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In-situ growth of oriented $PbTiO_3$ thin films by low temperature metalorganic chemical vapor deposition

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Oriented $PbTiO_3$ thin films were successfully grown on (200)-oriented $Pt/SiO_2/Si$ by metalorganic chemical vapor deposition at low temperature range from 350°C to 400°C, using β-diketonate complex of $Pb(tmhd)_2$ and titanium isopropoxide as source precursors. Dependences of orientation and formation of crystalline $PbTiO_3$ phase on Pb/Ti ratio and substrate temperature was investigated. Crystalline phases and preferred orientations were determined by X-ray diffraction technique, and surface morphology was identified with scanning electron microscopy. As the deposition temperature was raised from 350°C to 400°C at two fixed Pb/Ti ratios of 3.3 and 5.0, structures of $PbTiO_3$ films transformed from amorphous to polycrystalline and preferred orientation changed from random to [100] parallel to the surface. Similar results were also observed in the films deposited at 400°C with the increase of Pb/Ti ratio from 1.1 to 5.0. As the Pb/Ti ratio increased, the dielectric constant and current density increased due to crystallization of the $PbTiO_3$ films. It is found that the control of excess Pb precursor amount through Pb/Ti ratio change is the key process parameter for the formation of crystalline $PbTiO_3$ phase in the low temperature MOCVD process. © *2001 Kluwer Academic Publishers*

1. Introduction

Perovskite-type material of lead titanate ($PbTiO_3$) which has ferroelectric, piezoelectric and pyroelectric properties is very important 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 uses in the future electronic devices such as nonvolatile memory devices and microelectromechanical systems (MEMS) [1, 2]. Several deposition methods for ferroelectric thin films of $PbTiO_3$ such as sputtering, sol-gel and metalorganic chemical vapor deposition (MOCVD) have been examined [3–5]. Among these techniques, MOCVD technique has many advantages such as large area deposition with excellent step coverage over a patterned substrate, high growth rate, good film uniformity, and possibility of relatively low temperature deposition. Therefore, MOCVD has a strong potential as a manufacturable processing method.

In order to be compatible with Si-based technology, low temperature processes which produce thin films with good as-grown ferroelectric properties are attractive associated with the reaction between film and substrate, and maintenance of underlying circuitry like a metal-oxide-semiconductor field effect transistor (MOSFET). However, most of reports on the deposition of $PbTiO_3$ by MOCVD have required either relatively high temperature (500–700°C) [6–8] or a post annealing after a deposition to obtain crystalline phase of good ferroelectric properties [4]. 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.* [9] reported that multi-oriented $PbTiO_3$ films were formed at the growth temperature above Curie temperature of 490°C and (100) oriented films were grown at temperature range of 450–470°C on Si. Hwang and Kim [10] 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 [11]. 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 crystallization of $PbTiO_3$ thin films at low temperature below 500°C.

Metallic platinum on Ti/SiO_2 or SiO_2 is generally regarded as a potential electrode because of stability during subsequent oxide process. Pt films show preferred orientation of (111) plane parallel to the surface since (111) planes are close packed ones of the lowest

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surface energy. Only when Pt films were deposited on a single crystal like (100) MgO, they showed (100) and preferred orientation caused by formation of coherent interface due to small lattice constant difference [12]. A recent result has shown that it is possible to prepare (200)-oriented polycrystalline Pt on SiO_2/Si substrate by controlling Ar/O_2 gas plasma [13]. Since the c-axis oriented $PbTiO_3$ films corresponding to the spontaneous polarization vector is perpendicular to the plane of the substrate are advantageous in many applications, it would be better if the (200)-oriented Pt films could be used as a substrate because of its lattice match with the (001) plane of $PbTiO_3$ films.

In this paper, we are reporting the successful growth of oriented $PbTiO_3$ thin films on (200)-oriented Pt/SiO_2 at low temperature range from 350°C to 400°C by MOCVD process. The effects of the Pb/Ti ratio and deposition temperature 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 in order to obtain crystalline $PbTiO_3$ thin films by controlling the Pb/Ti ratio.

2. Experimental

The $PbTiO_3$ films were deposited on commercial substrate of (200)-oriented Pt/SiO_2/Si [13] (Inostek Inc. KOREA). The texture of (200) oriented Pt substrate was confirmed by x-ray pole figure measurement. 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. Thickness of Pt film was 1500 Å and their resistivity was about 20 $\Omega \cdot$ cm. The substrates were degreased in trichloroethylene (TCE), acetone, and methylalcohol and rinsed in deionized water at room temperature for 3 min, respectively. 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 : $Ti(OC_3H_7)_4$] were used as source precursors. Pure N_2 and O_2 gas were used as a carrier gas and an oxidizing gas, respectively. Table I shows the details of deposition condition of MOCVD process for $PbTiO_3$ thin films. 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 and the temperature and pressure of the bubbler. Then, Pb/Ti precursors input ratio was calculated [14]. In this experiment, calculated Pb/Ti input source ratio was changed from 1.1 to 5.0. We denote the Pb/Ti input source ratio as a Pb/Ti ratio in the current manuscript.

TABLE I Details of growth condition for $PbTiO_3$ thin films

Substrate	(200)-oriented Pt/SiO_2/Si
Substrate temperature	350 °C–400 °C
Working pressure	5 torr
Carrier and Oxidant gas	N_2 and O_2
Temperature of $Pb(tmhd)_2$	130 °C
Temperature of TIP	45 °C
$Pb(tmhd)_2$ carrier gas flow rate	40 sccm–300 sccm
TIP carrier gas flow rate	20 sccm
O_2 flow rate	100 sccm

MOCVD system used in this study has a 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. Heating tape was wrapped around metalorganic precursor transport lines, maintained at 140°C, to prevent condensation of vaporized precursors at cold spot and to hinder predecomposition at hot spot. In order to exclude reduction of vapor pressure caused by surface melting of the Pb precursor, the source was refreshed in every experimental set. After deposition, substrate was cooled down to room temperature at a rate of 150 °C/h under O_2 ambient. Thickness and growth rate of the films was about 200 nm–240 nm and 6.7 nm–8 nm/min, respectively. No post-annealing was carried out in this study.

Perovskite phase and orientation of $PbTiO_3$ thin films were identified by wide angle X-ray diffraction (XRD) measurement, using a Regaku X-ray diffractometer with a nickel-filter. Surface microstructure of films was examined by scanning electron microscopy (SEM, Hitachi 2700) while R_{ms} surface roughness of the $PbTiO_3$ films was quantitatively characterized by atomic force microscopy (AFM, Park Scientific Instrument). Furthermore, electrical properties such as frequency dependent dielectric constant and dissipation factor, and I-V characteristics were measured for Al/$PbTiO_3$/Pt capacitors.

3. Results and discussion

Fig. 1a and b shows the results of XRD as a function of deposition temperature from 350°C to 400°C at a fixed Pb/Ti ratio of 3.3 and 5.0, respectively. No evidence of any phases other than $PbTiO_3$ can be seen for all the films under current process conditions. With the decrease of deposition temperature from 400°C, crystallinity of $PbTiO_3$ 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 $PbTiO_3$ films were grown even at the low temperature of 350°C in the case of the Pb/Ti ratio of 5.0. Thickness of as-grown films is about 200 nm–240 nm irrespective of deposition temperature, which indicates thickness effect on diffraction intensity can be ignored. From the XRD results, it is clarified that formation temperature of single-phase crystalline $PbTiO_3$ thin film is as low as 350°C, which is the lowest temperature than previous results. Yom *et al.* [15] reported that polycrystalline $PbTiO_3$ films on platinized Si were grown at the temperature of 530°C, while Yen *et al.* [9] reported that (100) oriented $PbTiO_3$ films were grown on Si at temperature range of 450–470°C. The reason for the change of the phase formation of $PbTiO_3$ at the temperature range between 350°C to 400°C can be explained as follows; thermal decomposition temperature of $Pb(tmhd)_2$ is higher than that of TIP [16]. Then, thermal energy to activate the source precursor of $Pb(tmhd)_2$ at the temperature range from 350°C to 400°C is insufficient for formation of crystalline $PbTiO_3$ phase even though decomposition of TIP is vigorous to the extent of forming TiO-compound preferably. That means more amount of activated Pb precursors is required to deposit the crystalline $PbTiO_3$ phase at low temperature. From the

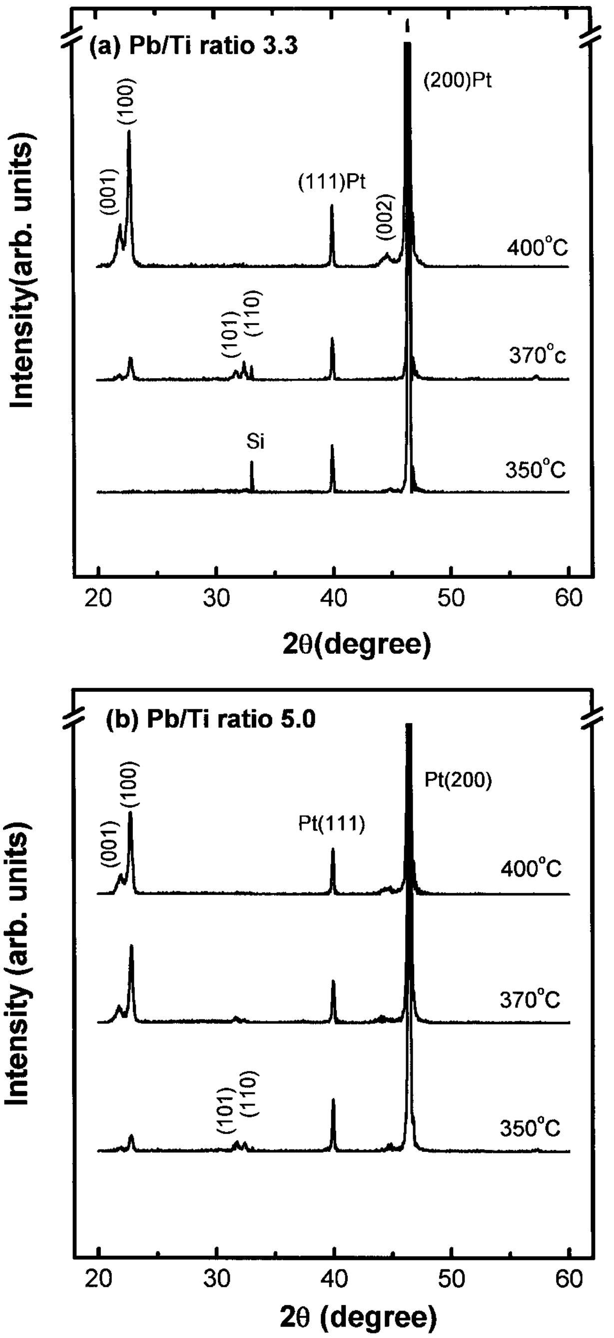

Figure 1 XRD patterns of $PbTiO_3$ films grown by MOCVD at fixed Pb/Ti ratios of (a) 3.3 and (b) 5.0 as a function of deposition temperature.

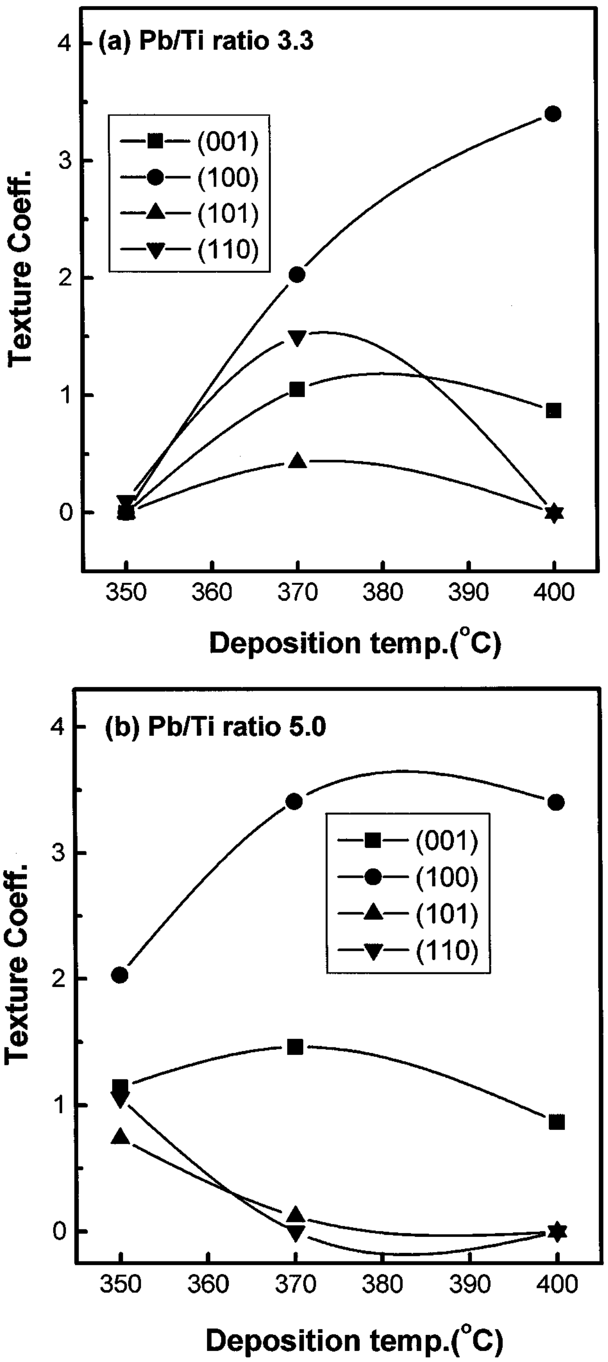

Figure 2 Texture coefficient of $PbTiO_3$ films deposited at fixed Pb/Ti ratios of (a) 3.3 and (b) 5.0 as a function of deposition temperature. When the structure is amorphous, every calculated values of TC are fixed by 0.

results, we can find that the effect of source concentration e.g. Pb precursor on the phase formation of $PbTiO_3$ at the low substrate temperature is significant even though adsorbing atoms on substrate surface have low surface mobility for the crystal growth [9].

A texture coefficient (TC) from Haris method [17] was calculated as a function of Pb/Ti ratio in order to observe the relative degree of preferred orientation among $PbTiO_3$ crystal planes. The equation for the texture coefficient (TC) is defined as

$$\mathrm{TC} = \frac{I(hkl)/I_0(hkl)}{(1/n)\sum I(hkl)/I_0(hkl)} \tag{1}$$

where, *I(hkl)* and I_0*(hkl)* are the intensities of *(hkl)* reflections measured for an experimental sample and a standard powder sample, respectively, and *n* is the total number of reflection planes, e.g. (001), (100), (101), and (110) planes were considered in the present study. When the TC value of any *(hkl)* plane is larger than unity, a preferred orientation exists in which grains are oriented with their *(hkl)* planes parallel to the Pt substrate. Fig. 2 indicates TC values of $PbTiO_3$ films as a function of deposition temperature at the fixed Pb/Ti ratio of 3.3 and 5.0. Since film grown at the Pb/Ti ratio of 3.3 at 350°C was amorphous confirmed by XRD result, every calculated TC value is fixed by 0. The results reveal that the degree of preferred orientation of $PbTiO_3$ films varied largely with the deposition temperature, and (100) diffraction are predominant at higher temperature range from 370°C to 400°C irrespective of the Pb/Ti ratio. The strong texturing in the [100] direction indicates that *c*-axis corresponding to the spontaneous polarization vector is parallel to the plane of the substrate. Note that (101) plane is the most intense diffraction one for $PbTiO_3$ powders [18]. Platinum substrate used in this study has a strong (200) texture and there is a good coincidence lattice match with (001) and (100) plane of $PbTiO_3$ even though the as-grown $PbTiO_3$ films show polycrystalline behavior in nature. Calculated lattice misfit parameters [19] are 0.56% along *a*-axis and −3.1% along *c*-axis parallel to the substrate. The reason for the dominant *a*-axis domain growth might be due to the anisotropic growth rate at low temperature reported by Yen *et al.* [9].

In order to testify an effect of Pb/Ti ratio on the structural properties of $PbTiO_3$ films, we changed the Pb/Ti ratio from 1.1 to 5.0 at a fixed temperature of 400°C. Fig. 3 shows results of X-ray diffraction measurements of $PbTiO_3$ films as a function of Pb/Ti ratio at 400°C. At the lowest Pb/Ti ratio of 1.1, films didn't show any peaks of crystalline perovskite phase, which indicating amorphous structure. As the Pb/Ti ratio increased, formation of tetragonal $PbTiO_3$ structure was observed from the Pb/Ti ratio of 1.4 upward. The results showed that change of crystallinity and phase formation of $PbTiO_3$ films with the Pb/Ti ratio was analogous to those of films with lowering the deposition temperature as indicated in Fig. 1, which could be explained by the facts that amount of activated Pb precursors is reduced as the Pb/Ti ratio decreases. Therefore, it is obvious that formation of polycrystalline $PbTiO_3$ phase is closely dependent on the Pb/Ti ratio during the low temperature MOCVD process.

Fig. 4 shows surface SEM images of the $PbTiO_3$ films grown at 350°C and 400°C with the fixed Pb/Ti ratio of 1.4, 3.3 and 5.0. As the Pb/Ti ratio changed from 1.4 to 5.0, surface morphology of the as-grown films at 350°C changed from hemisphere-shaped clusters [Fig. 4a] to polycrystalline grains of about 100 nm [Fig. 4c]. Uniform hemisphere-shaped clusters were confirmed as amorphous phase by XRD (not shown). Such structure was also observed in all the films grown at Pb/Ti ratio of 1.1 at both temperature of 350°C and 400°C. Films grown at the Pb/Ti ratio of 1.4 at 400°C [Fig. 4d] and 3.3 at 350°C [Fig. 4b] showed the mixed structure that amorphous and crystalline phase coexists. In the previous work [20], we have identified the phase and microstructure of locally formed grain-like structure in $PbTiO_3$ films grown at temperature of 400°C on (111)-oriented $Pt/Ti/SiO_2/Si$. From scanning electron microscopy, Auger electron spectroscopy, and micro-Raman results, it was found that locally formed grain-like structure is an aggregation of microcrystalline $PbTiO_3$ phases [20]. In contrast, we obtained a uniformly dense polycrystalline $PbTiO_3$ phase at the relatively higher Pb/Ti ratio of 5.0 at 350°C and 3.3 and 5.0 at 400°C [see Fig. 4c, e, and f]. Average R_{ms} roughness was calculated directly from three-dimensional AFM images so as to compare surface roughness of films quantitatively. The R_{ms} values of as-grown films with the Pb/Ti ratio of 1.1, 2.2, 3.3, and 5.0 are 12.4, 14.8, 14.7, and 14.5 nm, respectively. The increase of measured R_{ms} values with the Pb/Ti ratio are in reasonable agreement with the previous results [5] that surface of $PbTiO_3$ film became rougher with the deposition temperature due to *in-situ* crystallization. Structural properties of $PbTiO_3$ films deposited at both deposition temperature with the Pb/Ti ratio are tabulated in Table II. Combining SEM and AFM results, it is noticeable that microstructures of oriented $PbTiO_3$ films are also closely dependent on the Pb/Ti ratio for the low temperature MOCVD process.

The dielectric properties of $PbTiO_3$ films grown at 400°C as a function of the Pb/Ti ratio were investigated in terms of the dielectric constant and the dissipation factor as shown in Fig. 5. The dielectric measurements were performed on an $Al/PbTiO_3/Pt$ capacitor with a HP4192A impedance analyzer at room temperature. Dielectric constant increased as the Pb/Ti ratio increased up to 5.0. Dielectric constant at 100 kHz was 40, 60, 88, and 98 for the films grown at Pb/Ti ratio of 1.1, 2.2, 3.3, 5.0, respectively. The increase in dielectric constant may be attributed to the formation of grain structure, which was identified by the XRD and SEM measurements. The increase of dissipation factor at higher frequency region might be caused by a contact resistance between the probe and the electrode [21]. Fig. 6 shows the effect of Pb/Ti ratio on the current density versus electric field (I-V) characteristics of $PbTiO_3$

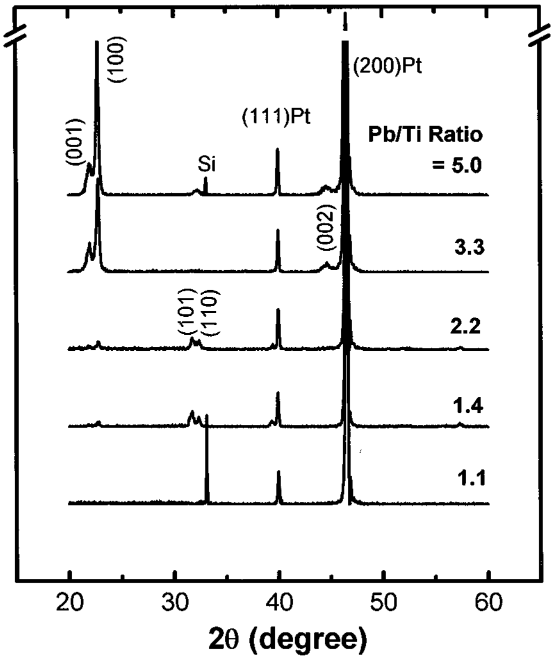

Figure 3 XRD patterns of $PbTiO_3$ films grown by MOCVD at 400°C as a function of Pb/Ti ratio.

TABLE II Summary of phases and structure of $PbTiO_3$ thin films confirmed by SEM and XRD

Pb/Ti ratio Temperature	1.1	1.4	3.3	5.0
350°C	AM	AM	AM + PC$^{(1)}$	PC
400°C	AM	AM + PC$^{(2)}$	PC	PC

Where, AM and PC represent the amorphous and polycrystalline phases, respectively. Locally crystallized phases are randomly distributed on the surface of the amorphous films with the density of about (1) 67,400/mm^2 and (2) 62,700/mm^2.

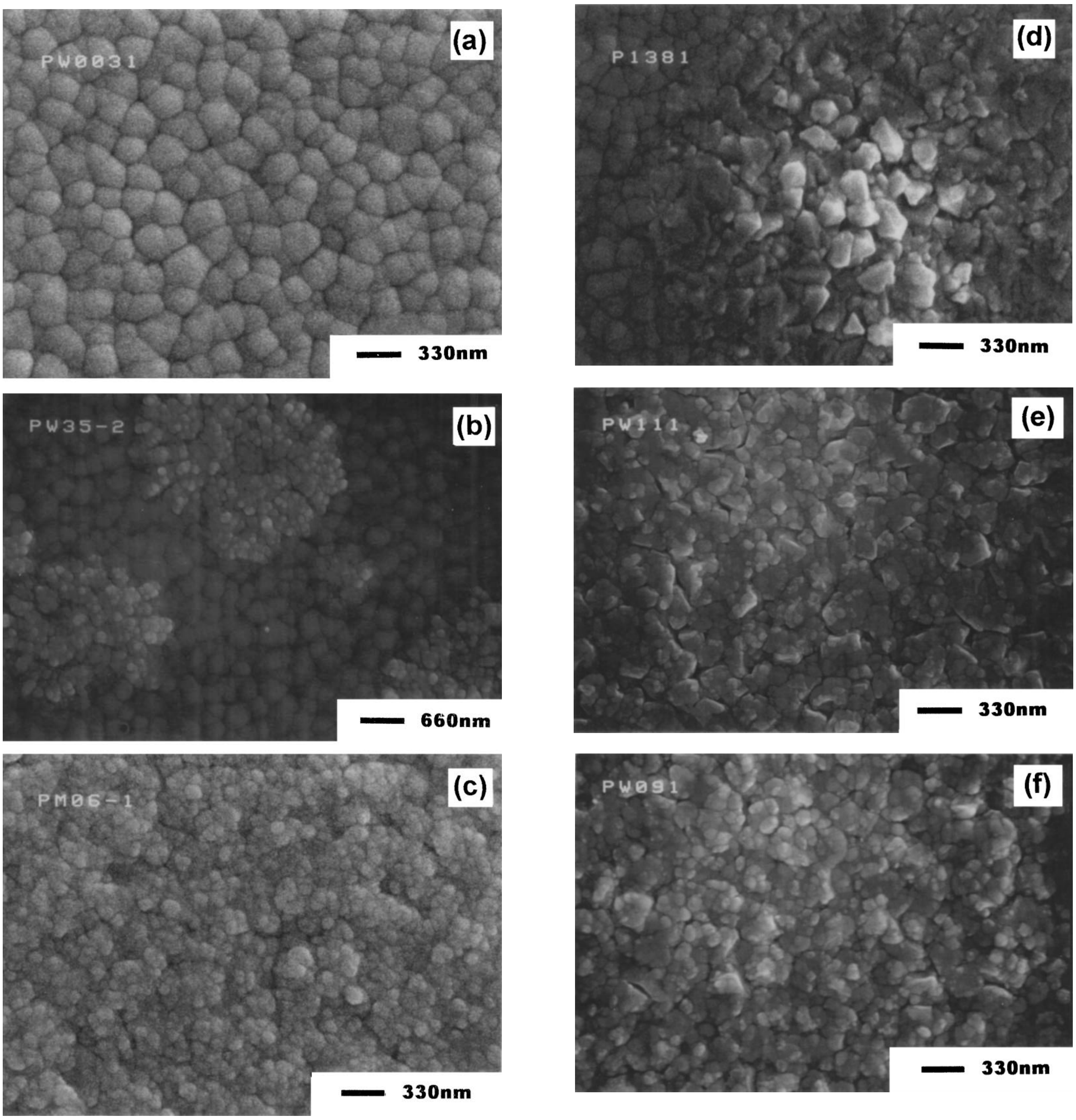

Figure 4 SEM surface morphology of $PbTiO_3$ thin films deposited at 350°C (a–c) and 400°C (d–f) with the Pb/ratio of 1.4 (a and d), 3.3 (b and e), and 5.0 (c and f).

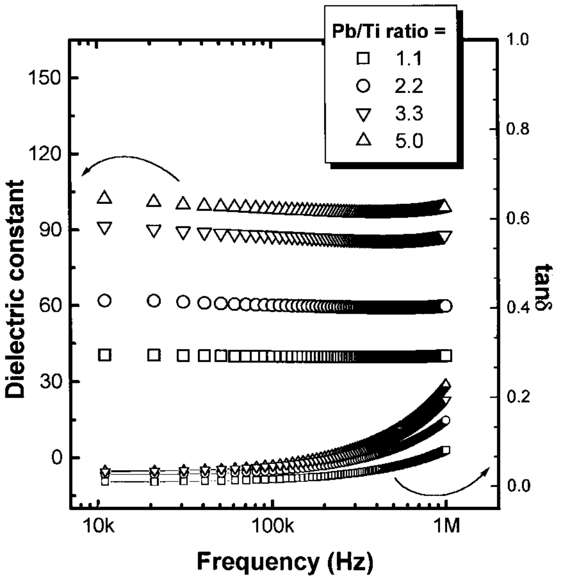

Figure 5 Frequency dependence of dielectric constant and dissipation factor for the $PbTiO_3$ films grown at 400°C as a function of the Pb/Ti ratio.

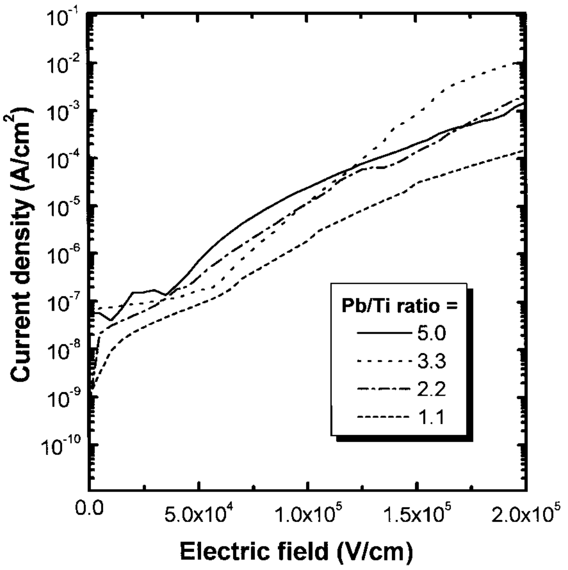

Figure 6 Leakage current characteristics of $PbTiO_3$ films grown at 400°C as a function of Pb/Ti ratio.

films deposited at 400°C. All of the I-V characteristics for the Al/$PbTiO_3$/Pt capacitor show the typical metal-insulator-metal (MIM) characteristics [22]. 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.

4. Conclusion

$PbTiO_3$ thin films were deposited on (200)-oriented Pt/SiO_2/Si by MOCVD at low temperature range from 350°C to 400°C. The a-axis oriented $PbTiO_3$ films were successfully grown at the low temperature range from 350°C to 400°C with the change of Pb/Ti ratio from 1.1 to 5.0. As the deposition temperature was raised from 350°C to 400°C at two fixed ratios of 3.3 and 5.0, structures of $PbTiO_3$ films transformed from amorphous to polycrystalline and preferred orientation changed from random to [100] parallel to the surface. Similar results were also observed in the films deposited at 400°C with the increase of Pb/Ti ratio from 1.1 to 5.0. The dielectric constant and current density of the $PbTiO_3$ films increase as the Pb/Ti ratio increases due to crystallization. Formation and microstructure of polycrystalline $PbTiO_3$ phase are closely 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, supply of excess Pb precursors at the initial stage of the film formation is required for the phase formation of the $PbTiO_3$ thin films at low temperature between 350°C and 400°C. Furthermore, the Pb/Ti ratio is the key process parameter to control crystalline $PbTiO_3$ phase formation at the low substrate temperature.

Acknowledgements

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References

1. D. BONDURANT, *Ferroelectrics* **112** (1990) 273.
2. D. L. POLLA and L. F. FRANCIS, *MRS Bulletin* **21** (1996) 59.
3. I. TAGUCHI, A. PIGNOLET, L. WANG, M. PROCTOR, F. LEVY and P. E. SCHMID, *J. Appl. Phys.* **73** (1993) 394.
4. C. J. LU, H. M. SHEN, J. S. LIU and Y. N. WANG, *J. Phys. D: Appl. Phys.* **30** (1997) 2338.
5. T. W. KIM, D. U. LEE, Y. S. YOON, C. H. WANG, S. S. YOM, S. J. LEE and C. O. KIM, *Solid State Comm.* **96** (1995) 95.
6. A. YAMASHITA and T. TATSUMI, *Appl. Phys. Lett.* **67** (1995) 1208.
7. T. YU, Y.-F. CHEN, L. SHUN, J.-X. CHEN and N.-B. MING, *Solid State Comm.* **96** (1995) 477.
8. Y.-F. CHEN, J.-X. CHEN, L. SHUN, T. YU, P. LI, N.-B. MING and L.-J. SHI, *J. Cryst. Growth* **146** (1995) 624.
9. B. M. YEN, D. LIU, G. R. BAI and H. CHEN, *J. Appl. Phys.* **76** (1994) 4805.
10. C. S. HWANG and H. J. KIM, *J. Electron. Mater.* **22** (1993) 707.
11. C. BYUN, J. W. JANG, Y. J. CHO, K. J. LEE and B. W. LEE, *Thin Solid Films* **324** (1998) 94.
12. H. FUJISAWA, M. SHIMIZU, T. HORIUCHI, T. SHIOSAKI and K. MATSUSHIGE, *Jpn. J. Appl. Phys.* **56** (1996) 4913.
13. M. H. KIM, T. S. PARK, D. S. LEE, E. YOON, D. Y. PARK, H. J. WOO, D. I. CHUN and J. HA, *J. Mat. Res.* **14** (1999) 634.
14. M. L. HITCHMAN and K. F. JENSEN, "Chemical Vapor Deposition" (Academic Press, San Diego, 1993) p. 33.
15. S. S. YOM and C. H. WANG, *J. Kor. Phys. Soc.* **29** (1996) s587.
16. C. H. PENG and S. B. DESU, *J. Amer. Ceram. Soc.* **77** (1994) 1799.
17. C. S. BARRET and T. B. MASSALSKI, "Structure of Metals" (Pergamon Press, London, 1980) p. 204.
18. ASTM card 6-0452, Powder Diffraction File, Philadelphia, 1975.
19. M. OHRING, "The Material Science of Thin Films" (Academic Press, San Diego, 1992) p. 315.
20. S. S. YOM, C. H. WANG and Y. T. KIM, *Integrated Ferroelectrics* **14** (1997) 77.
21. M. H. FRANCOMBE, *Thin Solid Films* **13** (1972) 413.
22. Z. Q. SHI, Q. X. JIA and W. A. ANDERSON, *J. Vac. Sci. Technol.* **A11** (1993) 1411.

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