Preparation of PbTiO₃ Thin Films by Ion- and Photo-Assisted Evaporation

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PbTiO₃ thin films were deposited on MgO (100) substrate using a newly developed "ion- and photo-assisted evaporation system". The composition and structure of the films were highly dependent on the evaporation rates of Pb and Ti and on the substrate temperature. Controlling the evaporation rates to yield the stoichiometry, the perovskite phase formation took place merely at 500 °C under the irradiation of oxygen ion. When an excimer laser beam was irradiated simultaneously with an oxygen ion beam, the perovskite phase formation took place as low as at room temperature. This remarkable lowering of the deposition temperature was caused by ion- and photo-activation of the surface during the film growth.

1. Introduction

Ferroelectric thin films of perovskite PbTiO₃ and its solid solution systems (such as P(T)) have received considerable attention. While various deposition methods have been studied, high deposition temperature above 600°C has been required to obtain the ferroelectric perovskite phase in-situ. So far, it has been difficult to produce good quality thin films due to serious problems in fabrication process such as lead loss and inter-diffusion of elements at the elevated deposition temperatures. For potential applications such as bistable memories, pyroelectric detectors and optical switches, it is crucial to integrate these films by the low temperature process compatibly with semiconductor device processing.

We have recently developed a new deposition technique named ion- and photo-assisted evaporation, expecting the enhancement and improvement of deposition by ion- and photo-activation of the substrate surface. In this paper, we wish to report the formation of PbTiO₃ films at low substrate temperatures using this technique.

2. Experimental

The deposition apparatus used is "Hybrid Ion Beam Deposition Apparatus (A)" of Ion Engineering Center Corporation schematically shown in Fig.1. The cryo-pumped vacuum chamber (base pressure 10⁻⁶ Torr) contained an electron beam gun with three evaporating sources, combined with an electron beam source and an excimer laser.

Pb and Ti metals were individually evaporated from the sources using the electron-beam gun. The individual evaporation rates were controlled by quartz crystal monitors and stabilized with a feedback system. Simultaneously with the evaporation beams of Pb and Ti, an oxygen ion beam and an XeCl excimer laser beam were irradiated onto MgO (100) substrates at an angle of incidence of 45°, respectively.

The oxygen ion beam was generated by the bucket-type ion source (150mm in diameter) introducing the oxygen gas at a flow rate of 15 cc/min. The energy of the ions was 100 eV and the current of ion beam was 40 mA (0.23 mA/cm²). The background O₂ pressure during the deposition was about 10⁻⁴ Torr.

The output from a Lambda Physik LPX100
XeCl excimer laser operating at 100 Hz and 308 nm was irradiated onto a substrate. The laser pulse energy was constant at 0.15 J. The laser fluence was ca. 0.1 J/cm² shot.

Depositions were performed at substrate temperatures ranging from room temperature to 500°C. Film composition was analyzed by electron probe x-ray microanalysis (EPMA). The structure of the films was investigated by X-ray diffraction measurements (XRD).

3. Results and Discussion

The composition of the deposited films was highly dependent on the substrate temperature and the evaporation rates of Pb and Ti. Figure 2 shows the relative lead content (Pb/Pb+Ti) of the films deposited under the irradiation of oxygen ion beam (100 eV, 0.23 mA/cm²). Propensity for Pb loss at the elevated temperatures is attributed to the high volatility of Pb and/or its oxide as compared to that of Ti. To yield the stoichiometry of metals in PbTiO₃, the evaporation rates must be adjusted according to the substrate temperature.

When the ratio of evaporation rates were adjusted to yield the stoichiometry at the substrate temperature of 500°C, the perovskite phase formation took place. Figure 3 shows a typical diffraction pattern of a film deposited at 500°C (Pb:2A/s, Ti:0.1 A/s), where peaks representing the (100) and (200) reflections of perovskite are evident.

Figure 4 shows the dependence of the film products on Pb- and Ti-evaporation rates at the substrate temperature of 500°C. It is suggested that the optimum perovskite phase formation takes place at around the ratio of the evaporation rates (Pb/Ti) = 20. While TiO₂ was produced at higher Ti-evaporation rate, little PbO or nothing was produced at higher Pb-evaporation rate. This system might be governed by a rate-dependent competition as well as the stoichiometric requirements of the perovskite phase.

![Graph of Pb/(Pb+Ti) ratio vs. substrate temperature](image)

Fig. 2. Temperature dependence of Pb/(Pb+Ti) ratio of the deposited films. Pb evaporation rate was kept at 2.0 A/s, and Ti evaporation rates were at 0.10 and 0.25 A/s.

![XRD pattern of PbTiO₃ film](image)

Fig. 3. Typical XRD pattern of a film deposited at 500°C (Pb:2A/s, Ti:0.1A/s) by the process of ion-assisted evaporation.

![Graph of PbTiO₃ deposition rate vs. Ti evaporation rate](image)

Fig. 4. Dependence of the film products on Pb- and Ti-evaporation rates at the substrate temperature of 500°C by the process of ion-assisted evaporation.

The substrate temperature of 500°C by the process of ion-assisted evaporation is considerably lower than those previously required to obtain the ferroelectric perovskite phase in-situ using other method such as sputtering. This may be caused by the special oxygen incorporation in this method.

The oxygen incorporation during the film growth is of significant importance for the crystal formation of perovskite PbTiO₃. Ionized beam deposition seems to be beneficial for the formation of ferroelectric thin films of Pb-based perovskite materials by oxidizing the metal sufficiently and by lowering the substrate temperature. The oxygen ion energy and current density are important factors in the present technique.

Simultaneously with an oxygen ion beam, an excimer laser beam was irradiated onto the substrate for an ion- and photo-assisted deposition. Noticeable effects were observed at low substrate temperatures. Clearly
distinguished from the dark color of the unirradiated part, the laser beam irradiated part were pale yellowish in color and almost transparent. Figures 5(a) and 5(b) show the XRD diffraction patterns of the laser beam irradiated and unirradiated parts of the film deposited at room temperature, respectively.

The (100), (001) and (200) peaks of perovskite structure were observed only on the pattern of the irradiated part although they were weak in intensity due to the small sample size and low crystallinity. Therefore, the present experimental results show that the perovskite phase formation can be induced as low as at the substrate temperature of room temperature.

Systematic experiments varying ion energy, ion current density, and laser fluence will be required to clarify the mechanism of this process.

In conclusion, we have developed an ion- and photo-assisted deposition technique. Perovskite PbTiO₃ films were synthesized at low substrate temperatures, 500°C by ion-assisted deposition and room temperature by ion- and photo-assisted one, respectively. This technique would be a promising process for multi-component oxide thin films. Further work in process characterization and optimization is in progress.

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References