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Preparation and characterization of $PbTiO_3$ thin films by metalorganic chemical vapor deposition on a $La_{0.5}Sr_{0.5}CoO_3$ metallic oxide electrode

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Abstract

(001)-oriented $PbTiO_3$ thin films have been grown in situ on $La_{0.5}Sr_{0.5}CoO_3/SrTiO_3$ by metalorganic chemical vapor deposition under reduced pressure, while thin films of $La_{0.5}Sr_{0.5}CoO_3$ (LSCO), which is an oxide perovskite metallic material, have been deposited on $SrTiO_3$ substrates by pulse laser deposition. The optimum growth conditions of (001)-oriented $PbTiO_3$ thin films were established. The natures of the films are characterized by X-ray diffraction, optical microscopy and scanning electron microscopy. The acoustic transducers operating at 9.58 GHz were made based on the $PbTiO_3/LSCO/SrTiO_3$ heterostructures. The characterization of $PbTiO_3$ thin films shows that the LSCO, at least in some applications such as piezoelectric transducers and resonators, is a suitable electrode material.

Keywords: Chemical vapour deposition; Heterostructures; Oxides; Piezoelectric effect

Lead titanate ($PbTiO_3$) is a well-known perovskite-type ferroelectric material with a large spontaneous polarization, a small dielectric constant, a high Curie temperature (490 °C) and a high electromechanical coupling constant, thus it is a promising material for piezoelectric and pyroelectric devices. In recent years, much effort aimed to develop the techniques of preparing device-quality ferroelectic thin films, e.g. $Pb(Zr_xTi_{1-x})O_3$ (PZT), $(Pb_xLa_{1-x})(Zr_yTi_{1-y})_{1-x/4}O_3$ (PLZT) and $PbTiO_3$, was stimulated by the tendency to integrate silicon integrated circuits with oxide dielectrics to develop integrated ferroelectric devices [1]. Some investigations have been reported successful to prepare epitaxial $PbTiO_3$ thin films on a $SrTiO_3$ substrate [2–5] by metalorganic chemical vapor deposition (MOCVD), which have been well developed to prepare compound semiconductor thin films and superlattices [6], and recently used to grow ferroelectric thin films. However, for some applications such as piezoelectric, pyroelectric and electro-optic devices, the high-quality ferroelectric thin film must be grown on an electrode/substrate. Conventionally, Pt was widely used as the base or top electrode for these applications. However, only poor-quality ferroelectric film had been grown on a Pt base electrode. Many studies had been made to improve traditional techniques, e.g. sputtering or sol–gel, in the hope of obtaining a high-quality ferroelectric film on a Pt base electrode. For example, Kushida and Takeuchi [7] reported that *c*-axis oriented $PbTiO_3$ films were formed on patterned Pt electrode films through seeded lateral overgrowth of $PbTiO_3$ on $SrTiO_3$. This experiment indicated that the growth mechanism of a $PbTiO_3$ thin film on Pt was different from that on $SrTiO_3$ because of the different surface free-energy of $PbTiO_3/Pt$ and $PbTiO_3/SrTiO_3$, which may imply that the $PbTiO_3$ thin films grown on Pt should be intrinsically of poor quality. The high-angle grain boundaries occurring in the poor-quality ferroelectric films lead to the degraded performance of the device. Recently, much effort [8,9] has been devoted to developing perovskite-type metallic oxides as electrodes to prepare device-quality ferroelectric heterostructures. Ramesh et al. reported the preparation of the heterostructure of PZT/YBCO [8] and PZT/$La_{0.5}Sr_{0.5}CoO_3$ (PZT/LSCO) [9], Eom et al. [10] used the pulse laser deposition (PLD) technique to prepare the heterostructure of PZT and $SrRuO_3$ which exhibited a superior fatigue characteristic.

In this paper we report our study on the preparation and acoustic properties of (001)-oriented $PbTiO_3$ thin films on LSCO/(001)$SrTiO_3$ substrates by MOCVD at reduced pressure. LSCO [11] is a pseudocubic perovskite, with a pseudocubic lattice parameter of 3.84 Å. The similar crystal structure and small lattice mismatch of LSCO and $PbTiO_3$ ($a_{PbTiO3}=3.9$ Å, mismatch ~1%) allow us to grow a high-

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quality ferroelectric film on a LSCO electrode. The (100)-oriented LSCO metallic thin films were deposited on a $SrTiO_3$ substrate by PLD during which the substrate temperature was held at 700 °C [12]. The wavelength of the excimer laser was 248 nm and the power was 12 mJ mm^{-2}.

The $PbTiO_3$ thin films were deposited in a low-pressure, horizontal quartz reactor described in more detail elsewhere [5]. The reaction chamber had an inner diameter of 47 mm and contained a resistor-heated stainless steel susceptor. The temperature of the susceptor was measured with a thermocouple inserted in its center. The metalorganic precursors titanium tetra-isopropoxide($Ti(O^iPr)_4$) and tetra-ethyl-lead (TEL) had been purified by ourselves and were held in electronically thermostatic stainless evaporators with the precision of the source temperature controlled within ±0.5 °C. The typical experimental conditions are summarized in Table 1.

The film thickness was measured with a surface profilometer on a delaminated portion of the films with a precision of ±10 Å. The deposition rate was about 0.15 μm h^{-1} at a substrate temperature of 650 °C and was almost independent of the growth temperature from 550 to 650 °C in this study. The surface of the films was mirror smooth and firmly attached to the substrates. However, films grown at substrate temperatures below 650 °C were easily peeled away from the substrate.

Analysis of the structure and identification of the phases were performed with a Ragaku X-ray diffractometer using nickel-filtered Cu Kα radiation. X-ray diffraction measurements of films deposited at 550–600 °C indicated that two stable phases, PbO(red) and $PbTiO_3$, coexisted in the films as shown in Fig. 1(b). With the rising of growth temperature, the PbO was successfully eliminated at a higher deposition temperature of 650 °C (Fig. 1(a)). Fig. 2 shows the dependency of (001)$PbTiO_3$ content (η) in the films on the growth temperature. Following Iijima et al. [13], η was calculated as below. Owing to the 100% PbTiO in film No. 1 (Fig. 1(a)), its intensity ratio of $PbTiO_3(001)$ and $SrTiO_3(001)$ $(I_{PbTiO3(001)}/(I_{PbTiO3(001)}+I_{SrTiO3(001)})$, was used as the ratio coefficient, α. Then η of the films including the PbO and (001) $PbTiO_3$ phases were defined as:

$$\eta=\alpha I_{PbTiO_3(001)}/(I_{PbTiO_3(001)}+I_{SrTiO_3(001)})$$

These calculated η using data of the (001) reflections (Fig. 1) were the same as the data of the (002) reflection within experimental error. Furthermore the results were consistent with the composition measurement of these films by an electronic probe analyzer (JAX-8800M). The grown films with a rough surface, loosely attached to the substrate, coincided with the occurrence of PbO in the films. An XRD pattern of the θ–2θ scan, in which only (001) reflections of $PbTiO_3$, LSCO and $SrTiO_3$ are observed, shows perfectly c-axis oriented $PbTiO_3$ thin film grown at 650 °C on LSCO/$SrTiO_3$. The c-axis lattice constant of the $PbTiO_3$ thin film is 4.090(±0.002) Å, which is less than the constants reported for both bulk $PbTiO_3$ (4.15 Å) and the epitaxial $PbTiO_3$ films grown on a $SrTiO_3$ substrate (4.126 Å) [2,5]. The more significant difference of the c-axis lattice constant for the $PbTiO_3$/LSCO/$SrTiO_3$ system than the $PbTiO_3$/$SrTiO_3$ sys-

Table 1
MOCVD process conditions

Substrate	LSCO/(001)$SrTiO_3$
Substrate temperature	~650 °C
Reactor pressure	15.0 Torr
Carrier gas	N_2
T_{TIP}	65 °C
T_{TEL}	35 °C
TEL carrier flow rate	~200 sccm
TIP carrier flow rate	~200 sccm
O_2 flow rate	~250 sccm

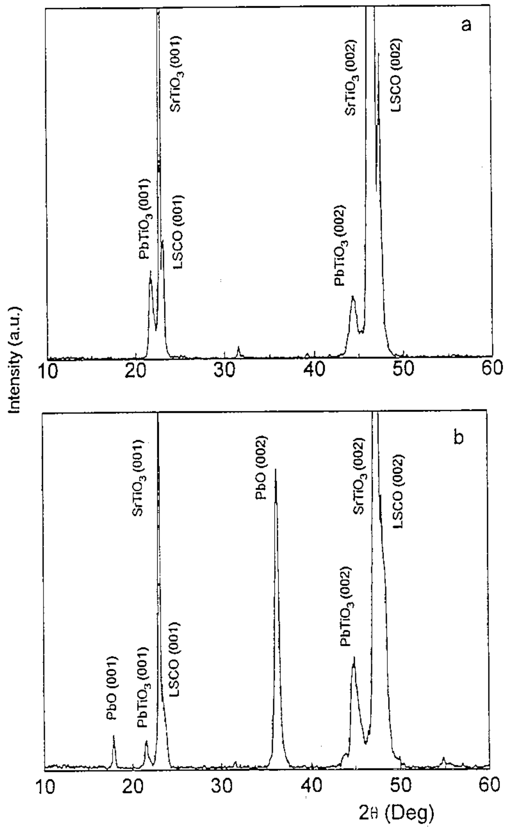

Fig. 1. X-ray diffraction patterns of MOCVD thin films on LSCO/$SrTiO_3$ at growth temperatures of 650 °C (a) and 550 °C (b). Below 650 °C, as-grown films were contaminated by PbO.

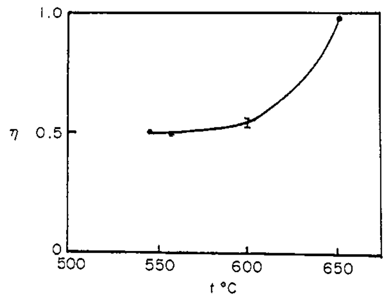

Fig. 2. Variation of the content of (001) $PbTiO_3$ in the thin films vs. the growth temperature.

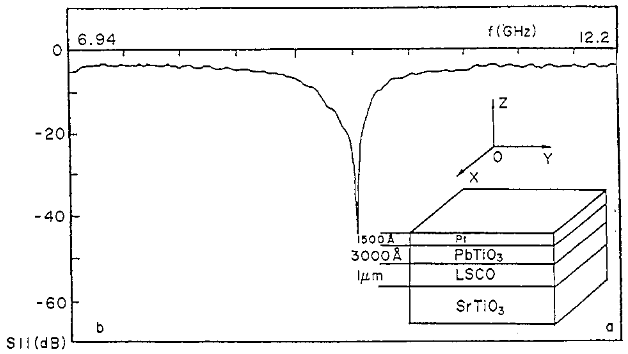

Fig. 3. (a) Schematic diagram of the resonator. (b) Measured reflection coefficient of the resonator No. 1. The rectangular coordinate indicates the magnitude of the reflection, the horizontal scale is frequency centered at 9.5 GHz with scanning width 5.3 GHz.

Table 2
Resonator measurements of the three samples

	f_0 (GHz)	Δf (MHz)	T (°C)	d (μm)	S_{11} (dB)	η
No. 1	9.58	940	650	0.3	−44.88	1.00
No. 2	9.73	640	600	0.27	−16.5	0.52
No. 3	9.77	630	550	0.27	−16.2	0.50

tem may indicate that the $PbTiO_3$ films on $LSCO/SrTiO_3$ suffer more serious tensile strain than $PbTiO_3$ on $SrTiO_3$ [2].

The surface morphology of $PbTiO_3$ films at growth temperature 650 °C was observed using Leitz optical microscopy with a magnification of 150× and scanning electronic microscopy (SEM) with a magnification of 7000×. At a higher magnification the film displays a polycrystalline nature.

Using these ferroelectric films with a thickness of ~0.3 μm, a set of transducers have been made. A schematic diagram of the resonator is shown in Fig. 3(a). The two electrodes are in the X–Y plane parallel to the surface of the films, i.e. perpendicular to the c axis of the $PbTiO_3$ thin films. Under the action of an external electric field, an acoustic wave is excited inside the resonator through the piezoelectric effect [14]. In theory, the resonance frequency of the resonator is determined by the velocity of the acoustic wave and thickness of the film [13].

With an Hp 8510C network analyzer ranging from 450 MHz–20 GHz, reflection coefficients of the resonators were measured. It is well-known that if the impedance of a load is not equal to that of the electric measurement system, the electric energy will be reflected by the load, i.e. with a great reflection coefficient, and when a resonator is in oscillation, the reflection coefficient will approach its minimum. The minimum of the reflection coefficient of the resonator made by a (001)-oriented $PbTiO_3$ film with a 0.3 μm thickness is −44 dB at the resonant point of 9.58 GHz (Fig. 3(b)). The measurements of the resonators are summarized in Table 2, where f_0 is the resonant frequency, Δf is the 3 dB bandwidth, T is substrate temperature, and S_{11} is the reflection coefficient. It should be noted that the reflection coefficients at the oscillation point of the resonators made of the thin film with PbO and $PbTiO_3$ were greater than that of the resonators made of a pure ferroelectric phase $PbTiO_3$ with a (001) orientation, and S_{11} of sample 2 was very close to that of sample 3, while the η values of samples 2 and 3 were close. The results may imply that the occurrence of the PbO phase in films degrades the electromechanical coupling coefficient of the $PbTiO_3$ film, and thus energy transforming from electric energy to acoustic energy decreases with increasing reflection coefficient, S_{11}, of the resonators.

In summary, we have shown that the (001)-oriented $PbTiO_3$ film can be grown on metallic LSCO /$SrTiO_3$ substrates by MOCVD much more conveniently than it can be grown on Pt. The suitable conditions for growth of the (001)-oriented $PbTiO_3$ thin film were investigated. The acoustic resonators of 9.58 GHz were prepared based on the $PbTiO_3$/LSCO/$SrTiO_3$ heterostructure. Future efforts will be focused on preparing epitaxial $PbTiO_3$ thin film on LSCO/$SrTiO_3$.

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