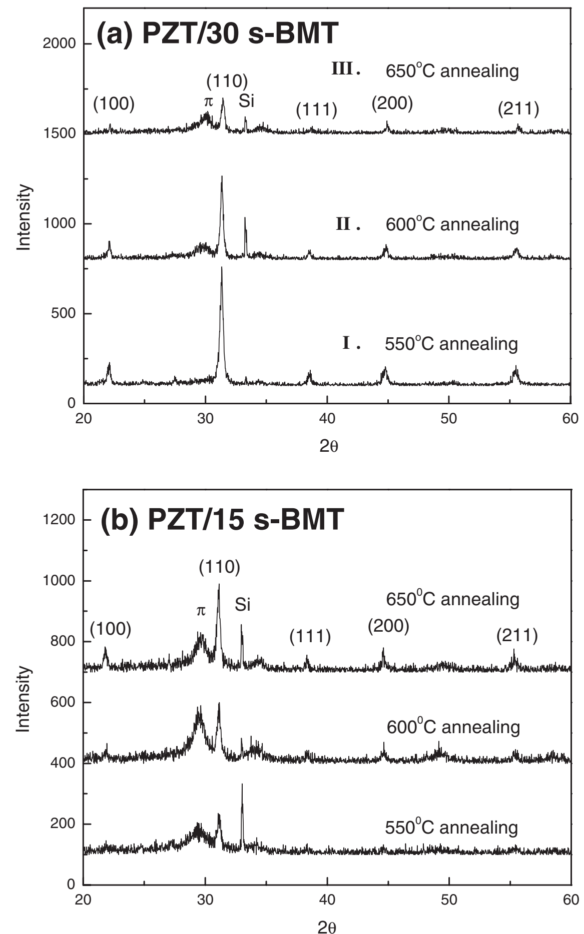


Fig. 5. XRD patterns of PZT films prepared on BMT buffer layers by two-step PLD, which is PLD at 300°C and then postannealing at 550–650°C, where the BMT buffer layer is PLD at 350°C for (a) 30 s and (b) 15 s.

than a continuous thin layer. This strongly suggests that BMT materials grew using the island-growth mechanism, such that the BMT materials cannot form a continuous layer when the PLD period is too short. Only when *in situ* PLD is long (60 s) can continuous BMT films served as buffer layers.

The nucleation behavior of the PZT films on these BMT islands was further investigated by preparing the PZT/BMt/Si thin films using a two-step PLD process, in which the PZT films were first deposited on BMT-buffered Si at 300°C, followed by postannealing at 550–650°C in O_2 atmosphere to crystallize the amorphous PZT films. For a 60 s-deposited BMT layer, pyrochlore-phase-free perovskite PZT films can be obtained, no matter how high the postannealing temperature is (not shown), which implies that the 60 s-deposited BMT layer is a continuous film and is capable of preventing interaction between the PZT and silicon materials.

Figure 5(a) reveals that, with the 30 s-deposited BMT buffer layer, a secondary-phase-free perovskite PZT phase can still be obtained by the two-step PLD process, provided that the postannealing temperature is not too high (550°C, curve I). On the basis of this result, infer we that the PZT materials sitting on top of the BMT islands were crystallized preferentially and grew laterally to form a continuous layer of perovskite PZT without the induction of PZT-to-Si interdiffusion. Crystallization proceeds very fast and the rate of interdiffusion between the perovskite PZT and silicon substrates is markedly lower than that between the amorphous PZT and Si materials. Thus, the occurrence of the pyrochlore phase is pronouncedly suppressed. However, postannealing at very high substrate temperatures (i.e., 600 and 650°C, curves II and III) still induces interaction between the PZT and Si materials. In contrast, Fig. 5(b) indicates that, with the 15 s-deposited BMT buffer layer, a large proportion of the pyrochlore phase is always present in conjunction with the perovskite PZT phase, regardless of postannealing temperature. Such a phenomenon indicates that the occurrence of PZT-to-Si interdiffusion cannot be completely suppressed if the proportion of crystallized PZT islands is too small to lateral growth, forming a continuous layer.

SEM micrographs in Figs. 6(a) and 6(b) show the microstructures of the PZT/BMT/Si thin films grown by *in situ* PLD on the 60 s- and 30 s-deposited BMT layers, respectively. The grain size of the PZT films grown on the 60 s-deposited BMT layer is markedly smaller than that of the PZT films grown on the 30 s-deposited BMT layer, indicating that the nucleation density of the latter is smaller than that of the former. Such a result supports the argument that, in the 60 s-deposited BMT layer, the PZT crystallizes simultaneously over the continuous BMT films, resulting in larger nucleation density. In contrast, for the 30 s-deposited BMT buffered films, the PZT crystals only form preferen-

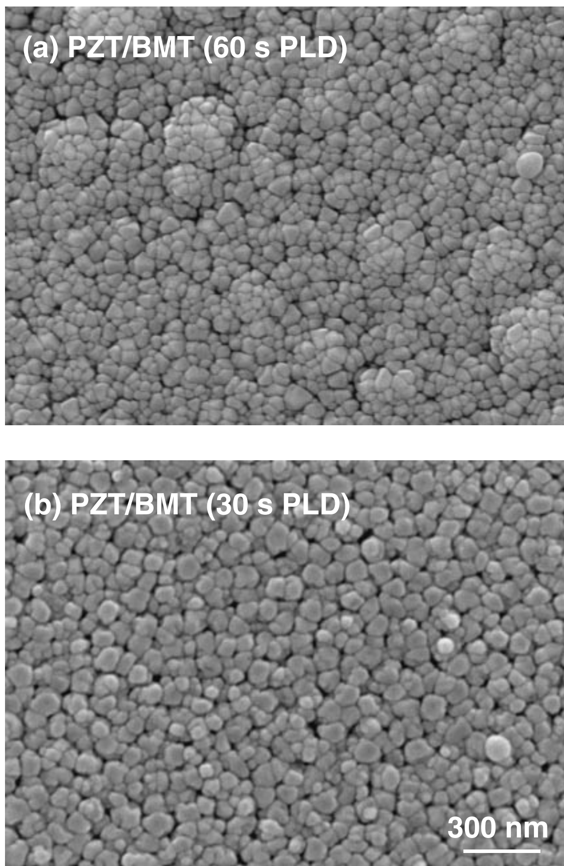


Fig. 6. SEM micrographs of PZT thin films synthesized by *in situ* PLD at 350°C substrate temperature with BMT buffer layer deposited for (a) 60 s and (b) 30 s.

tially on BMT islands and then grow laterally. The nucleation density is thus smaller. Restated, isolated BMT islands can still promote the crystallization kinetics of the subsequently grown PZT materials, forming secondary-phase-free perovskite PZT films provided that the number density of BMT islands is sufficiently large and the process temperature is not too high.

4. Conclusion

The effects of substrate temperature and oxygen pressure on the crystallinity and microstructure of PZT thin films prepared on the BMT buffer layer by *in situ* PLD were studied. The growth of the BMT buffer layer and that of PZT thin films on the BMT buffer layer were thus optimized. The BMT layer was observed to be a very good diffusion barrier and seeding layer. The (100)-preferred oriented PZT films with optical refractive index $n = 2.39$ and transmission loss $\beta = 2.86\,\mathrm{dB/cm}$ can be achieved by *in situ* PLD at 350°C substrate temperature and 0.18 mbar oxygen pressure.

Acknowledgements

The authors would like to thank the financial support of the National Science Council, R.O.C., through the grant NSC-92-2216-E-007-032.

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