

화학증착법에 의해 제조된 PbTiO₃ 박막의 전기적 특성에 관한 연구

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Electrical Properties of PbTiO₃ Thin Films Fabricated by CVD

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ABSTRACT

Lead titanate thin films were deposited on titanium substrates by a chemical vapour deposition(CVD) process involving the application of vapour mixtures of Pb, ethyl titanate(Ti(C₂H₅O)₄), and oxygen.

The lead titanate having a stoichiometric composition has a dc conductivity of $3.2 \times 10^{-12} \Omega^{-1} \text{cm}^{-1}$ at room temperature. The nonsaturating loops observed in present investigation may be attributed to the TiO₂ and TiO layers between the conductive substrate and the PbTiO₃ ferroelectric film. The ferroelectric properties of the stoichiometric PbTiO₃ film included a remanent polarization of 14.1 $\mu\text{C}/\text{cm}^2$ and a coercive field of 20.16 kV/cm.

I. INTRODUCTION

Much attention has been recently paid to ferroelectric thin films from a viewpoint of their wide applications in electronic (1), optoelectronic devices(2), and optical integrated circuit elements(3). In spite of the tremendous potential demand, practical devices have not yet been developed for many applications. The main reason why these devices are not feasible is that PbTiO₃ is usually employed in the form of ceramics. The ceramic device requires both high operating voltages and considerable cost for the microfabrication processing.

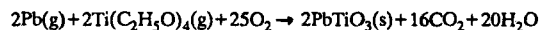
A number of efforts have been undertaken to prepare good ferroelectric thin films by various methods such as rf sputtering (4), electron beam evaporation(5), and ion beam sputtering(6).

The present work is concerned with the deposition of PbTiO₃ films by chemical vapour deposition(CVD). The films obtained by CVD were very uniform, and they do not require subsequent heat treatment. Though preparation of PbTiO₃ thin film by CVD had been regarded as very difficult, we obtained good films by CVD deposition on titanium substrates.

In our study, the electrical properties of the films were evaluated with respect to a wide range of deposition conditions.

II. EXPERIMENTAL DETAILS

The reaction chosen to produce the lead titanate films is written in over-all form as:



The growth system used for the lead titanate deposition consists of a mullite tube reactor of 38 mm inner diameter and a gas flow system. An alumina boat filled with Pb powder was placed at the highest temperature position near the gas inlet in a horizontal furnace, and a quartz boat holding a titanium disk substrate 14.9 mm in diameter and 2 mm thick was placed at the lower temperature part behind the Pb boat.

The temperature of the specimens was controlled by a k-type thermocouple in contact with the substrate. In our experiments, the reactor was kept at atmospheric pressure. The flow rate of Pb vapor was held constant at 200 sccm(standard cc/min), and the mole fraction of Ti(C₂H₅O)₄ vapor was varied from 0.02 to 0.23. The partial pressure of O₂ was varied from 0.06 to 0.32 atm. The temperature required to vaporize the Pb powder was about 1000 °C, and the Pb vapor was transported to the substrate by nitrogen(99.9999 %) as the carrier gas. The ethyl titanate(Ti(C₂H₅O)₄) vapor flowed from a nozzle at the ends of the delivery lines and was directed onto the substrate.

The thickness of the deposited PbTiO₃ films was determined from the change in weight(to microgram accuracy) of the titanium substrates of known surface area before and after depositing the PbTiO₃ films. The theoretical density of 7.9754 g/cm³ was used for thickness computation of the lead titanate film. This was confirmed by measuring the cross sections of fractured specimens with a scanning electron microscopy(SEM). Circular silver paste(Dupont 7095) electrodes were painted on the top surface of the film and were sintered for 30 min at 590 °C. The titanium substrates served as the bottom electrodes. The electrical properties measured for this study were the dielectric constant, dielectric loss, dc conductivity, and the

hysteresis behaviours.

III. RESULTS AND DISCUSSION

III-1. Electrical Properties of PbTiO₃ Films

The electrical behavior of the films was investigated in terms of the dielectric constant, dc conductivity, and polarization hysteresis.

III-1-1. Dielectric Constant

To characterize the ferroelectricity of the perovskite film, Curie point measurements were carried out. The dielectric constant and the loss tangent of films deposited on titanium substrates were obtained by measuring the capacitance and dissipation factor with a LCR meter (ANDO AG 4303) operated at 1 kHz. Figure 1 shows the variation of dielectric constant and loss tangent as functions of temperature for 4.7 μm thick films with stoichiometric composition. A phase transition is clearly present at about 480 °C which is about 10 °C lower than that of single crystals. Castellano et al.(7) also observed a shift in the transition temperature for PZT films. The dielectric constant changed by a factor of 5 in magnitude with variation of temperature from room temperature to the transition point. The presence of such peaks for films of thickness greater than 1 μm suggests that the grain size and the surface effects at the grain boundaries are important factors in the dielectric behavior of ferroelectric thin films(8).

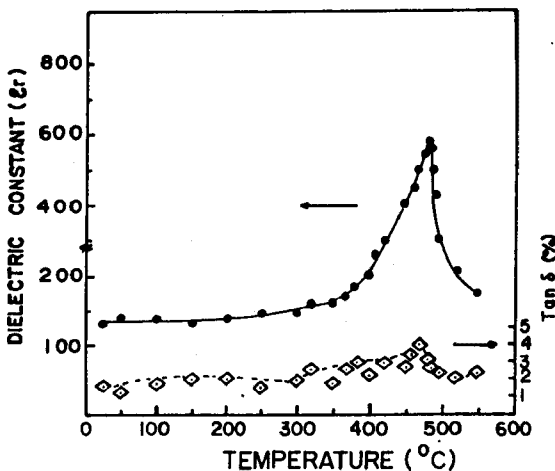


Fig.1 Variations of dielectric constant (ϵ_r) and dissipation factor ($\tan\delta$) with temperature. (deposition temperature, 750 °C; gas flow rate, 800 sccm; Ti(C₂H₅O)₄ fraction, 0.152; O₂ partial pressure, 0.06 atm)

III-1-2. dc Conductivity

The dc conductivity of the deposited PbTiO₃ films was measured using a ADVANTEST TR 8652 digital electrometer with a constant dc bias of 1.5 V applied to the sample.

The room temperature dc conductivity was a function of the substrate temperature. Figure 2 shows the effect of substrate temperature, and the conditions of film growth are indicated in the figure caption. dc conductivity decreases slightly with 10⁻¹⁰ order over the temperature range 600 - 700 °C. But dc conductivity of film deposited at 750 °C is almost similar that of the single crystal. In the deposition temperature range of 600 - 700 °C, in the deposition layer composed of the PbTiO₃ and TiO mixtures, the TiO phase seems to increase the electrical

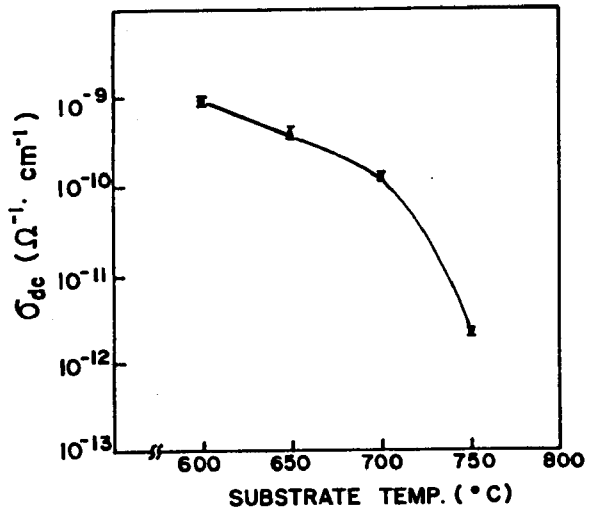


Fig.2 Variations of dc conductivity with substrate temperature.(gas flow rate, 800 sccm; Ti(C₂H₅O)₄ fraction, 0.152; O₂ partial pressure, 0.06 atm)

conductivity of the film. The variation of dc conductivity with temperature is shown in Fig.3. The variation of conductivity with temperature is similar to that reported by Krupanidhi et al.(9) for Pb(Zr,Ti)O₃ films. This exhibits a discontinuity at about 480 °C which is close to the temperature of the dielectric transition. At higher temperatures, the dc conductivity increased with a different slope. The activation energy(E) is calculated by the following equation:

$$\sigma = \sigma_0 \exp(-E/kT)$$

Numerical estimates of the activation energies in the ferroelectric and paraelectric phases are 0.73 and 1.17 eV, respectively. The different values of activation energy confirm the presence of ferroelectric and paraelectric phases in the deposited PbTiO₃. The important point to note is that an offset of dc conductivity

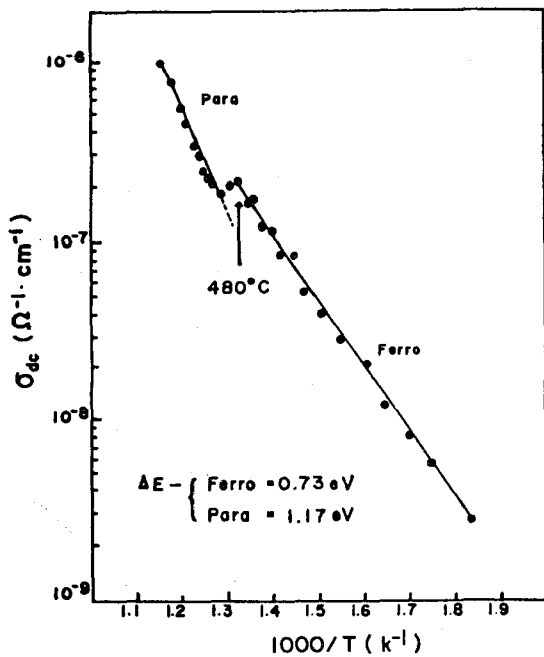


Fig.3 Variations of dc conductivity as functions of reciprocal temperature. (the same deposition condition as Fig. 2)

versus temperature is observed for the conductivity along the polar(C) axis for a single crystal and was found to be absent along the nonpolar(a or b) axes. The bend in the σ versus $1000/T$ plot near transition temperature and the different activation energies confirm the presence of ferroelectricity and preferred orientation along the C-axis in chemical vapour deposited thin films of $PbTiO_3$.

III-1-3. Polarization Hysteresis

The ferroelectric behavior of the $PbTiO_3$ film was examined by observing the polarization reversal using a Sawyer-Tower circuit. Figure 4 shows the ferroelectric hysteresis loops for a film deposited at various deposition temperatures. The loops observed in present investigations were nonsaturating , as can be seen from Fig.4. Further increase of electric field in the film caused its breakdown. Especially, a good hysteresis loop could not be obtained for films deposited at 750 °C(film with stoichiometric composition). This can be explained by the presence of the TiO_2 and TiO layers between the conductive substrate and the $PbTiO_3$ ferroelectric film which act as a lossy linear dielectric. The loop of Fig.4(C) actually represents the D vs. E characteristic of the $PbTiO_3$ film in series with the relatively high impedance of the linear dielectric intermediate layer. Since most of the applied voltage is dropped across the

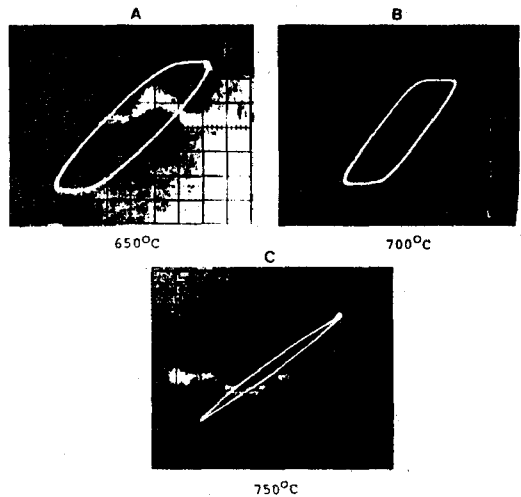


Fig.4 D-E hysteresis characteristic of $PbTiO_3$ film.
 A:deposition temperature,650 °C;Horizontal axis, 71.86 kV/cm/div; Vertical axis, 3.79 $\mu C/cm^2$ /div.
 B:deposition temperature,700 °C;Horizontal axis, 66.4 kV/cm/div; Vertical axis, 2.56 $\mu C/cm^2$ /div.
 C:deposition temperature,750 °C;Horizontal axis, 50.4 kV/cm/div; Vertical axis, 35.2 $\mu C/cm^2$ /div.
 (gas flow rate,800 sccm; $Ti(C_2H_5O)_4$ fraction,0.152; O_2 partial pressure,0.06 atm)

high impedance intermediate layer, the ferroelectric loop shows no approach to a saturation state.

The ferroelectric properties of the $PbTiO_3$ film having a stoichiometric composition were remanent polarization, 14.1 $\mu C/cm^2$, coercive field, 20.16 kV/cm.

IV. CONCLUSIONS

Chemical vapour deposition seems to be a suitable method for preparing $PbTiO_3$ films with better stoichiometry and crystallinity than those of conventionally prepared films. Both a well-defined dielectric anomaly and a break in dc conductivity were observed at the phase transition temperature 480 °C for films with stoichiometric composition. The nonsaturating loops observed in present investigation may be attributed to the presence of the TiO_2 and TiO layers between the conductive substrate and the $PbTiO_3$ ferroelectric film. The ferroelectric properties of the $PbTiO_3$ film having a stoichiometric composition were remanent polarization, 14.1 $\mu C/cm^2$, coercive field, 20.16 kV/cm.

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