The crystallographic properties of PbTiO₃ thin films fabricated by chemical vapour deposition

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Lead titanate, $PbTiO_3$, is a well-known material having remarkable ferroelectric, piezoelectric and pyroelectric properties. Thin films of lead titanate have been successfully fabricated by chemical vapour deposition on a titanium substrate. Layers deposited on the titanium substrate using PbO vapour and O_2 gas grow along the (1 0 1) preferred orientation. The maximum dielectric constant and loss tangent of $PbTiO_3$ thin film deposited on a titanium substrate are about 90 and 0.02, respectively. The electrical resistivity of the $PbTiO_3$ is about $10^9 \Omega$ cm. The deposition rates of $PbTiO_3$ deposited on the titanium substrate were 10 to 15 μm h^{-1}. A titanium dioxide interlayer formed between the $PbTiO_3$ film and titanium substrate materials. It might improve the adhesion of the film.

1. Introduction

Lead titanate is a well-known ferroelectric material having remarkable ferroelectric, pyroelectric, and piezoelectric properties [1, 2]. However, not many usable devices have so far been developed because $PbTiO_3$ is usually employed in the form of a ceramic, which requires a high operating voltage or is small in area. In order to break through these problems, a thin film of this material is effective because a large electric field can be applied to the film by an electric voltage; a fairly large area of film can be obtained easily and the film can be connected electrically to a peripheral circuit by depositing it on a silicon wafer [3].

Recently much attention has been paid to thin films of ferroelectric materials such as Pb(Zr, Ti)O₃ (PZT) and $PbTiO_3$ for opto-electronic devices, sensors and transducers [4]. These ferroelectric thin films are generally fabricated by r.f. sputtering, electron-beam evaporation and ion-beam sputtering at high substrate temperatures above 500° C and with subsequent heat treatment above 650° C. However, in the r.f. sputtering method there are some disadvantages as follows [5]:

(i) low deposition rate;
(ii) generation of surface defects and damage of substrate material by high-energy atoms, ions, and molecules;
(iii) stoichiometric change of the deposited film from the source material; and
(iv) surface roughness of the film.

The chemical vapour deposition (CVD) method can suppress these drawbacks compared with sputtering or the other deposition methods, so we have conducted a series of experimental trials for making $PbTiO_3$ thin films. In the study, the crystallographic and dielectric properties of the $PbTiO_3$ thin film fabricated by CVD were investigated.

2. Experimental procedure

The lead titanate coating was obtained by means of reactions between lead monoxide and titanium which was diffused from the titanium substrate at a temperature of 650° C. Chemically, the reaction can be described in the following way:

$$PbO + Ti\,(substrate) + O_2(in\,argon) \rightarrow PbTiO_3$$
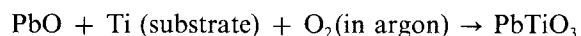
The growth system used for $PbTiO_3$ deposition consisted of a mullite-tube reactor of 27 mm inner diameter and a gas flow system, as shown in Fig. 1. An alumina boat filled with PbO powder was placed at the highest-temperature position near the gas inlet in a horizontal furnace, and a magnesia susceptor holding a titanium substrate in the form of a disc of diameter 10 mm and thickness 2 mm was put at the lower-temperature part behind the PbO boat. The temperature of the specimen was controlled by a K-type thermocouple in contact with the substrate.

In the experiments, the total pressure in the reactor was kept at atmospheric pressure. The temperature of the source was about 1150° C and PbO vapour was transported to the substrate by argon (99.99%) as the carrier gas. The equilibrium oxygen partial pressure of $PbTiO_3$ formation is very small, about 2.86 × 10^{-40} atm [6], so the available oxygen content in the reaction comes from the argon carrier gas. After the deposition, the reactor was cooled gradually to a temperature below 200° C at the highest-temperature point, in a flow of oxygen.

Crystallographic properties of the deposited $PbTiO_3$ layer were investigated by an X-ray diffractometer with Cu$K\alpha$ radiation and a nickel filter. A scanning electron microscope (SEM) was used to examine the surface morphologies of the $PbTiO_3$ deposits. The coating thickness was determined by observation of a cross-section through an optical microscope and an SEM. The dielectric properties of
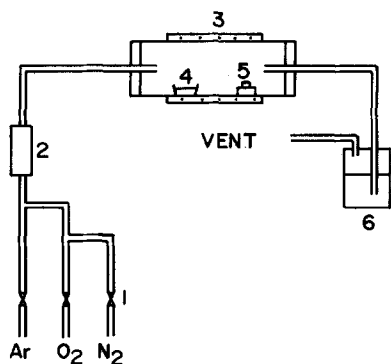
Figure 1 Schematic diagram of the CVD apparatus: (1) solenoid valve, (2) flowmeter, (3) resistance furnace, (4) PbO bath, (5) substrate, (6) trap.

the PbTiO₃ film were measured by an LCR meter (Ando AG 4303).

3. Results and discussion

3.1. The crystallographic properties of PbTiO₃ thin films

X-ray diffraction patterns of the PbTiO₃ thin films deposited on titanium substrates at 650°C for different argon gas flow rates are shown in Fig. 2. As shown in Fig. 2a, the pattern of PbTiO₃ powder exhibits many lines corresponding to the main crystallographic planes, but the patterns of the deposited films show that the diffraction lines correspond to several planes of tetragonal PbTiO₃.

Strong orientation was found in the patterns of the deposited films. As the flow rate of the argon carrier gas decreases, the peak of the (1 0 1) plane is higher than that of the other planes. The result shows that the deposit layer grows along the (1 0 1) preferred orientation. Also, in the X-ray pattern, a peak of TiO₂ (rutile) was found. Fig. 3 shows the effect of the total flow rate of the reactant gases on the deposition rate of PbTiO₃. The deposition rate increases almost linearly with an increase in the square root of the total flow rate. The PbTiO₃ deposition reaction is controlled by the mass transport of the reactant gases within the experimental range. This conclusion could be explained as follows.

On the assumption that the reactant gases are completely mixed and that mass transport of the reactant gases occurs through diffusion due to the concentration gradient of the reactant gases in the vicinity of the substrate surface, the flux J_D of the reactant gases by mass transport can be expressed by Fick's first law [7]:

$$J_D = -D_v \left(\frac{\Delta c(x)}{\Delta x} \right) \tag{1}$$

$$J_D = D_v \left(\frac{P_b - P_s}{\delta RT} \right) \tag{2}$$

Here D_v is the diffusivity of a reactant gas in the vapour phase, x is the distance from the substrate surface, $c(x)$ is the concentration of the reactant gas,
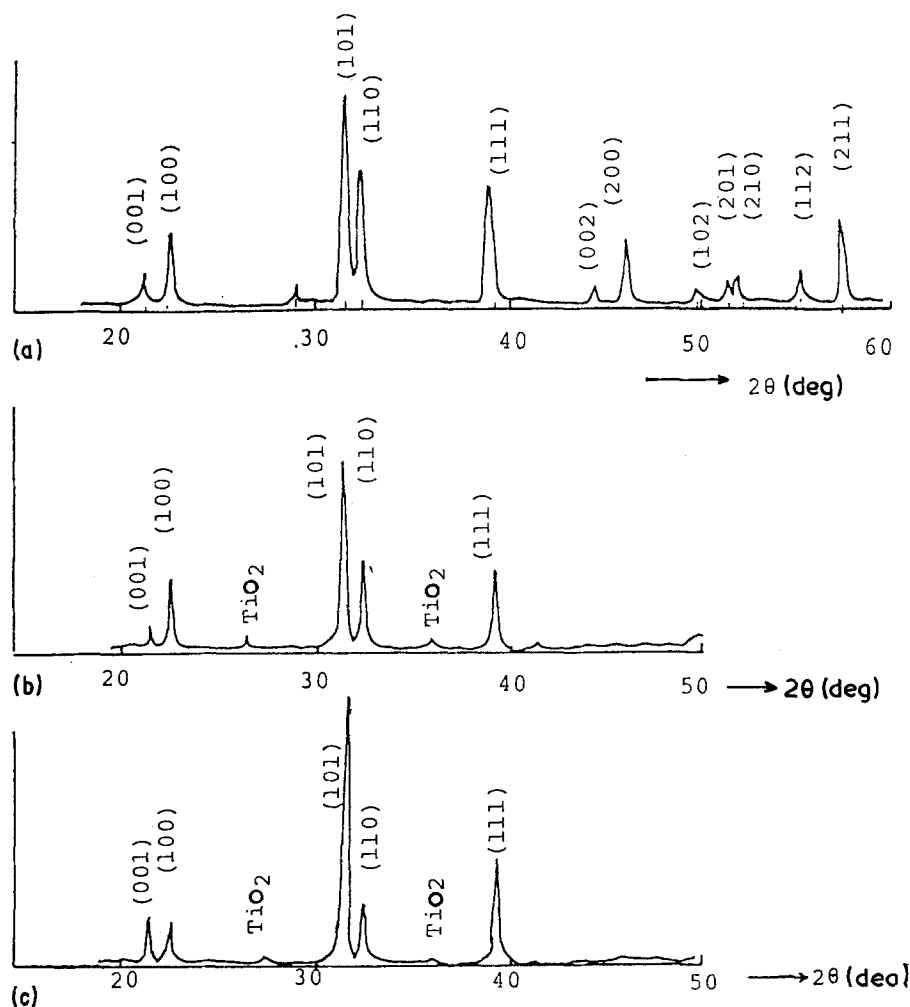

(a)

(b)

(c)

Figure 2 X-ray diffraction patterns of (a) well-reacted PbTiO₃ powder; (b, c) the films made from PbO on a titanium substrate at 650°C. Argon flow rate: (b) 600 cm³ min⁻¹, (c) 400 cm³ min⁻¹.

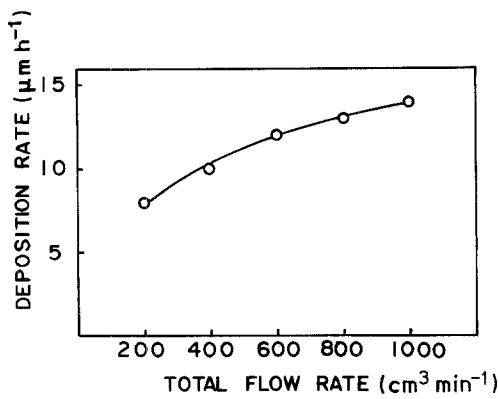Figure 3 The dependence of the deposition rate of PbTiO₃ on the total flow rate of the reactant gases (deposition temperature 650° C).

Figure 4 The dependence of the deposition rate of PbTiO₃ on the square root of the total flow rate (deposition temperature 650° C).

P_b and P_s are the partial pressures of the reactant gas in the bulk and at the substrate, respectively, δ is the boundary layer thickness, R is the gas constant and T the absolute temperature. Since D_v, P_b, P_s, R and T remain constant in this experiment, J_D is inversely proportional to δ.

Although δ increases along the length of the substrate, the average value of δ is given by following equation [8]:

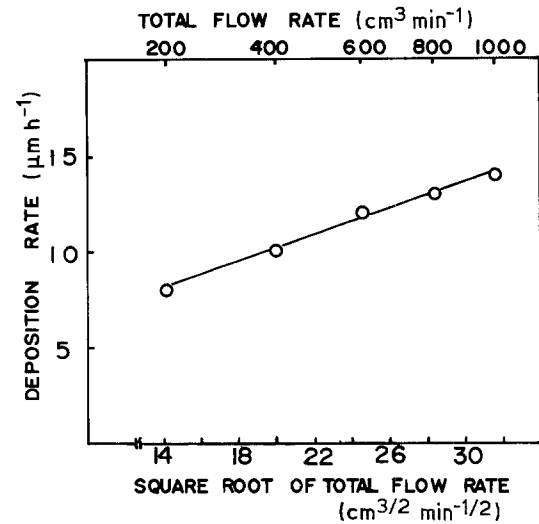$$\bar{\delta} = \tfrac{2}{3}L\left(\frac{\mu}{\varrho uL}\right)^{1/2} \tag{3}$$

In this equation $\bar{\delta}$ is the average boundary layer thickness, L is the length of the substrate, μ is the viscosity of the vapour phase, ϱ is the density of the vapour phase and u is the total velocity of the reactant gases. Since L, μ and ϱ are constant, $\bar{\delta}$ is inversely proportional to the square root of the total velocity u of the reactant gases.

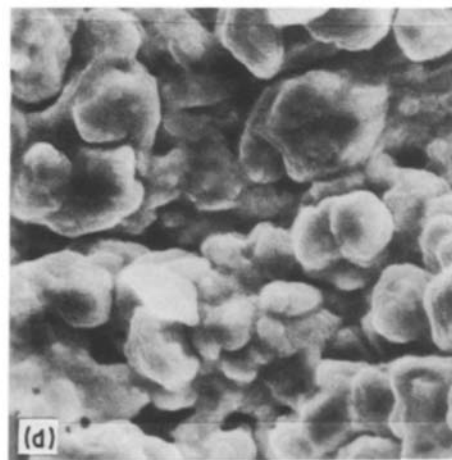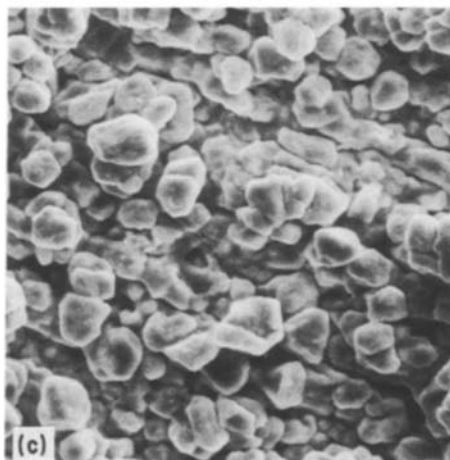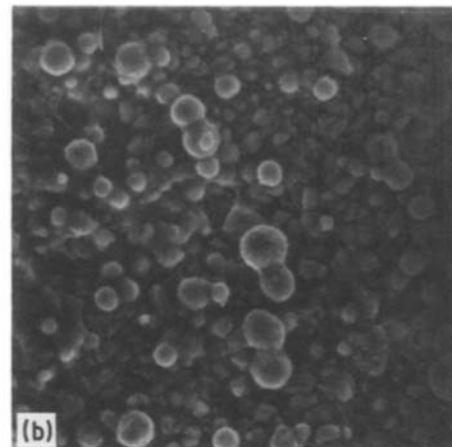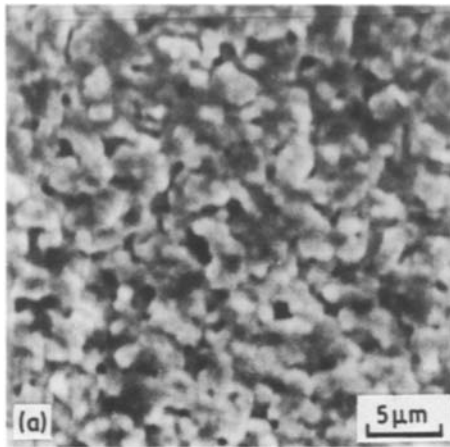Hence, the combination of Equations 2 and 3 gives

Figure 5 Scanning electron micrographs of the surface of PbTiO₃ crystals deposited at various total flow rates (deposition temperature 650° C, deposition time 1 h). Flow rate (cm³ min⁻¹): (a) 200, (b) 400, (c) 600, (d) 1000.
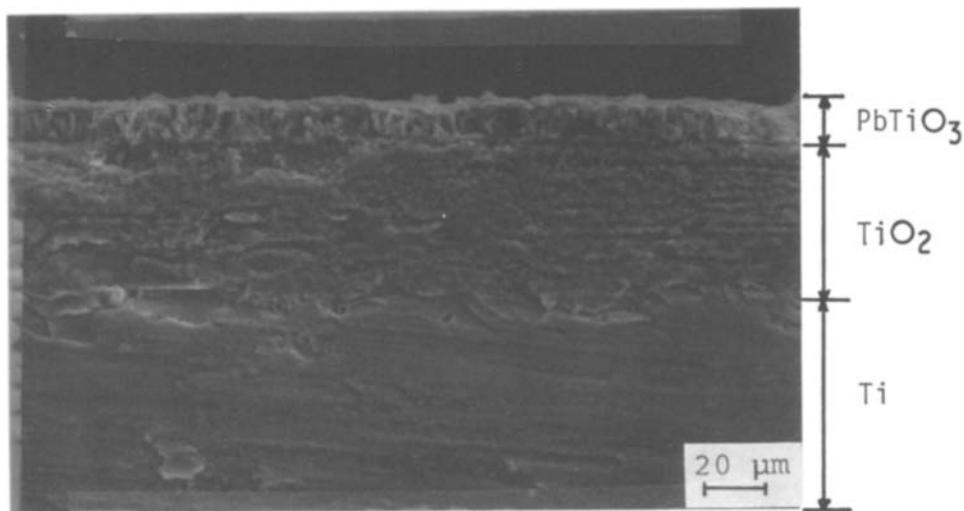
Figure 6 Scanning electron micrograph of fracture surface of PbTiO$_3$ coating layer deposited for 1 h (deposition temperature 650° C, total gas flow rate 400 cm^3 min^{-1}, system pressure 1 atm).

the following:

$$J_D = C_0 q^{1/2}$$

where C_0 is a constant and the total flow rate q is used instead of u (where q is the product of u and the cross-sectional area of the deposition chamber). When the deposition reaction is controlled by the mass transport of the reactant gases, the deposition rate of PbTiO$_3$ is proportional to the mass transport flux J_D. Therefore, the deposition rate of the PbTiO$_3$ is proportional to the square root of the total flow rate (Fig. 4).

The morphologies of PbTiO$_3$ deposited at 650° C and 1 h for various flow rates are shown in Fig. 5. The grain size of the deposited PbTiO$_3$ increases with an increase in the flow rate of the argon carrier gas. In particular, above 800 cm^3 min^{-1} the surface appearance is porous as if a homogeneous reaction has happened.

A scanning electron micrograph of the fracture sur-

face of a PbTiO$_3$ coating layer deposited for 1 h at 650° C is shown in Fig. 6. Fig. 6 shows that a second layer is formed. The grain morphologies of the second layer seem to be equiaxed and its thickness is very great. The second layer turned out to be TiO$_2$ (rutile) by X-ray diffraction and energy-dispersive spectrometry (EDS) analysis.

As the formation of a TiO$_2$ layer is kinetically very fast, a TiO$_2$ (rutile) layer is formed at the initial nucleation stage of the deposition and a PbTiO$_3$ layer, which is the most stable phase, is formed at the growth stage. Ultimately, the growth of the TiO$_2$ layer is suppressed by the formation of the PbTiO$_3$ layer. Thus the grain morphologies of the TiO$_2$ layer were presupposed to be equiaxed. The PbTiO$_3$ layer has a columnar structure and grows vertically on the substrate.

Fig. 7 shows EDS analysis of the fracture surface of PbTiO$_3$ deposited at 650° C. As shown in the EDS analysis, elemental lead is found only in the first layer.
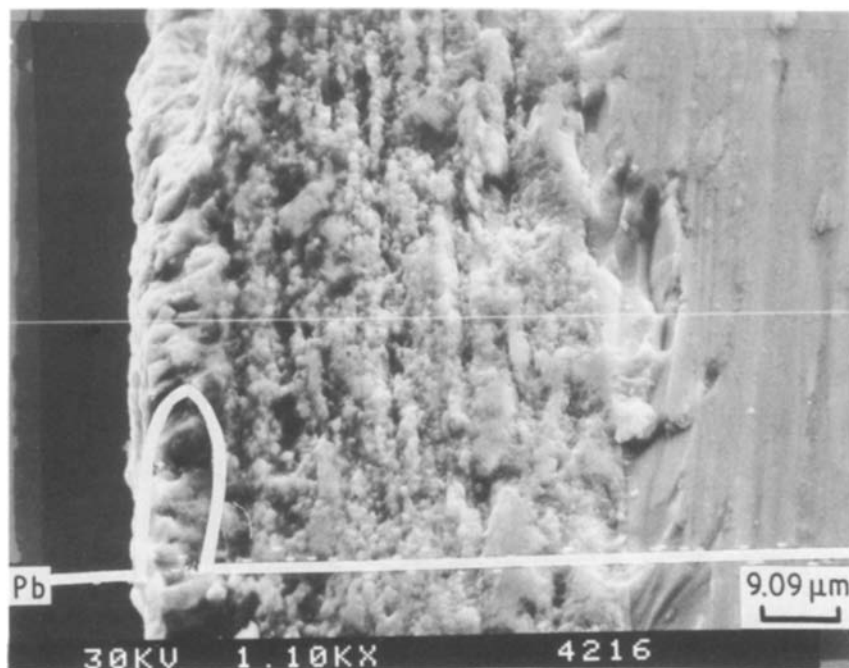

Figure 7 Line scanning micrograph of the fracture surface of PbTiO$_3$ coating layer deposited for 1 h (deposition temperature 650° C, total gas flow rate 400 cm^3 min^{-1}).
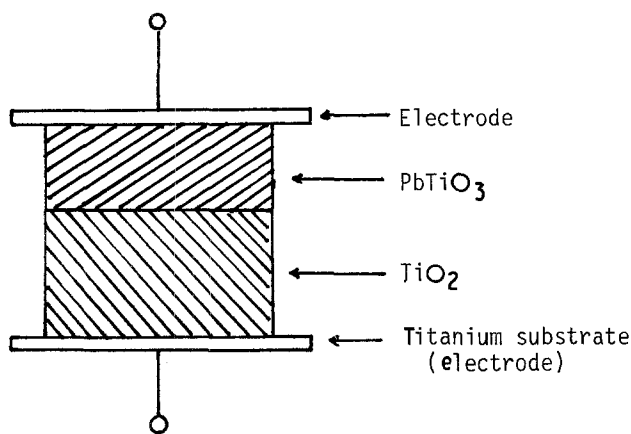
Figure 8 Schematic diagram of arrangement used to measure the dielectric properties of layers having different characteristics in a dielectric.

Therefore, the first layer turns out to be the $PbTiO_3$ deposit layer. Titanium is present in the entire layer.

3.2. Electrical properties of $PbTiO_3$

Some fundamental dielectric properties of the $PbTiO_3$ thin films deposited on a titanium substrate have been measured. A schematic diagram of the arrangement used to measure the dielectric properties is shown in Fig. 8.

Mixtures of dielectrics can be most simply considered on the basis of layer materials with the layers normal to the applied field [9]. When the layers are parallel to the capacitor plates, and the inverse capacitances are additive, then

$$\frac{1}{\kappa'} = \frac{v_1}{\kappa'_1} + \frac{v_2}{\kappa'_2}$$

where v_1 and v_2 are the volume fractions of TiO_2 and $PbTiO_3$ phases equal to the relative plate thicknesses, respectively; κ' is the total dielectric constant, κ'_1 the dielectric constant of TiO_2 and κ'_2 the dielectric constant of $PbTiO_3$.

The dissipation factor (tan δ) of $PbTiO_3$ was also obtained. As the dissipation factor of the TiO_2 layer is much lower than that of $PbTiO_3$, the value of the measured dissipation factor is considered to be that of $PbTiO_3$. The dielectric properties of $PbTiO_3$ are shown in Table I. The dielectric constant and the

TABLE I Electrical properties of $PbTiO_3$ thin films deposited on a titanium substrate

Film thickness (μm)	Dissipation factor, tanδ	Dielectric constant, ε_r
10	0.019	88
12	0.019	88
14	0.021	90

dissipation factor are nearly constant irrespective of the thickness of $PbTiO_3$.

4. Conclusions

$PbTiO_3$ thin films have been grown on a titanium substrate by chemical vapour deposition. The $PbTiO_3$ deposition reaction is limited by a mass-transport-controlled mechanism within the experimental range and the deposit layer grows along the (1 0 1) preferred orientation. The $PbTiO_3$ layer has a columnar structure and grows vertically on the substrate. A titanium dioxide interlayer is formed between the $PbTiO_3$ film and the titanium substrate material. This might improve the adhesion of the film. The obtained $PbTiO_3$ film has nearly constant dielectric properties irrespective of the film thickness and shows good dielectric properties.

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