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1995 J. Phys.: Condens. Matter 7 9075

(http://iopscience.iop.org/0953-8984/7/47/023)

J. Phys.: Condens. Matter 7 (1995) 9075–9080. Printed in the UK

(001)-oriented $PbTiO_3$ ferroelectric thin films grown on Si by metal-organic chemical vapour deposition

Wen-Hui Ma, Ming-Sheng Zhang, Li Shun, Yang-Feng Chen and Nai-ben Ming

National Laboratory of Solid State Microstructures and Center for Advanced Studies in Science and Technology of Microstructures, Nanjing University, Nanjing 210093, People's Republic of China

Received 27 June 1995

Abstract. $PbTiO_3$ ferroelectric thin films have been prepared on Si (001) by metal–organic chemical vapour deposition. The as-grown films were characterized by scanning electron microscopy, x-ray diffraction and Raman spectroscopy. It is shown that the films were highly (001) oriented and had essentially the same lattice constants as the bulk single crystal. However, the as-grown films were subject to internal stress as shown by a downshift in the Raman modes when compared with a bulk single crystal.

1. Introduction

Perovskite-type oxides, such as $PbTiO_3$, $BaTiO_3$ and $PbZr_xTi_{1-x}O_3$, are ferroelectric materials which have remarkable ferroelectric, pyroelectric and electro-optic properties. Potential applications of these oxides in non-volatile memories, infrared sensors, space optical modulators, etc, have stimulated the development of thin-film growth [1]. Epitaxial films would be advantageous for device applications. Recently, much effort has been given to the epitaxial growth of thin films of perovskite-type oxides; for example, epitaxial films have been achieved on single-crystal substrates such as MgO, $SrTiO_3$ and $LaAlO_3$ [2–4], while films grown on fused quartz were polycrystalline [5]. However, in order to integrate ferroelectric thin films into CMOS technology, it is desirable to prepare high-quality thin films on a Si substrate.

In the past few years, a series of techniques for the preparation of thin films has been developed, including sputtering, sol–gel and metal–organic chemical vapour deposition (MOCVD) [2–10]. Of these techniques, MOCVD shows some advantages over the others, such as good uniformity of composition, high probability of achieving epitaxial growth, high deposition rate, adaptability to multicomponent deposition and large-scale commercial production. By using MOCVD, many epitaxial ferroelectric thin films have been achieved, including $PbTiO_3$ [2–4], $BaTiO_3$ [8] and PZT [9]. However, it is still difficult to obtain high-quality $PbTiO_3$ thin films on Si substrates. Kim *et al* [10] have grown polycrystalline $PbTiO_3$ thin films with random orientation, which was attributed to the formation of an amorphous interfacial layer, and Okada *et al* [2] obtained polycrystalline films with some [001] texture. Although epitaxial or single-crystal films are preferred, the c-axis-oriented thin films are sufficient and suitable for piezoelectric, pyroelectric and other applications. A c-axis-oriented $PbTiO_3$ film may have a small dielectric constant and a large pyroelectric coefficient

0953-8984/95/479075+06$19.50

because the c axis is the polarization axis. In this paper, we report the preparation of highly (001)-oriented $PbTiO_3$ thin films on Si (001) single-crystal substrates and characterization of the as-grown films by scanning electron microscopy (SEM), x-ray diffraction (XRD) and Raman spectroscopy.

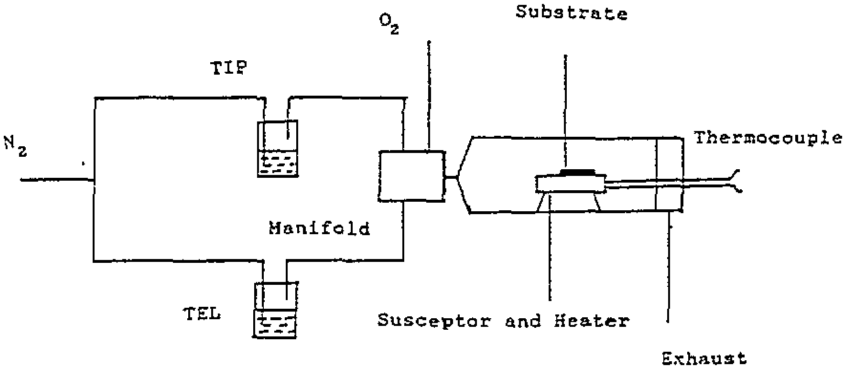

Figure 1. Schematic diagram of the MOCVD apparatus used in this work.

2. Experimental methods

The $PbTiO_3$ films were grown on *Si (001)* by MOCVD. The MOCVD apparatus is shown schematically in figure 1. It is mainly composed of three parts: a gas supply system, a horizontal quartz reactor and an exhaust gas-handling system. In the present work, two purified metal-organic precursors, namely titanium isopropoxide (TIP) and tetraethyllead (TEL) were used. The temperatures of the two precursors TIP and TEL were maintained at 65 °C and 35 °C, respectively. The substrate temperature was elevated using a resistive heater and kept at 600 °C. The flow rates of TIP, TEL and O_2 were 200 sccm, 250 sccm and 200 sccm, respectively, with the total pressure of the reactor chamber set at 10 Torr.

The surface mophologies of the as-grown $PbTiO_3$ films were investigated by SEM. Before examination, a thin layer of gold was deposited on the surface. The crystallinity and orientation of the films were examined using XRD. XRD measurements were performed on a Ragaku x-ray diffractometer with nickel-filtered Cu Kα radiation. Raman spectroscopy measurements were performed on a Spex 1403 Raman spectrometer using the back-scattering geometry. The 488 nm line of an Ar^+ laser with 100 mW output power was used. The widths of both the entrance and the exits slits were set at 150 μm.

3. Results and discussion

A scanning electron micrograph is shown in figure 2. A few particulate structures with a size of about 1 μm can be observed. Considering that the typical film thickness is 1.5 μm, such surface fluctuation or roughness is understandable. The surface roughness is expected to reduce as the film thickness is decreased. In fact, for the intergrated ferroelectrics applications, films of only a few hundred nanometres thickness are generally needed. From figure 2, some equilateral triangular faceted grains of about 0.5 μm in size can be observed. These are related to the (111)-oriented texture of the film, consistent with the following XRD measurements.

Figure 2. A scanning electron micrograph showing the surface morphology of the $PbTiO_3$ films on Si(001).

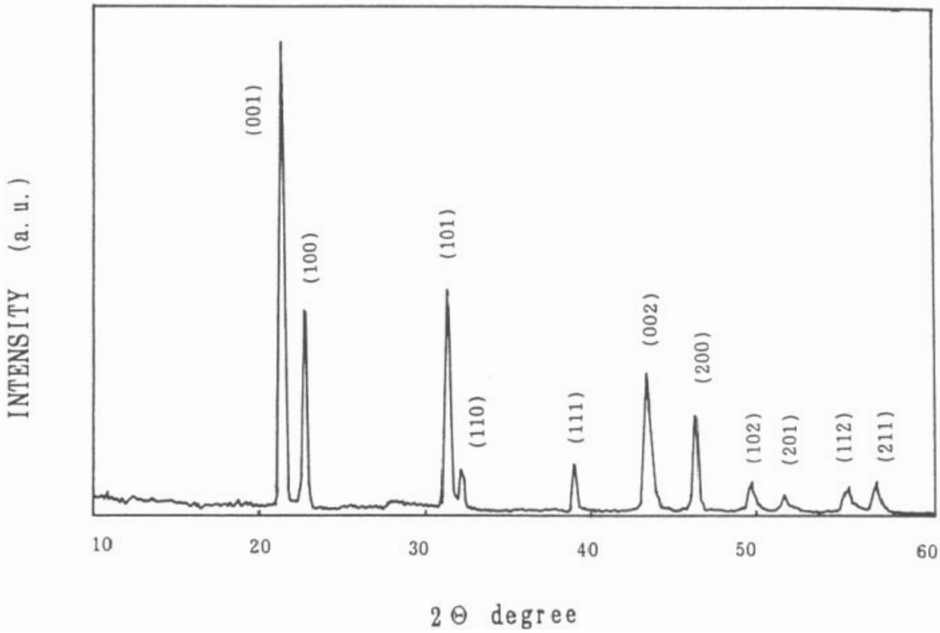

Figure 3. XRD pattern of highly (001)-oriented $PbTiO_3$ films on Si by low-pressure MOCVD (a.u., arbitrary units).

Figure 3 shows the XRD pattern from the as-grown $PbTiO_3$ films on an Si substrate by MOCVD. The XRD data are also clearly listed in table 1. It is shown that the film is polycrystalline but highly (001) textured and has no secondary phases. Careful checks by focusing the x-rays on different regions were performed and similar patterns were obtained, indicating good uniformity of the films. The c-axis orientation ratio α is calculated to be 0.71, which is, to our knowledge, the highest value ever reported on Si. Tetragonality of

Table 1. XRD data for MOCVD-grown $PbTiO_3$ films on Si.

	001	100	101	110	111	002	200	102	201	210	112	211
Film	100	42	46	9	10	28	20	6	3	—	5	7
JCPDS No. 6-452	25	50	100	55	40	16	30	14	10	12	20	40

the film was calculated to be 1.063 which is comparable to that reported for bulk single crystals.

Raman spectroscopy is used conventionally to characterize the frequencies of optical phonons or long-wavelength lattice vibrations. Raman scattering from bulk $PbTiO_3$ single crystals has been fully studied [11, 12]. Recently Taguchi *et al* [13] reported a Raman scattering study of $PbTiO_3$ thin films prepared by RF sputtering and post-annealing treatment. It was found that phonon frequencies are generally more sensitive than XRD peaks to microstructural changes in the films. So Raman spectroscopy can give more subtle information on the microstructure of the as-grown films and should be a good supplement to the XRD measurements. Here, Raman spectroscopy measurements were performed to examine further the crystalline quality of the as-grown films.

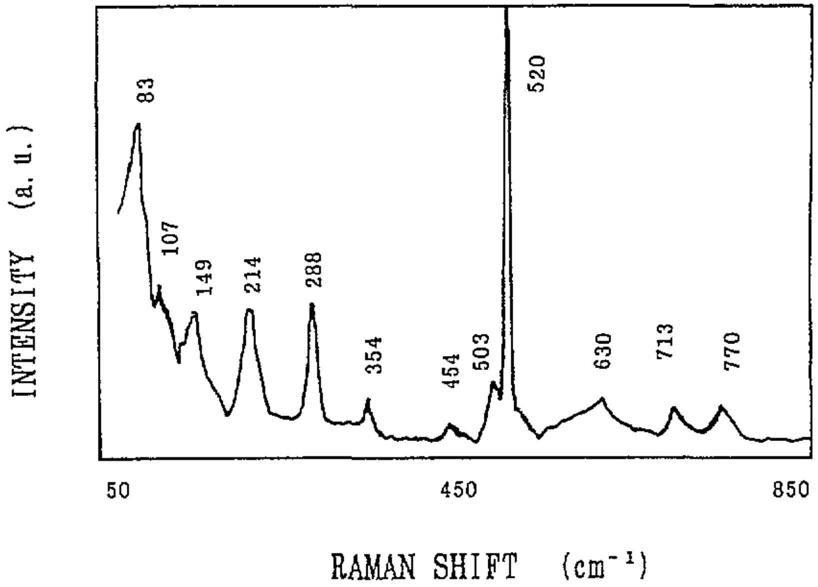

Figure 4. Raman spectrum of the as-grown $PbTiO_3$ film on Si obtained at room temperature (a.u., *arbitrary units*).

Figure 4 displays the Raman spectrum from the $PbTiO_3$ films at room temperature. It closely resembles the Raman spectra from bulk single crystals. The 520 cm^{-1} mode is a first-order mode from the Si substrate. All the other phonon modes were from $PbTiO_3$ and clearly resolved. No extra Raman modes indicative of impurities or interfacial phases were detected. We suppose that the 650 °C growth temperature used here, which was higher than that used by Kim *et al* [10], had restrained the formation of interfacial phases. The 83 cm^{-1} mode is a well known soft mode [11]. Near 634 and 734 cm^{-1} there are two broader lines with relatively lower intensities. It is reported that the linewidths of these two modes are sensitive to microstructure [11]; their broadening was expected and consistent with highly textured polycrystalline films with some randomly oriented grains.

Table 2. Mode frequencies of optical phonons in $PbTiO_3$ single crystal and $PbTiO_3$ film at room temperature (cm^{-1}).

Mode	Single crystal			Present work
	0 Gpa[a]	0 GPa[b]	1 GPa[c]	
E(1TO)	89	89	83	83
A_1(1TO)	127	148	120	109
E(1LO)	128	130		149
A_1(1LO)	215			
E(2TO)	221	220	218	214
B_1 + E	290	290	289	288
A_1(2TO)	364	362	349	354
E(2LO) + A_1(2LO)	445	440		454
E(3TO)	508	508	515	503
A_1(3TO)	651	650	634	630
E(3LO)	717	720	718	713
A_1(3LO)	797			770

[a] — [11]
[b] — [12]
[c] — [14]

All the phonon modes are listed in table 2 for comparison with the Raman data on bulk single crystals. From table 2 it is found that the phonon frequencies for the films are somewhat lower than those for single crystals. This downshift of Raman lines or mode-softening behaviour can be attributed to pressure effects [14] induced by internal stress in the thin films. The frequency of phonon mode versus pressure could be described as

$$\omega^2 = \omega_0^2(1 - P/P_1) \tag{1}$$

where ω_0 is the phonon frequency at zero pressure and P_1 is the pressure under which the phonon frequency goes to zero. The internal stress in the films may be caused by different expansion coefficients between the film and the substrate, or it may form when domain splitting was hindered by the neighbouring grains with different orientations. As shown in table 2, the mode frequencies in thin films are basically comparable to those in bulk single crystals under 1 GPa pressure, which is lower than that of sputter-prepared films [13]. It should be noted that, in addition to internal stresses, finite domain effects may be another cause leading to the phonon softening in the $PbTiO_3$ ferroelectric thin films.

4. Conclusion

We have successfully prepared highly (001)-textured $PbTiO_3$ films on a Si substrate using low-pressure MOCVD. We have carefully examined the as-grown films using SEM, XRD and Raman spectroscopy; the results indicate that the films were of fairly good quality.

Acknowledgment

This work was supported by the National 863 High Technology Program of China.

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