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Raman scattering of ferroelectric lead lanthanum titanate thin films grown on fused quartz by metalorganic chemical vapor deposition

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Abstract

Highly textured lead lanthanum titanate $(Pb_{1-x}La_x)TiO_3$ (PLT) thin films have been grown on fused quartz substrates by metalorganic chemical deposition (MOCVD). A series of PLT with different x between 0 and 0.32 were prepared and studied by Raman scattering. Raman spectra, measured at 300 K and 80 K, showed the features from the PLT film and quartz substrate. By using a “difference Raman” technique, more PLT modes are shown. The variations of the PLT Raman modes with the La composition and the measurement temperature are studied, and related physical phenomena and problems are discussed.

Keywords: Lead lanthanum titanate; PLT; Raman scattering

1. Introduction

Lead lanthanum titanate $(Pb_{1-x}La_x)TiO_3$ (PLT) is an important ferroelectric ceramic material that attracts much research interest currently [1–3]. It is also a necessary partner of lead lanthanum zircinate titanate (PLZT) [4–6] and lead lanthanum stannate zircinate titanate (PLZST) [7]. These PLT and related materials possess various novel properties, such as piezoelectricity, pyroelectricity, elasto-optic effect, linear or quadratic electro-optic effect, which are useful in applications for nonvolatile memory devices, detectors, sensors, and optical switches [1–8]. Efforts have been made to deposit PLT thin films on sapphire [9], MgO [10], and Pt/MgO [11] substrates by rf magnetron sputtering technique, on Si by excimer laser ablation [12] and by metalorganic chemical vapor deposition (MOCVD) [13], on (0 0 0 1) sapphire by the sol–gel process [14], and recently on composite substrates of $ZrO_2/SiO_2/Si$ by metalorganic deposition (MOD) [1] and $Pt/TiO_2/SiO_2/Si$ by pulsed laser deposition [2,3].

MOCVD is a useful technique for the deposition of various electronic and optoelectronic materials, and has been successfully applied by us to the growth of a series of ferroelectric thin films of $BaTiO_3$ [15], $PbTiO_3$ [16,17], and $PbZrTiO_3$ (PZT) [18] on various substrates. We have also reported on the deposition and investigation of highly textured $(Pb_{1-x}La_x)TiO_3$ (PLT) thin films on Si(1 0 0) by MOCVD [13]. These ferroelectric films have been characterized and investigated by X-ray diffraction (XRD) [16–18], scanning electron microscopy (SEM) [16], Rutherford backscattering spectroscopy (RBS) [13,16,17] and Raman scattering [13,17].

In this paper, we report on the deposition of a series of $(Pb_{1-x}La_x)TiO_3$ $(0 < x < 0.32)$ thin films on fused quartz by MOCVD and characterizations by Raman scattering.

2. Experiment

The MOCVD growth of PLT on fused quartz was similar to the case of PLT deposition on Si substrates [13]. Tetraethyl

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lead [$Pb(C_2H_5)_4$], titanium isopropoxide [$Ti(OC_3H_7)_4$], and lanthanum diketonate [$La(thd)_3$, thd = $C_{11}H_{19}O_2$] were metalorganic sources for PLT. Argon was used as the carrier gas with the flow rates of 800, 100, and 200 sccm for Ti-, Pb-, and La-sources, respectively. Temperatures for Pb- and La-sources were between 12–14 °C and 120–140 °C, respectively, while Ti-source temperature was in 28–31 °C. The substrate temperature was set at 550 °C. The reactor pressure was 70 Torr. An oxygen flow of 50 sccm was used to enhance the pyrolysis, and more importantly, to eliminate the carbon incorporation in the film. The film thickness in this study ranging between 1500 and 3000 Å, and the La compositions ranging from 0 up to 0.32 were determined by RBS (not shown here).

All PLT thin films were first examined by XRD. Results are briefly described below. The 2θ diffraction patterns are obtained for all samples with peaks corresponding to (0 0 1), (1 0 0), (1 0 1), (1 1 0), (1 1 1), (0 0 2), and (2 0 0) crystalline planes, indicating that the films are polycrystalline in nature. The separation between (0 0 1) and (1 0 0) peaks decreases with increasing *x*. This demonstrates that the degree of tetragonality in these films decreases as the lanthanum concentration increases. This is consistent with the changes seen in PLT films grown on MgO by rf magnetron sputtering [11], and our MOCVD-grown PLT films on Si [13]. Detailed calculation of these PLT lattice constants *a* along the *a*-axis parallel to the surface and *c* along the *c*-axis normal to the surface for various La-concentrations as well as their tetragonality, *c*/*a*, will be given elsewhere together with XRD scan patterns.

Raman scattering measurements were performed in a near-backscattering geometry with the excitation source of 457.9 nm lines from an Ar^+ laser, using a triple spectrometer-optical multichannel analyzer (OMA) system [13,17]. Two gratings were used to achieve different scanning range and resolution ability.

3. Results and discussion

Figs. 1 and 2 show Raman spectra from five PLT/quartz samples with $x = 0$, 0.054, 0.167, 0.212, and 0.319 measured at 300 K and 80 K, respectively, in the spectral range below 400 cm^{-1}. Three major bands below 400 cm^{-1} characterize PLT modes [13]: the lowest frequency mode is a so-called soft mode, i.e. a transverse optical (TO) mode with the E symmetry E(1TO) at 78 cm^{-1}, the secondary E symmetry TO mode E(2TO) is located at 197 cm^{-1}, and a silent mode at 283 cm^{-1}. These three major modes of E(1TO), E(2TO), and silent can be seen in all four samples, although they are weak for the $x = 0.319$ PLT film, and also almost unrecognized for the $x = 0.212$ PLT film, indicating the poor quality of this sample. An additional A_1(1TO) mode at 150 cm^{-1} is seen for PLT with $x < 0.167$ and sharper at 80 K than 300 K. The E(1LO) mode at 125 cm^{-1} is observed at 80 K measurements only. Also, a mode near 330–340 cm^{-1} is seen and assigned to A_1(2TO) [14,19].

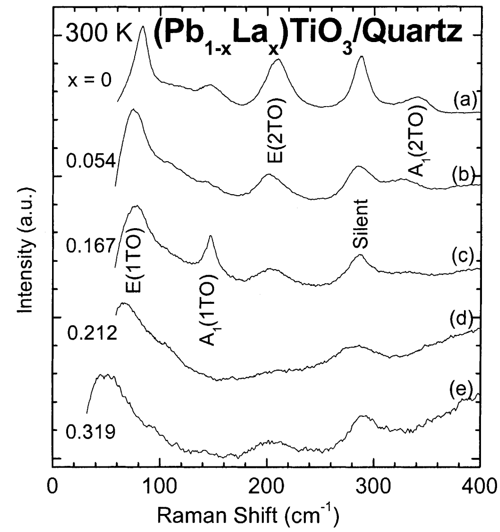

Fig. 1. Raman spectra taken at 300 K under excitation of 457.9 nm and 100 mW, showing the major PLT phonon bands below 400 cm^{-1}, from MOCVD-grown ($Pb_{1-x}La_x$)TiO_3/quartz for *x* values of: (a) 0, (b) 0.054, (c) 0.167, (d) 0.212, and (e) 319.

We have previously used the difference Raman scattering technique to treat Raman spectra of $PbTiO_3$ thin films grown on substrates of $KTaO_3$ and quartz by MOCVD [17], by way of which, Raman modes from the ferroelectric film can be recognized clearly. We are now employing this method to further study the PLZ films grown on quartz. Figs. 3 and 4 show the Raman spectra for a typical ($Pb_{1-x}La_x$)TiO_3 ($x = 0.10$) thin film grown on quartz by MOCVD, its bare

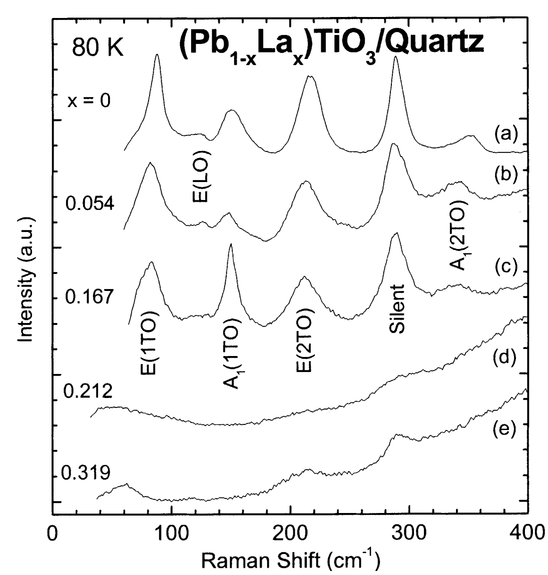

Fig. 2. Raman spectra taken at 80 K under excitation of 457.9 nm and 100 mW, showing the major PLT phonon bands below 400 cm^{-1}, from ($Pb_{1-x}La_x$)TiO_3/quartz for *x* values of: (a) 0, (b) 0.054, (c) 0.167, (d) 0.212, and (e) 0.319.

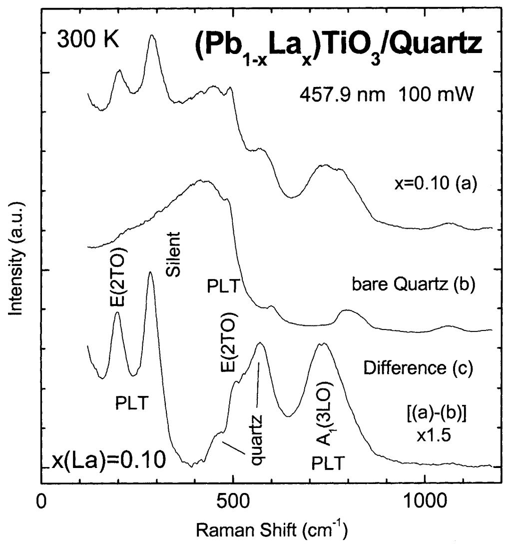

Fig. 3. Raman spectra (300 K) under excitation of 4579 Å and 100 mW, from (a) $x = 0.10$ $(Pb_{1-x}La_x)TiO_3$ quartz, (b) bare quartz region, and (c) difference of (a−b).

substrate and the difference between them in the frequency range of 100–1200 cm^{-1} and measured between 300 and 80 K, respectively. The secondary E(2TO) at 197 cm^{-1} and the silent mode at 283 cm^{-1} are seen directly from the Raman spectrum without subtracting the contributions from substrate (Figs. 3a and 4a). They are superposed upon the low frequency side of a broad Raman band, peaked near 400 cm^{-1}, from quartz, and this is same also for the soft mode when we changed a grating to scan (not shown here). Two weak bands located at 123 and 148 cm^{-1}, respectively, can bee seen from the LT difference spectrum, Fig. 4c, which

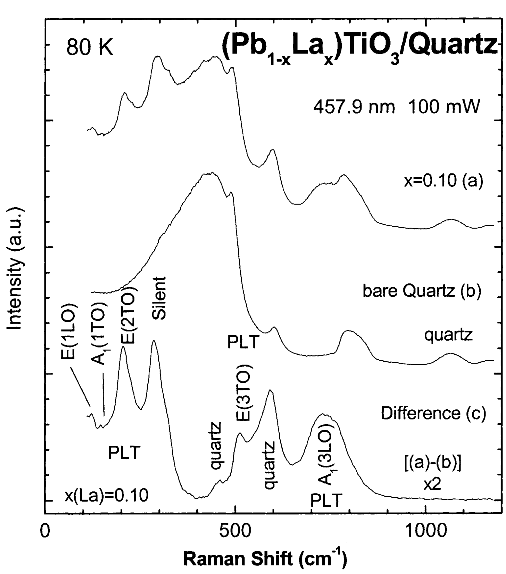

Fig. 4. Raman spectra (80 K) under excitation of 4579 Å and 100 mW, from (a) $x = 0.10$ $(Pb_{1-x}La_x)TiO$ quartz, (b) bare quartz region, and (c) difference of (a−b).

had been observed for powder PLT [19] and can be assigned as E(1LO) and A_1(1TO), respectively, following the assignments for $PbTiO_3$ [20].

Beyond 400 cm^{-1}, the spectrum of PLT/quartz (Figs. 3a and 4a) consists of contributions from both PLT and quartz, which can not be distinguished simply. In comparison with the spectrum from bare quartz (Figs. 3b and 4b), it is seen that the Raman feature at 1060 cm^{-1} from quartz does not appear from the difference spectra, Figs. 3c and 4c. The quartz mode at 800 cm^{-1} does not appear in Figs. 3c and 4c also, leaving a broad band between 650 and 950 cm^{-1} and with the peak at about 730 cm^{-1}. This band is recognized to be a PLT longitudinal optical (LO) phonon mode with an A_1 symmetry and assigned as A(3LO) from PLT.

Between 400 and 650 cm^{-1}, there exist a small bump slightly below 500 cm^{-1} and band at 600 cm^{-1} which are from the quartz substrate. In the difference spectrum of Fig. 4c, these two features still exist. But a third band exhibits clearly between these two modes located at 515 cm^{-1} which is assigned as E(3TO) from PLT film. At the RT difference spectrum, Fig. 3c, this E(3TO) mode and a quartz mode in its lower frequency side appear not so sharp as they appear at LT spectrum, Fig. 4c. LT (80 K) measurements can produce better results.

The dependence of the mode frequencies on x for our PLT/quartz samples can be obtained from above Raman spectra. The data are consistent with that for PLT/Si(1 0 0) [13] and that from Katiyar [14]. All modes except for the so-called “silent mode” show some systematic changes as a function of the composition and temperature. The “silent mode”, which is not Raman or infrared active [21], exhibits a unique compositional and temperature dependence where the position (287–288 cm^{-1}) almost does not vary with either the La composition or temperature. Its appearance in Raman spectra might be due to the disorder in samples.

The frequency of the E(TO) soft mode decreases in wavenumber with an increase of x for both 300 K and 80 K, which is consistent with the results of $PbTiO_3$ thin films [17] and PLT/Si [13].

4. Conclusion

In summary, we have successfully grown lead lanthanum titanate (PLT) thin films on fused quartz substrates by metalorganic chemical vapor deposition. Films with the La composition less than 0.32 were characterized by X-ray diffraction, Raman spectroscopy, and Rutherford backscattering. X-ray diffraction showed the polycrystalline nature of these films. Raman spectra were studied and compared with that from our MOCVD-grown PLT on Si(1 0 0). Difference Raman technique was used to exhibit better the features from PLT films by subtracting the contributions from quartz substrates. More features from PLT films can be recognized or distinguished at low temperature (80 K) measurements. The composition and temperature dependent behaviors of the Raman modes of PLT with $0 < x < 0.32$ are obtained. Some empirical trends can be seen that the TO-like and LO-like modes decrease and increase, respectively, with increasing *x*, and that the silent mode does not depend on *x* in the range studied. The success of the growth of the complex PLT ferroelectric films on the widely available quartz substrates by MOCVD may enhance further the development and application of ferroelectric thin film materials.

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