Structural properties of mocvd-grown PbTiO$_3$ thin films at low temperature

Chae Hyun Wang* and Doo Jin Choi

Department of Ceramic Engineering, Yonsei University, 134 Shinchon-dong, Sudaemun-ku, Seoul 120-749, Korea

Oriented PbTiO$_3$ thin films were successfully grown on Pt/SiO$_2$/Si by metalorganic chemical vapor deposition at low temperature range from 350°C to 500°C, using β-diketonate complex of Pb(tmhd)$_2$ and titanium isopropoxide as source precursors. Effects of Pb/Ti ratio and substrate temperature on the orientation and formation of crystalline PbTiO$_3$ phase were investigated. Structure of the as-grown films changed from amorphous to polycrystalline with the increase of Pb/Ti ratio from 0.8 to 5.0 at a fixed temperature of 400°C and with the raise of deposition temperature from 350°C to 400°C at fixed Pb/Ti ratios of 3.3 and 5.0. As the Pb/Ti ratio and deposition temperature increased, the leakage current density increased due to crystallization of the PbTiO$_3$ films. As-deposited PbTiO$_3$ films were analyzed by X-ray diffraction measurements, scanning electron microscopy, and micro-Raman. It is found that the control of excess Pb precursor through Pb/Ti ratio change is the key process parameter for the formation of crystalline PbTiO$_3$ phase in the low temperature MOCVD process.

Key words: PbTiO$_3$, MOCVD, Crystallization.

Introduction

Perovskite-type material of lead titanate (PbTiO$_3$), which has ferroelectric, piezoelectric and pyroelectric properties, is very significant due to its possible applications in electronic devices including sensors, actuators and capacitors. Recently, perovskite-type oxide films have become more attractive because of their high potential use in the future electronic devices such as nonvolatile memory devices and microelectromechanical systems (MEMS) [1, 2].

In order to be compatible with Si-based technology, low temperature processes that produce thin films with good as-grown electrical properties are attractive considering the reaction between film and substrate, and maintenance of underlying devices. However, most reports on the deposition of PbTiO$_3$ by MOCVD have required either relatively high temperature (500~700°C) [3-5] or a post annealing after deposition to obtain good ferroelectric properties [6]. Recently, therefore, many works have been done to lower the process temperature below 500°C and to obtain crystalline phases having preferred orientation at low substrate temperature. Yen *et al*. [7] reported that (100) oriented PbTiO$_3$ films were grown on Si at temperature range of 450~470°C. Hwang and Kim [8] have also succeeded to deposit polycrystalline PbTiO$_3$ films on Pt/SiO$_2$/Si at 350°C using Pb(tmhd)$_2$ and titanium isopropoxide by atmospheric pressure MOCVD. There was a new report on successful deposition of polycrystalline PbTiO$_3$ films at 450°C on various substrates of Si, TiO$_2$ buffered Si, and platinized Si without carrier gas [9]. To our knowledge, there have been no reports on single phase of PbTiO$_3$ films having *a*- and *c*-axis preferred orientation at the temperature below 400°C. Additionally, there has been no proper explanation on crystalline phase formation of PbTiO$_3$ thin films at low temperature below 500°C. In this paper, we are reporting a low temperature MOCVD process of perovskite PbTiO$_3$ thin films. The effects of the Pb/Ti ratio on phase formation, microstructure, and crystallization of PbTiO$_3$ thin films are discussed. From the results, it will be suggested that it is possible to lower the deposition temperature for crystalline PbTiO$_3$ thin films by controlling the Pb/Ti ratio.

Experimental

The PbTiO$_3$ films were deposited on commercial substrate of (200)-oriented Pt/SiO$_2$/Si (Inostek Inc. KOREA). A root-mean-square roughness (R$_{ms}$) value measured by atomic force microscopy (AFM) was about 141 Å for the surface of (200)-oriented Pt. The thickness of Pt film was 1500 Å and its resistivity was about 20Ω · cm. The substrates were degreased in trichloroethylene (TCE), acetone, methyl alcohol and rinsed in deionized water at room temperature for 3 min, respectively. Organometallic precursors of β-diketonate complex of Pb(tmhd)$_2$ [tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionate : Pb(C$_{11}$H$_{19}$O$_2$)$_2$] and titanium isopropoxide [TIP : Ti(OC$_3$H$_7$)$_4$] were used as source precursors. Pure N$_2$ and O$_2$ gas were used as a carrier gas and an oxidizing gas, respectively. The partial pressure and flow rate of Pb(tmhd)$_2$ and TIP in the reactant flow were changed by varying the carrier gas flow rate, the temperature and the pressure of the bubbler. Then, Pb/Ti precursors

*Corresponding author:
 Tel : +82-2-2123-2852
 Fax: +82-2-365-5882
 E-mail: chwang@yonsei.ac.kr

input ratio was calculated. MOCVD system used in this study has cold-wall type vertical reactor, having resistively heated susceptor, with a tube-typed Pb precursor bath for fresh evaporation and a common bubbler bath of Ti. In order to exclude reduction of vapor pressure caused by surface melting of the Pb precursor, the source was refreshed in every experimental set. The thickness and the growth rate of the films were about 200 nm~240 nm and 3.3 nm~4 nm/min regardless of the Pb/Ti ratio variation, respectively. No post-annealing was carried out in this study.

Results and Discussion

Figure 1 shows results of X-ray diffraction measurements of PbTiO₃ films on (200)-oriented Pt/SiO₂/Si as a function of Pb/Ti ratio at 400°C and 500°C. At the lowest Pb/Ti ratio of 1.1 and 0.8, films at 400°C and 500°C didnt show any diffraction peaks of crystalline perovskite phase, which indicating amorphous structure. As the Pb/Ti ratio increases, formation of tetragonal PbTiO₃ structure was observed from the Pb/Ti ratio of 2.2 upward for the 400°C and 1.0 for the 500°C. From the XRD results, it is obvious that formation of polycrystalline PbTiO₃ phase is closely related to the Pb/Ti ratio during the low temperature MOCVD process in respect that amorphous and polycrystalline phase were observed with the Pb/Ti ratio change. It is also clarified that the higher Pb/Ti ratio is required for the formation of single-phase crystalline PbTiO₃ thin film when the deposition temperature become lower.

A texture coefficient (*TC*) from Haris method [10] was calculated as a function of Pb/Ti ratio in order to observe the relative degree of preferred orientation among planes. Figure 2 indicates *TC* values of PbTiO₃ films on (200)-oriented Pt substrate as a function of Pb/Ti ratio at 400°C. The results reveal that the degree of preferred orientation of PbTiO₃ films varied largely with Pb/Ti ratio, and (100) and (001) diffraction are dominant at higher ratio. There exist a strong texturing
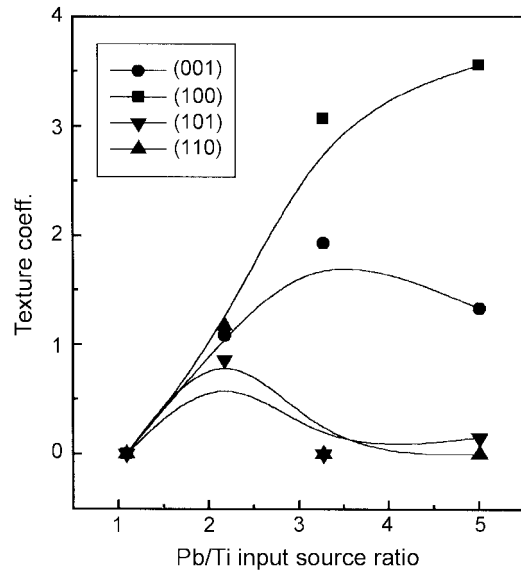

Fig. 2. Texture coefficient of PbTiO₃ films deposited at 400°C as a function of Pb/Ti ratio. When Pb/Ti ratio is 1.1, every calculated values of TC are fixed by 0.
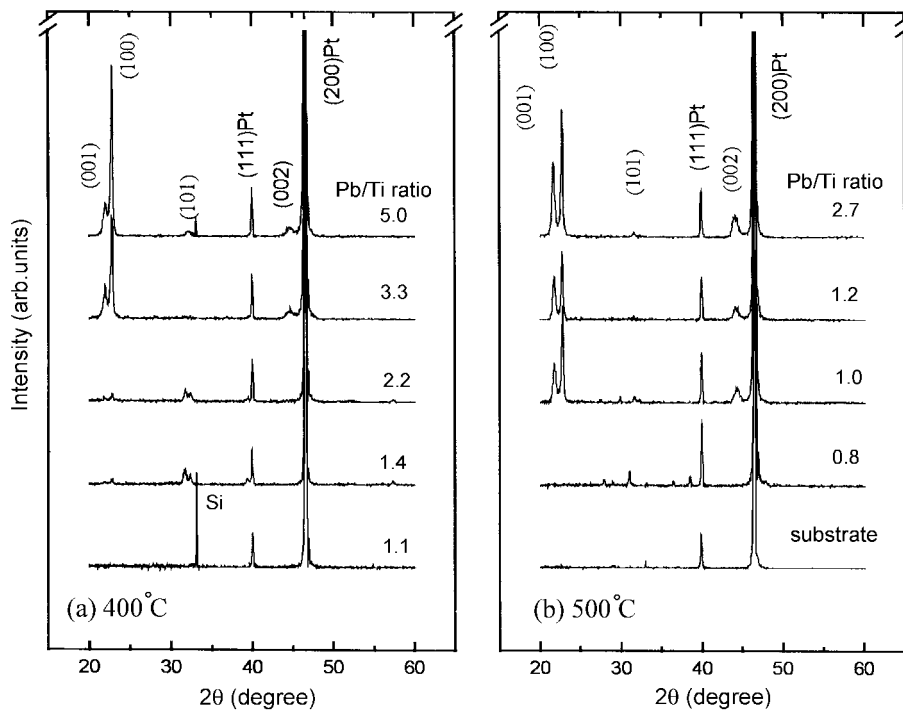

Fig. 1. XRD patterns of PbTiO₃ films deposited by MOCVD on (200)-oriented Pt/SiO₂/Si substrates as a function of Pb/Ti ratio at (a) 400°C and (b) 500°C.
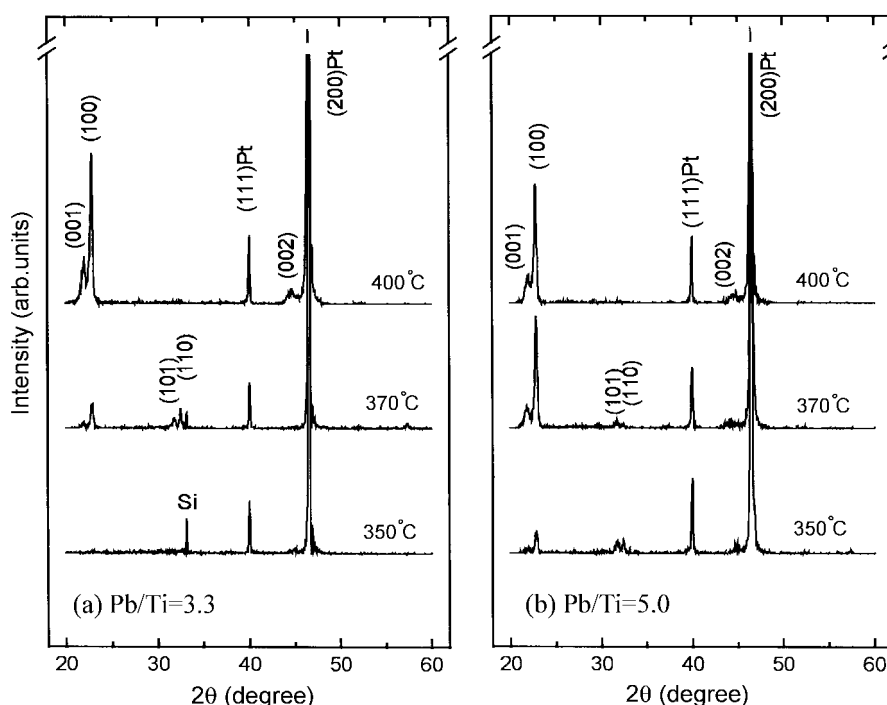
Fig. 3. XRD patterns of PbTiO₃ films grown by MOCVD at fixed Pb/Ti ratios of (a) 3.3 and (b) 5.0 as a function of deposition temperature.

indicates that c-axis corresponding to the spontaneous polarization vector is parallel to the plane of the substrate. The reason for dominant a-axis domain growth at the Pb/Ti ratio of 3.3 and 5.0 might be due to the anisotropic growth at the low temperature reported by Yen *et al.* [7] even though all the (001) and (100) plane of PbTiO₃ show good coherent lattice match with (200) plane of Pt. The clarification for dependence of preferred orientation on Pb/Ti ratio has not been clearly understood yet but is thought to be related to phase formation of PbTiO₃.

Since oriented PbTiO₃ thin films were successfully grown at the temperature of 400°C with both Pb/Ti ratio of 3.3 and 5.0, we tried to investigate temperature dependence of the Pb/Ti ratio on phase formation and microstructure of PbTiO₃ thin films. Figure 3(a) and 3(b) show the results of XRD as a function of deposition temperature at fixed Pb/Ti ratio of 3.3 and 5.0, respectively. The results showed that change of crystallinity and phase formation with the decrease of the deposition temperature was similar to results of films with the Pb/Ti ratio change as indicated in Fig. 1(a). With the decrease of deposition temperature, crystallinity of PbTiO₃ film at the Pb/Ti ratio of 3.3 decreases, which result in amorphous phase at the temperature of 350°C. On the contrary, polycrystalline PbTiO₃ films were grown even at low temperature of 350°C in the case of Pb/Ti ratio of 5.0.

Figure 4 shows surface SEM images of the PbTiO₃ films grown as a function of the Pb/Ti ratio and deposition temperature. As the Pb/Ti ratio increased from 1.1 to 5.0, surface morphology of the as-grown films at

400°C changed from uniform hemisphere-shaped clusters [Fig. 4(a)], confirmed as amorphous by XRD, to polycrystalline grains of about 200 nm [Fig. 4(d)]. The same structure is also observed in the films grown at the temperature of 350°C with the Pb/Ti ratio of 3.3 (not shown). Films grown with the Pb/Ti ratio of 1.4 and 2.2 at 400°C [Fig. 4(b) and Fig. 4(c)] and 5.0 at 350°C [Fig. 5(e)] showed the mixed structure that amorphous and crystalline phase might coexist. In order to confirm the partial crystallization, micro-Raman and AES analysis was carried out for center and edge in Fig. 4(b). Spatial resolution of laser spot size was less than ~3 mm so that Raman spectra of inside/outside of local structure can be distinguished. Raman spectra of the area 1 and area 2 for the film deposited at the Pb/Ti ratio of 1.4 were not analogous as shown in Fig. 5(a) and Fig. 5(b). Fig. 5(c) shows Raman spectra of polycrystalline PbTiO₃ films grown at the Pb/Ti ratio of 5.0, which is similar to published Raman peaks for the polycrystalline PbTiO₃ thin films deposited by sputtering [10]. AES surface energy survey for the center and the edge of Fig. 2(b) was also carried out to clarify local composition fluctuation between crystalline and amorphous. There was little difference in stoichiometry between the center and edge after 16 min etching by 10 keV Ar⁺ ions (not shown). From these results, it is found that locally formed grain-like structure is an aggregation of micro-crystalline PbTiO₃ phases. Consequently, we assure that the micro-structure of PbTiO₃ films observed at the intermediate Pb/Ti ratios indicate mixed structure, which is caused by the transition from amorphous to crystalline phase during the deposition of
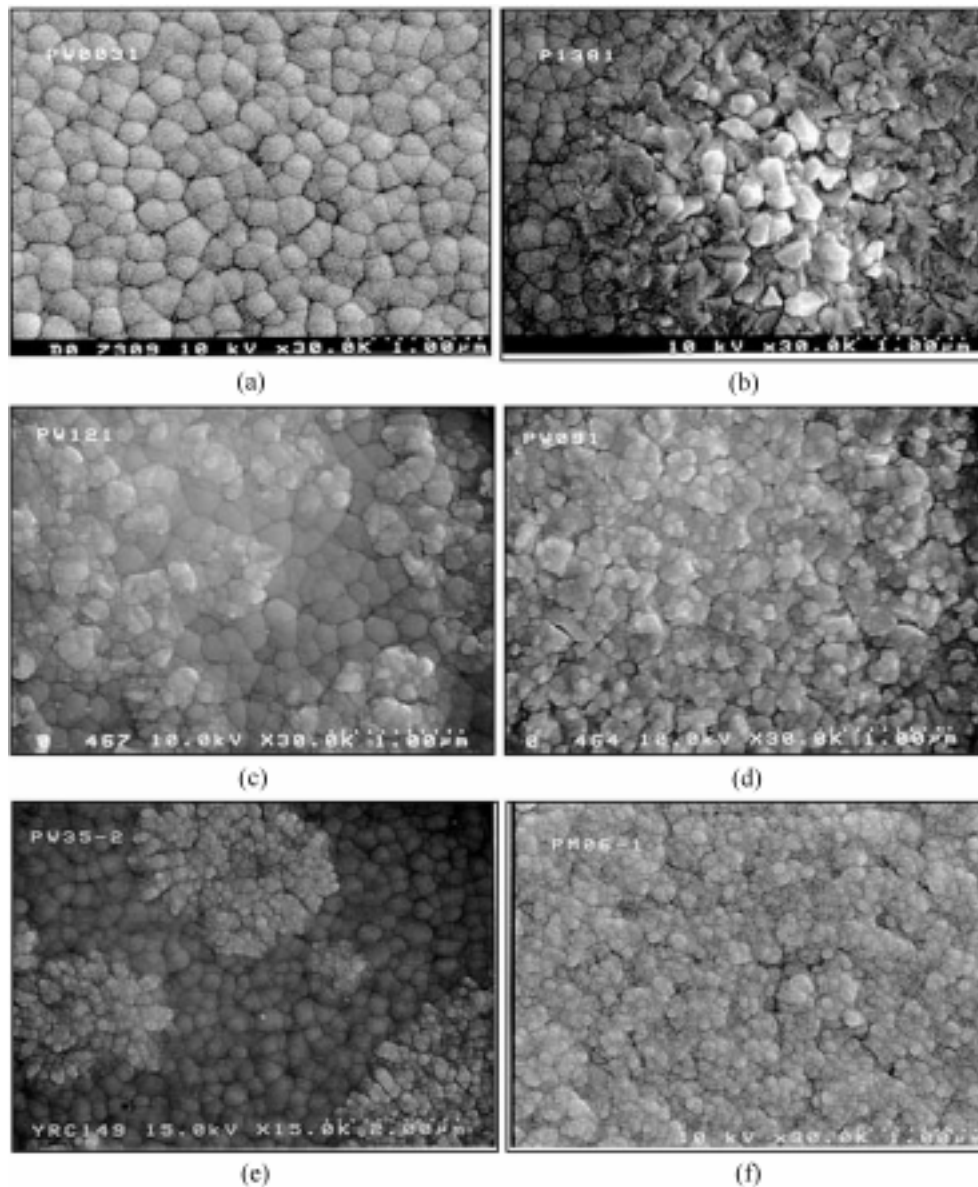
Fig. 4. SEM surface morphology of PbTiO$_3$ thin films deposited at 400ºC [(a), (b), (c) and (d)] with the Pb/Ti ratio of 1.1, 1.4, 2.2 and 5.0 respectively and 350ºC with the Pb/ ratio of 3.3[(e)], and 5.0[(f)].

PbTiO$_3$ films.

Figure 6 shows the effect of Pb/Ti ratio on the current density versus electric field (I-V) characteristics of PbTiO$_3$ films deposited at 400ºC. All of the I-V characteristics for the Al/PbTiO$_3$/Pt capacitor show the typical metal-insulator-metal (MIM) characteristics [11]. The leakage current density for the amorphous film grown at the lowest Pb/Ti ratio of 1.1 was smaller than other films. Increase in the current density with the increase of Pb/Ti ratio is attributed to the structural imperfections like a grain boundary, which was formed due to the crystallization of PbTiO$_3$ films with the increase of Pb/Ti ratio, as confirmed by the SEM measurement.

Since metalorganic sources contribute to a quite complicated growth process of PbTiO$_3$ thin films, just a qualitative idea of the growth mechanism can be sug-

gested for the crystalline phase formation at the low temperature with the change of Pb/Ti ratio. It is experimentally confirmed that the formation of crystalline PbTiO$_3$ phase below 500ºC is closely related to the Pb/Ti ratio. Because Pb concentration on the surface *i.e.* amount of activated Pb species adsorbed on the surface increases with the raise of the Pb/Ti ratio[8], crystalline phase grown at low temperature is thought to be dependent on the adsorption of activated Pb species. Also, thermal decomposition temperature of Pb(tmhd)$_2$ is higher than that of TIP [12]. Then, thermal energy to activate the source precursor of Pb(tmhd)$_2$ at the temperature range from 350ºC to 400ºC is insufficient for formation of stoichiometric crystalline PbTiO$_3$ phase even though decomposition of TIP is vigorous to the extent of forming TiO compound preferably. That means
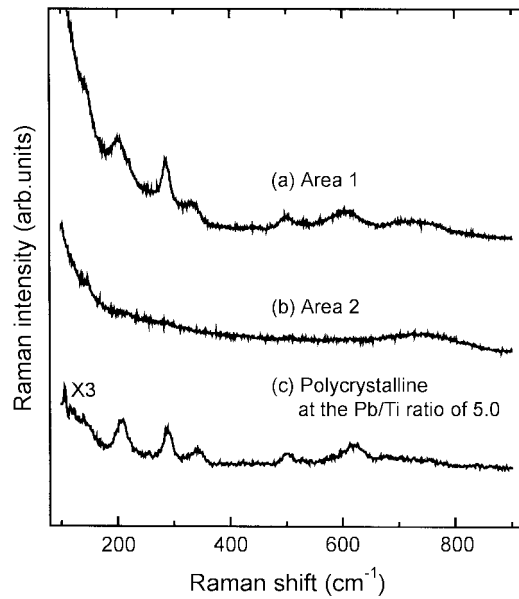
Fig. 5. Micro-Raman spectra for the (a) center, and (b) edge of Fig. 4(b).
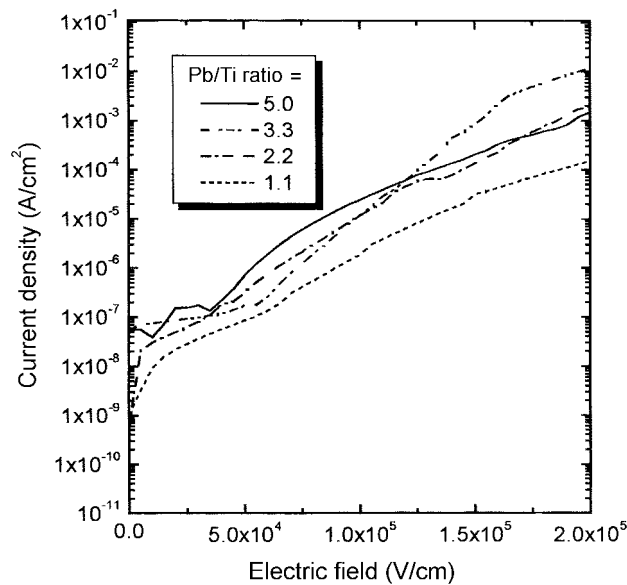

Fig. 6. Leakage current characteristics of PbTiO₃ films grown at 400°C as a function of Pb/Ti ratio.

amount of activated Pb precursors is reduced as the deposition temperature become lower, which is analogous to down control of Pb/Ti ratio at 400°C. Our explanation for the crystalline film formation also can be confirmed by the structural properties of PbTiO₃ films as tabulated in table1. Therefore, it is inevitable to supply excess Pb precursor for formation of PbTiO₃ phase at low temperature process.

Conclusion

PbTiO₃ thin films were deposited on (200)-oriented

Table 1. Summary of phases and structure of PbTiO₃ thin films confirmed by SEM and XRD

Temp.	Pb/Ti 1.1	1.4	3.3	5.0
350°C	AM	AM	AM+PC	PC
400°C	AM	AM+PC	PC	PC
500°C	PC	PC	PC	PC

where, AM and PC represent the amorphous and polycrystalline phases, respectively.

Pt/SiO₂/Si by MOCVD at low temperature range from 350°C to 500°C. The *a*- and *c*-axis oriented PbTiO₃ films were successfully grown at the temperature of 400°C with the change of Pb/Ti ratio from 1.1 to 5.0. Preferably oriented growth of tetragonal PbTiO₃ phase was observed in the PbTiO₃ films deposited at as low temperature as 370°C. Formation and microstructure of polycrystalline PbTiO₃ phase are completely dependent on the amount of activated Pb precursors during the low temperature MOCVD process in respect that amorphous, mixed, and polycrystalline phase were observed with the change of Pb/Ti ratio and deposition temperature. Therefore, the Pb/ ratio is the key process parameter to control crystalline PbTiO₃ phase formation at the low substrate temperature.

Acknowledgement

References

1. J. F. Scott, and C. A. Araujo, Science 246 (1989) 1400-1405.
2. D.L. Polla, and L.F. Francis, MRS bulletin 21 (1996) 59-65.
3. A. Yamashita, and T. Tatsumi, Appl. Phys. Lett. 67 (1995) 1208-1210.
4. T. Yu, Y-F. Chen, L. Shun, J-X. Chen, and N-B. Ming, Solid State Comm. 96 (1995) 477-480.
5. C.J. Lu, H.M. Shen, J.S. Liu, and Y.N. Wang, J. Phys. D: Appl. Phys. 30 (1997) 2338-2342.
6. B.M. Yen, D. Liu, G.R. Bai, and H. Chen, J. Appl. Phys. 76 (1994) 4805-4810.
7. C.S. Hwang, and H.J. Kim, J. Electron. Mater. 22 (1993) 707-716.
8. C. Byun, J.W. Jang, Y.J. Cho, K.J. Lee, and B.W. Lee, Thin Solid Films 324 (1998) 94-99.
9. C.S. Barret, T.B. Massalski, Structure of Metals, (Pergamon, Oxford, 1980) p.204.
10. I. Taguchi, A. Pignolet, L. Wang, M. Proctor, F. Levy, and P.E. Schmid, J. Appl. Phys. 73 (1993) 394-399.
11. Z.Q. Shi, Q.X. Jia, and W.A. Anderson, J. Vac. Sci. Technol. A11 (1993) 1411-1413.
12. C.H. Peng, and S.B. Desu, J. Am. Cerm. Soc. 77 (1994) 1799-1812.