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Ion Beam Assisted Crystallization Behavior of Sol-Gel Derived $PbTiO_3$ Thin Films

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Ion beam assisted crystallization behavior of sol-gel derived $PbTiO_3$ thin films, deposited on bare silicon (100) substrates by spin-casting method, has been investigated. Ar ion bombardment was directly conducted on the spin-coated film surface with or without heating the film from room temperature to 300°C. Ion dose was changed from 5×10^{15} to 7.5×10^{16} Ar^+/cm^2. Formation of (110) oriented perovskite phase was observed with ion dose above 5×10^{16} Ar^+/cm^2. Crystallization of $PbTiO_3$ thin film could be enhanced with increasing the Ar ion dose, or heating the substrate during ion bombardment. Crystallization of the $PbTiO_3$ films by ion bombardment was related to the local heating effect during ion bombardment.

Key words : $PbTiO_3$, Ferroelectric thin film, Perovskite, Ion bombardment, Crystallization

I. Introduction

Ferroelectric thin films, particularly Pb related materials such as $Pb(Zr,Ti)O_3$, $PbTiO_3$, $(Pb,La)TiO_3$, $(Pb,La)(Zr,Ti)O_3$, have been extensively investigated in recent years due to their potential applications for non-volatile memory, integrated electro-optic devices, infrared sensors, and microactuators.[1-10] Ferroelectric thin films have been fabricated using a variety of deposition techniques such as sputtering,[1,2] chemical vapor deposition,[3,4] ion beam deposition,[5] sol-gel,[6-9] and laser ablation.[10]

In order to crystallize as-deposited $PbTiO_3$ or $Pb(Zr,Ti)O_3$ films into ferroelectric perovskite phase, *in-situ* or post heat-treatments are required. However, lead volatility during annealing process at elevated temperatures usually hinders the formation of perovskite phase, resulting in deterioration of the ferroelectric properties of films. Thus, various methods, such as rapid thermal processing and control of PbO stoichiometry in sol-gel solutions, have been applied to prevent the lead deficiency of heat-treated films.[1,6,11]

Recently, it has been often reported that ion beam processing could be effective for modification of the sol-gel derived film properties. Shacam-Diamond *et al.* showed that the properties of sol-gel derived silica films could be modified by ion implantation with silicon and phosphorous ions.[12] Levine *et al.* also reported the crystallization of sol-gel derived zirconia films using Xe ion beam.[13] There has been few report up to now, however, which is concerned to the crystallization of perovskite materials using ion bombardment. Instead of post annealing process, ion bombardment may be applied as an alternative method for crystallization of sol-gel derived $PbTiO_3$ and $Pb(Zr,Ti)O_3$ films since heating for crystallization can be minimized with ion beam processing.

In this work, ion beam assisted crystallization behavior of sol-gel derived $PbTiO_3$ thin films was investigated with high energy Ar ion bombardment.

II. Experimental

Pb acetate trihydrate and Ti *iso*-propoxide were used as precursors, and 2-propanol was selected as a solvent. Chemical additives were added to modify hydrolysis and condensation rates of the complexed sol for long-time stability. $PbTiO_3$ thin films were deposited on bare silicon (100) substrates (1×1 cm) by spin-casting at 3000 rpm for 30 seconds. Deposited films were dried and pyrolized at 300°C for 2 minutes. This process was repeated several times to obtain the desired film thickness of 300 nm.

Deposited $PbTiO_3$ thin films were bombarded with 80 keV Ar ions at temperatures ranged from ambient to 300°C. Ar ion doses were selected to be 5×10^{15}, 5×10^{16}, or 7.5×10^{16} Ar^+/cm^2. Ion beam current density was fixed at 1.5 $\mu A/cm^2$ with the base pressure of 4×10^{-7} torr.

Thickness of the films was measured using scanning electron microscopy (SEM) and ellipsometry. Crystallization behavior of the films with ion bombardment was characterized using X-ray diffraction (XRD). Morphology of the ion-bombarded film surface was observed using SEM, and compositional analysis on the film surface was performed with Auger electron spectroscopy (AES).

III. Results and Discussion

XRD patterns of the films (Fig. 1), bombarded at room

temperature with ion doses ranged from 5×10^{15} to 7.5×10^{16} Ar^+/cm^2, clearly illustrate the effect of ion bombardment on crystallization of sol-gel derived $PbTiO_3$ films. With Ar ion dose of 5×10^{15} Ar^+/cm^2, there was no trace of XRD peaks, indicating amorphous state of the thin film. With appearance of (110) peak of the perovskite structure, however, it is clearly shown that perovskite phase was crystallized by increasing the Ar ion dose above 5×10^{16} Ar^+/cm^2. Small increase of the Ar ion dose from 5×10^{16} to 7.5×10^{16} Ar^+/cm^2 results in a large increase of (110) peak intensity, probably indicating the existence of a threshold in the ion dose for the crystallization of sol-gel derived $PbTiO_3$ films.

Fig. 2 shows the influence of heating temperature during Ar ion bombardment on the crystallization behavior of sol-gel derived $PbTiO_3$ films. Obviously, the overall peak intensities were enhanced with increasing heating temperature from 100°C to 300°C at the ion dose of 5×10^{15} Ar^+/cm^2. At heating temperature of 300°C, a peak around $\theta=36°$, which was presumed to be pyrochlore phase, appears with increase of all peak heights.

SEM micrographs of the surface morphology of $PbTiO_3$ films, bombarded with various Ar ion doses at room temperature, are given in Fig. 3. Morphology of the as-de-

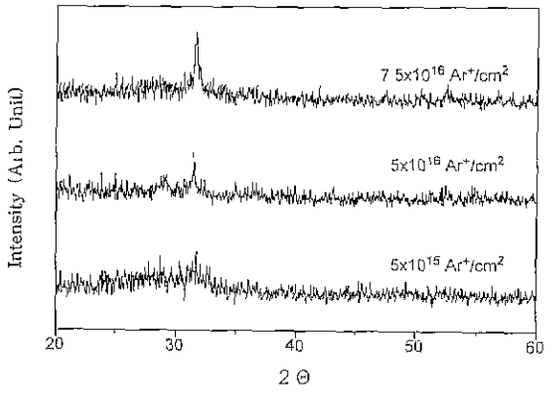

Fig. 1. XRD patterns of $PbTiO_3$ films bombarded with various Ar ion doses at room temperature.

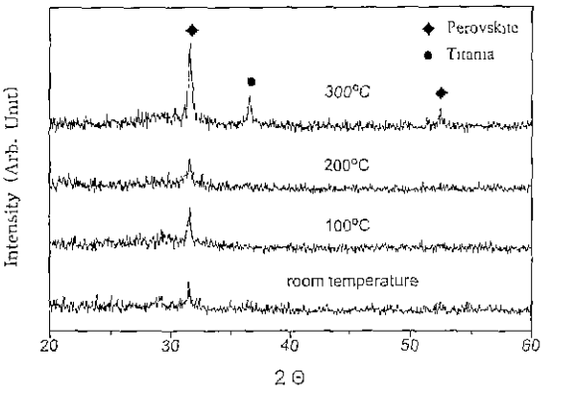

Fig. 2. XRD patterns of $PbTiO_3$ films bombarded with ion dose of 5×10^{15} Ar^+/cm^2 at various temperatures.

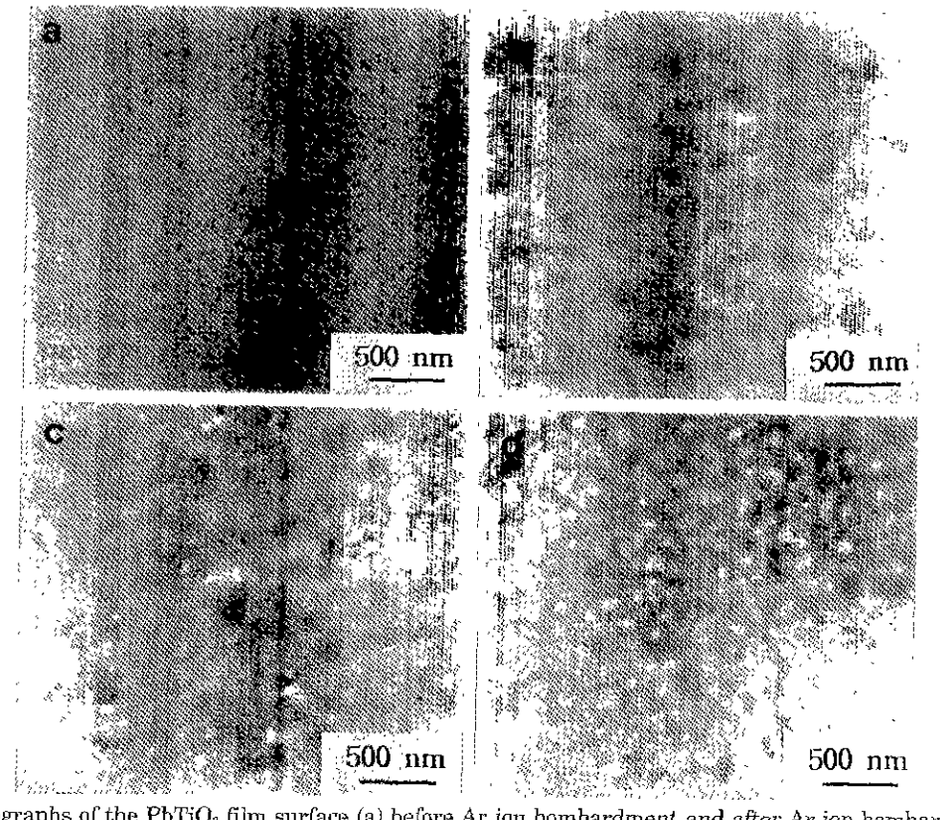

Fig. 3. SEM micrographs of the $PbTiO_3$ film surface (a) before Ar ion bombardment and after Ar ion bombardment at room temperature with ion dose of (b) 5×10^{15} Ar^+/cm^2, (c) 5×10^{16} Ar^+/cm^2, and (d) 7.5×10^{16} Ar^+/cm^2.

posited film surface, smooth and flat, was changed significantly with Ar ion bombardment. Surface of the films became rougher by ion bombardment with the ion dose of 5×10^{16} Ar^+/cm^2. However, small white particulates began to appear on the film surface bombarded at 5×10^{16} Ar^+/cm^2. The number of white particulates was increased and the size became larger with increasing Ar ion dose to 7.5×10^{16} Ar^+/cm^2. As shown in Fig. 4, which illustrates the surface morphology of films bombarded with Ar ions of 5×10^{16} Ar^+/cm^2 at various temperatures, white particulates were formed more heavily with increasing *in-situ* heating temperature during Ar ion bombardment. By comparing microstructures of $PbTiO_3$ films (Figs 3 and 4) with XRD data in Figs. 1 and 2, it can be suggested that crystallinity of the ion-bombarded $PbTiO_3$ films is associated with the formation of these white particulates.

Compositions of white particulates and the matrix were analyzed using AES equipped with fine focused beam (resolution: 50 nm) and scanning Auger microscopy (SAM). Fig. 5(a) and (b) show SAM image and Pb elemental mapping for films processed with Ar ion dose of 5×10^{16} Ar^-/cm^2 at 100°C. White particulates (area 1) and the matrix (area 2) in Fig. 5(a) corresponds to bright spot and dark area in Fig. 5(b), respectively. With Pb elemental mapping in Fig. 5(b), it can be clearly seen that white particulates (area 1) are Pb-rich compared to the matrix (area 2). Nano-probe AES spectra in Fig. 6 also confirm that there is a significant difference in Pb content between white particulates (area 1) and the matrix (area 2).

As composition of the film at spin-coated state could be thought to be uniform on whole film surface, occurrence of the compositional variation in the ion bombarded $PbTiO_3$ films (Figs. 5 and 6) should be due to Ar ion bombardment. Sputtering rate of Pb during ion bombardment has been reported to be faster than the sputtering rate of Ti.[14] When Ar ion beams impinge the film surface, some of Pb, Ti and O atoms are sputtered out[15] and heat is generated by thermal spike mixing process. Then, the temperature of the surrounding area would be locally increased high enough to crystallize the perovskite phase (area 1 in Fig. 5). Thus, the crystallization of sol-gel derived $PbTiO_3$ films by ion bombardment could be resulted from local heating during ion bombardment. Since the sputtering rate of Pb is faster than that of Ti,[14] the overall composition of the films was changed to be Pb-deficient from the stoichiometry by ion bombardment. With increasing Ar ion dose and heating temperature during ion bombardment, crystallization of the perovskite phase was promoted and white particulates, which were Pb-rich than the matrix, were formed more heavily (Fig. 1 to Fig. 4). Then, the composition of the matrix became Pb-deficient further, and pyrochlore phase was

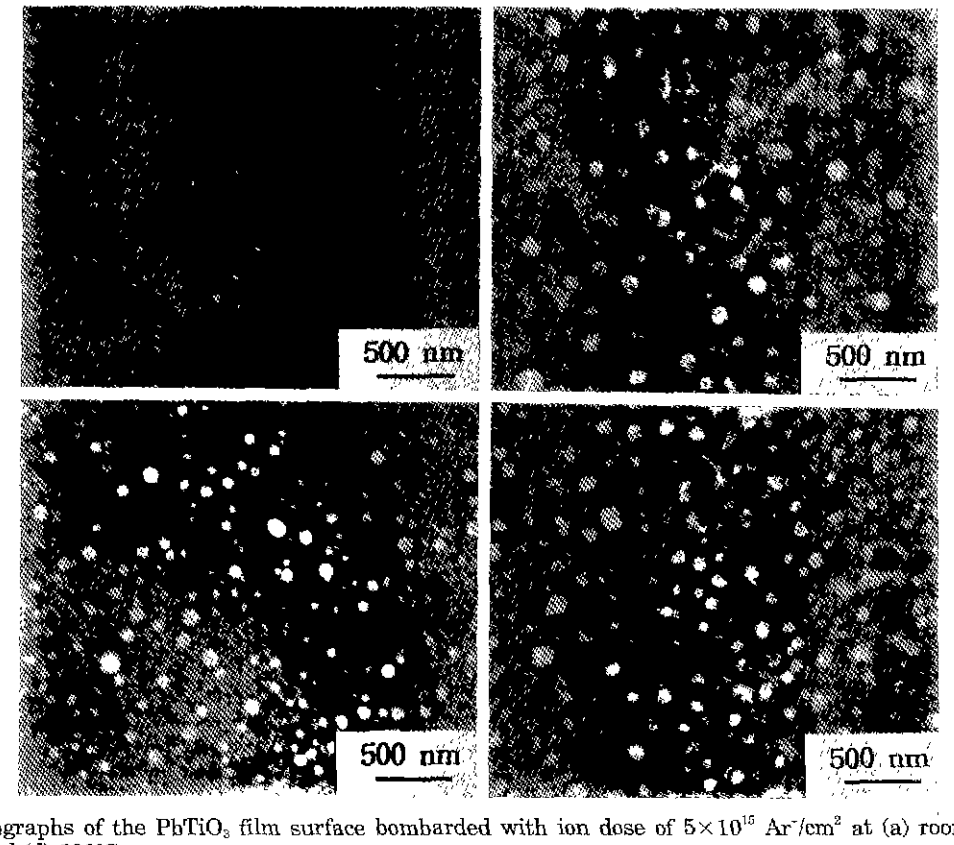

Fig. 4. SEM micrographs of the $PbTiO_3$ film surface bombarded with ion dose of 5×10^{16} Ar^-/cm^2 at (a) room temperature, (b) 100°C, (c) 200°C, and (d) 300°C.

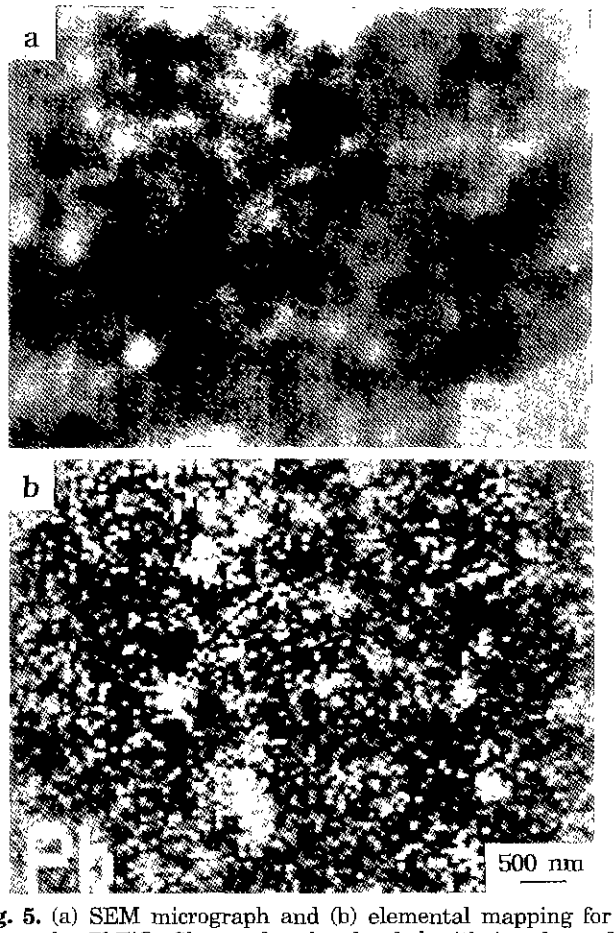

Fig. 5. (a) SEM micrograph and (b) elemental mapping for Pb on the $PbTiO_3$ film surface bombarded with ion dose of 5×10^{15} Ar^+/cm^2 at 100°C.

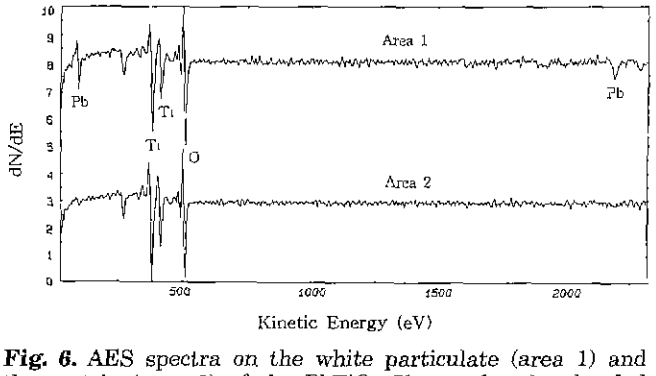

Fig. 6. AES spectra on the white particulate (area 1) and the matrix (area 2) of the $PbTiO_3$ film surface bombarded with ion dose of 5×10^{16} Ar^+/cm^2 at 100°C.

formed as shown in Fig. 2.

As there is a certain temperature range for post-annealing under which sol-gel derived $PbTiO_3$ or $Pb(Zr,Ti)O_3$ films could not be crystallized,[1,6,11] a critical ion dose would exist for ion bombardment under which local heating is not sufficient to obtain the crystallization of sol-gel derived films. This may explain the crystallization behavior of $PbTiO_3$ films with Ar ion doses, shown in Fig. 1. Enhancement of perovskite phase formation with increasing the *in-situ* heating temperature during ion bombardment, illustrated in Fig. 2, may be thought to be equivalent to crystallization behavior of the $PbTiO_3$ films with increasing the post-annealing temperature. With XRD data, microstructural observation and composition analysis on the ion-bombarded $PbTiO_3$ films, thus, it can be suggested that the crystallization of sol-gel derived $PbTiO_3$ films by high energy Ar ion bombardment was associated with local heating by thermal spike process during ion bombardment.

IV. Summary

Perovskite phase could be formed in sol-gel derived $PbTiO_3$ thin films by Ar ion bombardment with ion doses above 5×10^{15} Ar^+/cm^2. Crystallization of $PbTiO_3$ thin films could be enhanced by increasing Ar ion dose and increasing *in-situ* heating temperature during ion bombardment. Small white particulates, Pb-rich compared to the matrix, were formed on the $PbTiO_3$ film surface by Ar ion bombardment with ion doses above 5×10^{16} Ar^+/cm^2. Crystallinity of the ion bombarded $PbTiO_3$ films is associated with the formation of these white particulates. With XRD data, microstructural observation and composition analysis on the ion-bombarded $PbTiO_3$ films, it can be suggested that the crystallization of sol-gel derived $PbTiO_3$ films by high energy Ar ion bombardment is related to local heating of the films by thermal spike process during ion bombardment.

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