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Formation of $PbTiO_3$ films from multilayered structures of primitive oxides

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Abstract−The possibility of the formation of $PbTiO_3$ from a multilayer structure of PbO and TiO_2 layers on Pt-coated Si substrates prepared by rapid thermal metal organic chemical vapor deposition (RTMOCVD) followed by an appropriate annealing process was examined. The metal organic precursors of PbO and TiO_2 were $Pb(C_2H_5)_4$ and $Ti(O\text{-}i\text{-}C_3H_7)_4$, respectively. The composition of the $PbTiO_3$ thin film was adjusted by control of the thickness of each binary oxide layer of PbO and TiO_2. The multilayer structure was converted into crystalline $PbTiO_3$ by rapid thermal annealing under O_2 ambient at temperature greater than 550 °C. As the annealing temperature was increased from 550 to 750 °C, the peaks related to perovskite $PbTiO_3$ in the XRD patterns became stronger and sharper. From this study, it was confirmed that the crystalline $PbTiO_3$ thin films could be prepared from the interdiffusion reaction of multilayer structure composed of primitive binary oxides through the appropriate post annealing process.

Key words: $PbTiO_3$, Multilayered Structure, Perovskite, MOCVD, Interdiffusion

INTRODUCTION

Ferroelectric $PbTiO_3$ thin film with applications to piezoelectric, pyroelectric, electro-optic and several electronic devices has recently received a great deal of attention. A variety of methods for ferroelectric $PbTiO_3$ thin film growth, including metal organic chemical deposition [1,2], plasma enhanced chemical vapor deposition [3], pulsed laser deposition [4], sol-gel [5], RF sputtering [6] and spray pyrolysis [7], have been used. Among these, chemical vapor deposition (CVD) using metal organic precursors is extensively used, as this method offers a high level of controllability of the film crystallinity and electrical properties as well as good step coverage, a high deposition rate and the possibility of commercial-based production.

In the preparation of multi-component ferroelectric oxide thin films, the control of their composition is usually considered as one of the most difficult tasks. Because the composition of ferroelectric material can influence its ferroelectric properties [8], considerable efforts have been made to clear this issue. As binary oxides such as PbO and TiO_2 can be fabricated easily using several deposition techniques, if a multi-component ferroelectric oxide can be fabricated from a multilayer structure composed of binary oxides by a solid state interdiffusion reaction, it would be a very promising method to prepare the ferroelectric oxide films with a suitably well controlled stoichiometry. A similar concept for an interdiffusion reaction technique has been used widely in the preparation of electronic materials such as silicides [9].

However, few works dealing with this technique have been reported in the field of multi-component ferroelectric thin films. In the work of Tochitsky and Romanova [10], $PbTiO_3$ thin film was prepared by the thermal evaporation of Pb/Ti metals layer by layer on an NaCl substrate followed by annealing in O_2 ambient and oxide formation. Li and Desu [11,12] reported that $PbTiO_3$ thin films on Al_2O_3 substrates can be prepared using a metallic Pb/Ti and oxide PbO/TiO_2 multilayer and a subsequent annealing process.

In the present study, perovskite $PbTiO_3$ thin film is prepared from a multilayer structure of PbO and TiO_2 thin films using an appropriate annealing process. In addition, the morphologies and crystalline structure of the $PbTiO_3$ thin films are analyzed to confirm the viability of the proposed method in detail.

EXPERIMENTAL

A Pt-coated Si wafer was used as a substrate. The metal organic precursors of PbO and TiO_2 were $Pb(C_2H_5)_4$ (TEL, 5 N purity) and $Ti(O\text{-}i\text{-}C_3H_7)_4$ (TTIP, 5N purity), respectively. A rapid thermal metal organic chemical vapor deposition (RTMOCVD) reactor was equipped with thermal components and a quartz tube with a 65 mm OD. Bubblers containing TEL and TTIP were heated to 23 °C and 36 °C. Each vapor was carried into the reactor by nitrogen. Oxygen was used as an oxidizing gas. The typical growth conditions of PbO and TiO_2 thin film are shown in Table 1; the details of the RTMOCVD process are available in the literature [13]. The multilayer structure of binary oxides was prepared as follows. First, an initial oxide layer

Table 1. Growth conditions of PbO and TiO_2 thin film in a rapid thermal metal organic chemical vapor deposition

Layer	PbO	TiO_2
Metalorganic source	$Pb(C_2H_5)_4$ (TEL)	$Ti(O\text{-}i\text{-}C_3H_7)_4$ (TTIP)
Substrate temperature	380 °C	400 °C
Carrier N_2 flow rate	40 sccm	20 sccm
Chamber pressure	500 mtorr	400 mtorr
Bubbler temperature	23 °C	36 °C
Reactant O_2 flow rate	20 sccm	10 sccm
Reactor type	Hot wall	
Substrate	Si wafer and Pt-coated Si wafer	

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of either PbO or TiO_2 was deposited and its thickness was controlled by the process time. Second, all reactant species were eliminated by venting, and the substrate temperature was simultaneously changed to support alternating layers. After a multilayer structure with a designed thickness was prepared, subsequent rapid thermal annealing was done under O_2 ambient at the temperature range of 550-750 °C to convert the structure into a perovskite $PbTiO_3$ thin film. The composition of the $PbTiO_3$ thin film could be controlled by the thickness ratio of each binary oxide layer of PbO and TiO_2.

The compositions of the films were analyzed by energy dispersive X-ray spectroscopy (EDX). The crystal structure was evaluated through X-ray diffraction (XRD). Field emission scanning electron micrography (FESEM) was used to observe the cross-sectional view and surface morphology and also to verify the film thickness. Atomic force microscopy (AFM) was used to check the surface roughness of thin films. Ellipsometry and FESEM were used for the thickness measurement of the deposited films in this study.

RESULTS AND DISCUSSION

It was supposed that stoichiometric $PbTiO_3$ could be obtained simply by alternately pulsing two metal-containing precursors, TEL and TTIP, and an oxygen source, and that the growth rate of the ternary oxide could be predicted by summing the growth rates of the constituent oxides. However, in actuality, both assumptions often fail due to the different reactivities of the precursors [14]. The effects of the surface chemistry usually cause changes in the relative growth rates, which can be determined by comparing the observed film thickness with the theoretical thickness calculated from the growth rates of the binary oxides. This explains why a novel method for the control of the composition is required. In this study, the formation of a multilayer structure of PbO and TiO_2 and the interdiffusion of these two materials are evaluated as a novel method for the fabrication of perovskite $PbTiO_3$ as shown in Fig. 1.

Theoretically, the thickness ratio of a PbO and TiO_2 layer is required to produce precise stoichiometric $PbTiO_3$ thin film. As the composition of ferroelectric materials could have a considerable influence on the ferroelectric properties, compositional controllability is very important to obtain some useful properties from multicomponent ferroelectric oxides [15]. First, the relationship between the thickness ratio of PbO/TiO_2 deposited by RTMOCVD and the actual atomic ratio of Pb/Ti was evaluated, as shown in Fig. 2. The result indicates that if PbO and TiO_2 have the same thickness, the

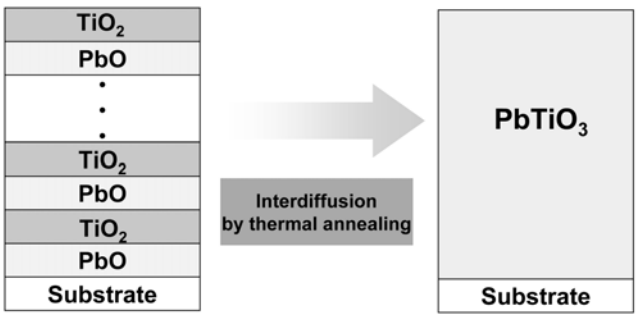

Fig. 1. Schematic of the preparation of $PbTiO_3$ thin film from the multilayer films composed of PbO and TiO_2.

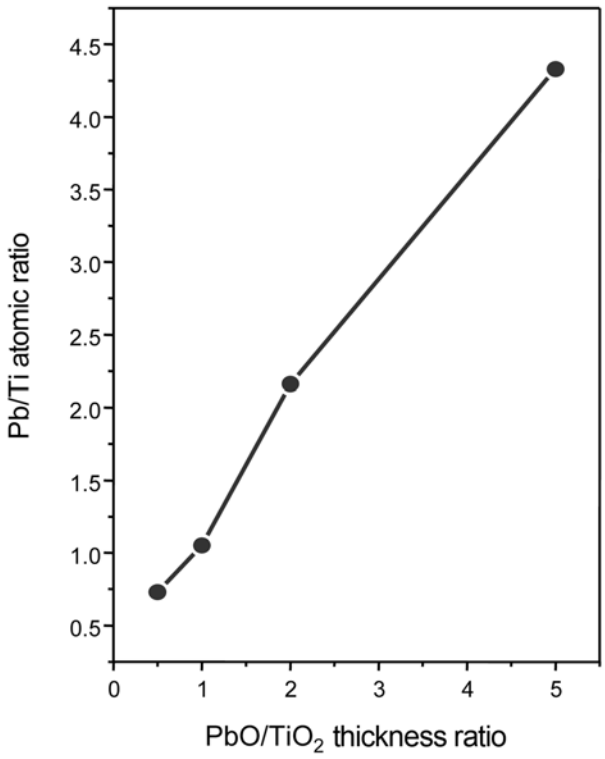

Fig. 2. Correlation between the thickness ratio of PbO/TiO_2 and the related atomic ratio of Pb/Ti.

atomic concentration of Ti would be lower than that of Pb. The atomic ratio of Pb/Ti is 1/0.94.

However, if there is a change in the atomic ratio during a post treatment such as an annealing process, it becomes crucial to obtain or sustain the desired material properties. Therefore, variation of the atomic ratio in $PbTiO_3$ thin films after an annealing process should be minimized. It was reported [3] that Pb reduction in $PbTiO_3$ film increases with an increase in the annealing temperature due to the high volatility of the Pb compounds. It appears that structure capping with a TiO_2 layer suitably protects against the evaporation

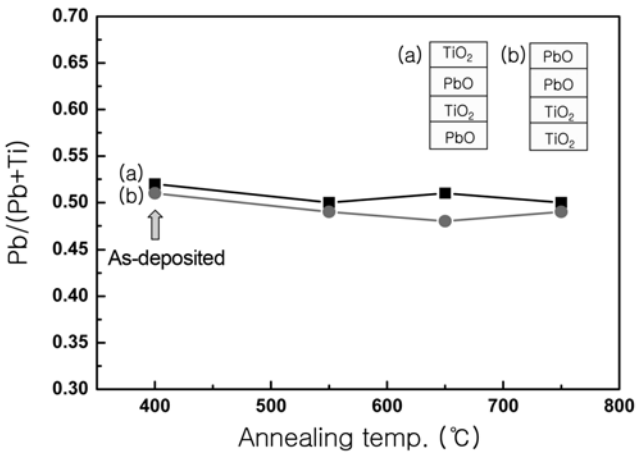

Fig. 3. Effect of annealing temperatures on the atomic ratio of annealed $PbTiO_3$ thin films from (a) TiO_2 capped and (b) PbO capped.

of the Pb element during the annealing process, whereas with a film topped with a PbO layer, it can be expected that the volatility of the Pb would be accelerated during the annealing step. However, the loss of Pb was not severe, though the annealing temperature ranged from 550 to 750 °C; this compares well with the result of the Ti capped specimen as shown in Fig. 3. The reduction of the total annealing time due to the fundamental capability of a rapid thermal annealing process may contribute to the suppression of Pb loss [20].

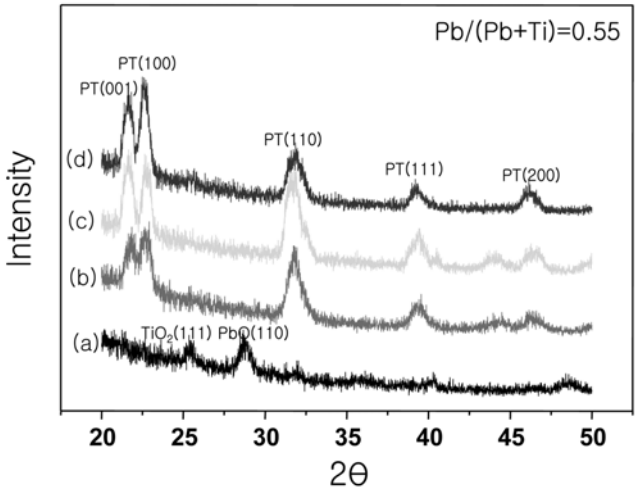

Fig. 4. XRD patterns of the film: (a) as-deposited, (b) annealed at 550 °C, (c) annealed at 650 °C and (d) annealed at 750 °C for 1 hr in oxygen ambient. Atomic ratio of as-deposited film, Pb/(Pb+Ti) is 0.55.

The crystalline structure of $PbTiO_3$ films was studied in the films annealed between 550 and 750 °C. Fig. 4 shows the XRD patterns of $PbTiO_3$ thin films on a Pt-coated silicon substrate as a function of the annealing temperatures. The as-deposited film with an atomic ratio, Pb/(Pb+Ti), of 0.55 had the structure of $(PbO/TiO_2)_2$ and showed the crystalline peaks of TiO_2 (111) and PbO (110). The indexed peaks refer to the crystalline tetragonal phase of $PbTiO_3$ according to the JCPDS (6-452) data card. Well-defined crystalline peaks for perovskite $PbTiO_3$ were observed in all annealed films and the peaks were determined to be at the (001), (100), (101) and (111) orientations. As the annealing temperature was increased from 550 to 750 °C, these peaks in the XRD patterns became stronger and sharper, indicating better crystallization. This result shows that perovskite $PbTiO_3$ can be prepared successfully by the interdiffusion of multilayer binary oxides after an appropriate post-annealing process.

Fig. 5 shows AFM surface images of as-deposited thin films annealed at 550, 650 and 750 °C for 1 hr. The surface roughness and grain size increased as the annealing temperature increased. The values of R_{rms} were 12.661, 13.698, 14.034 and 15.475 nm for the as-deposited and annealed films at 550, 650 and 750 °C, respectively. The grain size in the ferroelectric thin films has an influence on a number of properties. An increase in the grain size leads to an increase in the coercive field, a decrease in the remnant polarization, a depression in the dielectric constant and a smearing of the ferroelectric transition [16].

It is well known that the crystal structure of $PbTiO_3$ thin film is

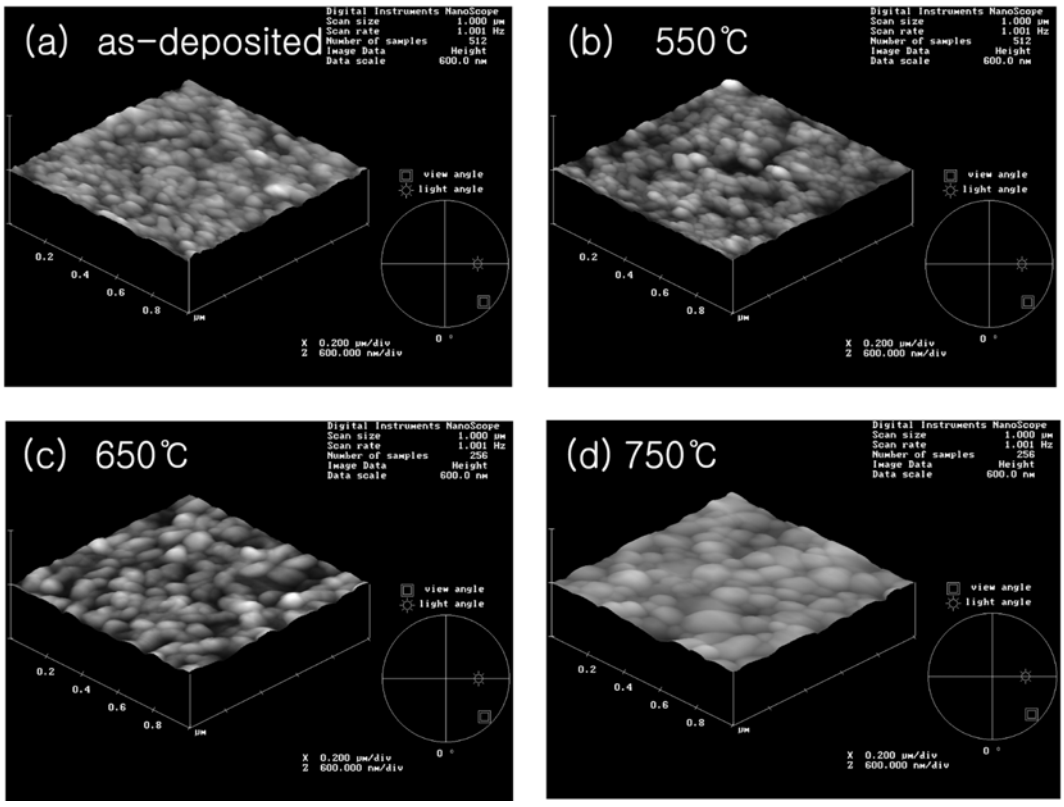

Fig. 5. AFM images of the film: (a) as-deposited, (b) annealed at 550 °C, (c) annealed at 650 °C and (d) annealed at 750 °C for 1 hr in oxygen ambient. Atomic ratio of as-deposited film, Pb/(Pb+Ti) is 0.55.

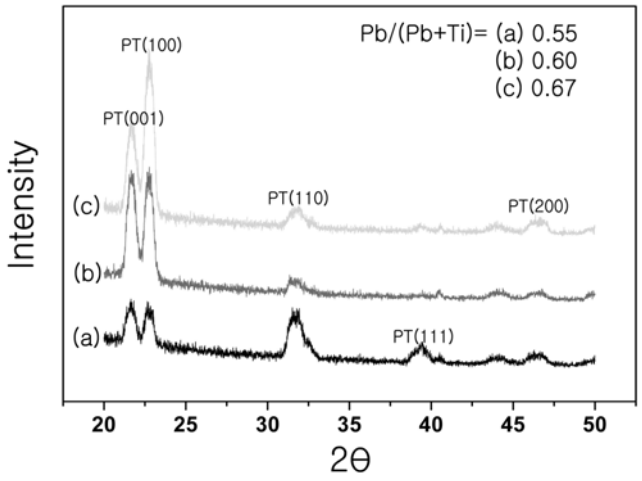

Fig. 6. XRD patterns of the annealed $PbTiO_3$ thin films at 650 °C for 1 hr under oxygen ambient. Atomic ratios, Pb/(Pb+Ti), of each film are (a) 0.55, (b) 0.60 and (c) 0.67.

sensitive to the substrate temperature and the Pb/Ti atomic ratios. Fig. 6 shows the diffraction patterns of perovskite $PbTiO_3$ thin films annealed at 650 °C for 1 hr under oxygen ambient, where the Pb/(Pb+Ti) atomic ratios of the films were (a) 0.55, (b) 0.60 and (c) 0.67 in the successive images. All of the specimens showed diffraction patterns related to the perovskite structure, where the peak of the strongest intensity had changed from the (001) to the (100) peak and (110) peak. Moreover, the (110) peak was weakened as the Pb content increased. Interestingly, it was reported [3] that when lead-rich films with Pb/(Pb+Ti) ratios between 0.55-0.65 were annealed above 600 °C, the presence of excess Pb, probably in the form of amorphous lead oxide, somehow promoted the crystallization of the $PbTiO_3$ phase.

Fig. 7 shows the surface morphologies of annealed $PbTiO_3$ thin films according to the variation of Pb content in the film. As the Pb content increased from Pb/(Pb+Ti)=0.38 to 0.60, the grain size was bigger and smoother. The stoichiometric amount of Pb reacts with the Ti element to form perovskite $PbTiO_3$ during annealing. The excess Pb element exists as a PbO compound of amorphous and/or microcrystalline phase, which fills up the grain boundary and reduces the leakage current path in the grain boundary region [17]. The formation of PbO networks in $PbTiO_3$ thin films remarkably decreased the electrical conductivity of the film [18]. In contrast, as the Ti content in films increased, the domains of the TiO_2 crystal with a high leakage current increased; additionally, the leakage current of the films may be predominated by the properties of the crystalline TiO_2 [19].

CONCLUSION

Perovskite $PbTiO_3$ thin films on Pt-coated Si wafer were successfully prepared through an interdiffusion process of PbO and TiO_2 multilayer films prepared by rapid thermal metal organic chemical vapor deposition (RTMOCVD). The exact composition of the $PbTiO_3$ thin film could be controlled by the thickness ratio of each constituent binary oxide layer of PbO and TiO_2. As the annealing temperature increased, the peaks related to perovskite $PbTiO_3$ in the XRD patterns became stronger and sharper. The surface roughness and grain size were increased as the annealing temperature increased. From this study, it was confirmed that a well defined perovskite $PbTiO_3$ thin film could be prepared by the interdiffusion of a multilayer structure of binary oxides PbO and TiO_2 with an appropriate post-annealing process.

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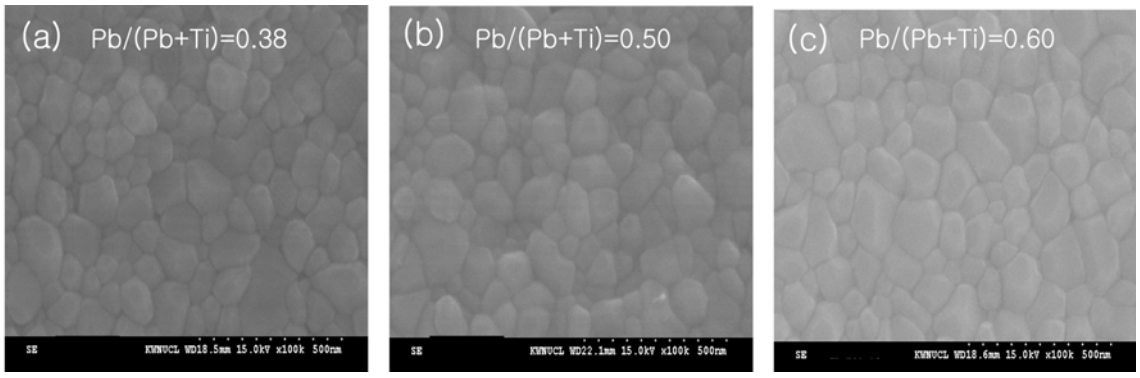

Fig. 7. Surface morphologies of $PbTiO_3$ films annealed at 750 °C under oxygen ambient for 1 hr. Atomic ratios, Pb/(Pb+Ti), of each film are (a) 0.38, (b) 0.50 and (c) 0.60.

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