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RAMAN SPECTRA OF MOCVD-GROWN FERROELECTRIC PbTiO_3 THIN FILMS

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ABSTRACT

Lead titanate (PbTiO_3) has been grown on a variety of substrates by using the metalorganic chemical vapor deposition (MOCVD) technique. The substrates employed included Si, GaAs, MgO, fused-quartz, sapphire, and KTaO_3 . Raman spectra from these heterostructures are presented. All of the films exhibited the strong, narrow spectral features characteristic of PbTiO_3 perovskite-oxide crystals and indicative of high crystalline quality. The temperature behavior of the Raman modes, including the so-called "soft-mode," was studied. A "difference-Raman" technique was used to distinguish the contributions of the PbTiO_3 film and the KTaO_3 single-crystal substrate.

INTRODUCTION

Lead titanate (PbTiO_3) is an important ferroelectric material for applications in electronic and optical devices. In recent years, a great deal of interest in the epitaxial growth of PbTiO_3 thin films by various techniques and on different substrate materials has arisen. The metalorganic chemical vapor deposition (MOCVD) technique is one of the most powerful of the current practical methods for the growth of PbTiO_3 thin films,¹⁻⁴ and we have grown various PbTiO_3 thin films on a variety of substrates by using this method. The substrates employed here included Si, GaAs, MgO, sapphire, fused-quartz, and KTaO_3 .

The selection of these substrates is significant since Si and GaAs are the most important elemental and compound semiconductor materials and are very attractive for potential combinations of ferroelectric devices with Si-based integrated circuits and GaAs-based optoelectronics. Such heterostructures represent a new field for the application of ferroelectric thin films, and ferroelectrics with high dielectric constants may replace SiO_2 to form waveguides and to reduce conventional device sizes.

Oxides of MgO, sapphire ($\alpha\text{-Al}_2\text{O}_3$), and fused quartz were employed because of their widespread use as substrate materials for various devices and thin-film structures—including superconductors. The perovskite oxide, potassium tantalate or KTaO_3 , was chosen in order to investigate the combination of two different perovskite oxides.

In the present study, Raman scattering was employed to characterize the resulting PbTiO_3 thin films. Raman spectra from these heterostructures, taken at both room and low temperature and under different excitations, are presented. All of the films exhibited the strong, narrow spectral features characteristic of PbTiO_3 perovskite-oxide crystals and indicative of high crystalline quality.

EXPERIMENT

The PbTiO_3 depositions were performed in an inverted, vertical, warm-wall reactor with a resistively heated susceptor. Tetraethyl-lead $[\text{Pb}(\text{C}_2\text{H}_5)_4]$, and titanium isopropoxide $[\text{Ti}(\text{OC}_3\text{H}_7)_4]$, were chosen as the reactive gases. Argon was used as the carrier gas. The detailed growth conditions used in forming the lead titanate films have been described elsewhere.^{1,3,4} The film thickness in this study ranged between one thousand and several thousand angstroms, as determined by Rutherford backscattering spectroscopy.

All of the PbTiO_3 thin films were first examined by XRD techniques in a Siemens digitized horizontal diffractometer with a monochromatized $\text{CuK}\alpha$ radiation source. The sample stage was equipped with rotational and rocking capabilities to insure statistically correct averaging over the reciprocal lattice points.

Raman-scattering measurements were performed in a near-backscattering geometry with an Ar^+ laser excitation source having different lines between 4579 and 5145 Å. The samples were mounted on a Cu block in a liquid nitrogen vacuum dewar, which was set on a micrometer-adjustable stage to allow for precise positioning of the samples. The scattered light from the sample was dispersed by a triple spectrometer and subsequently detected by an optical multichannel analyzer (OMA) using a Si-detector array. The signals were accumulated under computer control to achieve a high signal-to-noise ratio.

RESULTS AND DISCUSSION

PbTiO_3 on Si and GaAs

Figure 1 shows the Raman spectra for a $\text{PbTiO}_3/\text{Si}(100)$ sample measured at 300 and 80 K. The lines at 520 cm^{-1} (300 K) and 522 cm^{-1} (80 K), which are from the Si substrate, are the strongest features and are not fully displayed in the figure. The broad bands between 900 and 1150 cm^{-1} are due to the second-order scattering of the Si phonon modes, which shift up slightly as the temperature is decreased from 300 K to 80 K.

Figure 2 shows the spectra of MOCVD-grown PbTiO_3 on GaAs at 300 and 80 K. The bands at 258 cm^{-1} (300 K) and 262 cm^{-1} (80 K) are due to the GaAs TO mode. The GaAs LO mode appears as shoulders at the high-frequency side of the silent mode (located at 290 cm^{-1} (300 K) in Fig. 2a and 293 cm^{-1} (80 K) in Fig. 2b), and is clearly split further from the silent band at low temperature than at room temperature.

All other features in Figs. 1 and 2 are characteristic of bulk PbTiO_3 with the assignments and notations following those of Burns and Scott.⁵ Below 800 cm^{-1} , there exist several longitudinal optical (LO) and transverse optical (TO) phonon modes with E or A_1 symmetries. We use the numbers 1, 2, and 3 to label the mode numbers prior to the TO or LO inside the parenthesis which follows the symmetry notation E or A_1 , as shown in the figures. The lowest bands in Figs. 1a and 1b are the so-called soft modes⁶ with E(TO) symmetry, E(1TO), which are located at 84 cm^{-1} (300 K), and 87 cm^{-1} (80 K), respectively.

Near 150 cm^{-1} , an E-symmetric LO mode E(1LO) appears in all four spectra with the band intensity relatively stronger at high temperature than at low temperature.

Features between E(1TO) and E(1LO) are not well-resolved in Fig. 1 for PbTiO₃/Si, but are distinguishable in Fig. 2a and are well-resolved with a clear A₁(1TO) peak in Fig. 2b for PbTiO₃/GaAs. This indicates that the quality of the PbTiO₃ film on GaAs is better than that on Si.

The mixture of A₁(1LO) and E(2TO) is located just above 200 cm⁻¹. The “silent” (or B₁+E) mode,⁵ located at 287–288 cm⁻¹ for all four spectra, exhibits a unique temperature dependence where the position of the feature does not vary appreciably with temperature. Figures 1 and 2 also show other PbTiO₃ characteristic modes: A₁(2TO) near 350 cm⁻¹, A₁(2LO)+E(2LO) near 450 cm⁻¹, E(3TO) just above 500 cm⁻¹ (unrecognizable in Fig. 1 due to a strong Si phonon mode near 520 cm⁻¹), A₁(3TO) close to 550 cm⁻¹, and E(3LO) above 700 cm⁻¹. The comparison between Figs. 1 and 2 indicates that the E(3TO) and A₁(3TO) bands for PbTiO₃/Si in Fig. 1 are much broader than those for PbTiO₃/GaAs in Fig. 2. This broadening may be caused by disorder, which gives additional evidence that the film quality of PbTiO₃ on Si is poorer than that of PbTiO₃ on GaAs.

PbTiO₃ on Oxides of MgO, Fused-Quartz, and Sapphire

Figure 3 displays the Raman spectra for an MOCVD-grown PbTiO₃ film on MgO with all of the PbTiO₃ characteristic features mentioned above. The increasing background with increasing wavenumber in the figure is due to the MgO substrate.

Figure 4 shows three Raman spectra: (a) MOCVD-grown PbTiO₃ on quartz, (b) the bare quartz substrate, and (c) the difference spectrum, which also clearly shows all of the PbTiO₃ characteristic bands as noted above. We observe that most of PbTiO₃ characteristic Raman lines for PbTiO₃ on MgO in Fig. 3 are narrower than that for PbTiO₃ on quartz as shown in Fig. 4. This indicates that the film quality of PbTiO₃ grown on MgO is better than that of PbTiO₃ grown on quartz.

Figures 5 and 6 exhibit Raman spectra of MOCVD-grown PbTiO₃ on sapphire, i.e. α-Al₂O₃, under excitation at 501.7 nm in the range of 40–470 cm⁻¹ and under excitation at 457.9 nm in the range of 150–900 cm⁻¹. Comparative Raman spectra from the sapphire substrate with seven typical Raman lines⁷ from α-Al₂O₃ are shown in Figs. 5c and 6c. These seven α-Al₂O₃ lines also appear clearly in the spectra for PbTiO₃ on sapphire measured at 300 and 80 K. The comparison between Figs. 5 and 6 shows that, under excitation at 501.7 nm, the intensities of characteristic PbTiO₃ Raman lines are much weaker than those of the α-Al₂O₃ lines, while under excitation of 457.9 nm, the intensities of the PbTiO₃ lines with respect to the α-Al₂O₃ lines become much stronger than in the case of 501.7 nm excitation. Similar phenomena were observed for PbTiO₃ films grown on other substrates. This may be due to the approach toward the energy gap or to impurity-defect mid levels within the wide energy gap (>10 eV) of PbTiO₃. Further investigations will be performed in the future on these phenomena.

PbTiO₃ on KTaO₃

We have grown PbTiO₃ on another perovskite oxide KTaO₃, but, the Raman spectrum for PbTiO₃/KTaO₃ is very similar to that from pure KTaO₃,⁸ as shown in Figs. 7a and 7b. By a direct examination, one cannot find obvious differences between these two spectra. However, when accumulated >5000 times, the “difference spectrum”

(Fig. 7c) shows the major features of PbTiO₃ as observed in Figs. 1–6 for PbTiO₃ grown on other substrates. Particularly, the first four modes in the low-frequency range below 300 cm⁻¹ stand out sharply. Other PbTiO₃ features between 400 and 800 cm⁻¹ are also seen. A strong band near 600 cm⁻¹ in Fig. 7c is due to KTaO₃, which may be caused by the different dispersion properties between PbTiO₃ and KTaO₃.

Different Temperature Behavior of Raman Line Shifts

As mentioned above, the “silent mode” has a frequency that is almost unchanged with temperature. All of the other PbTiO₃ modes, including the soft mode E(1TO), vary in frequency with temperature. The temperature dependence of the mode frequency w can be described by the soft mode theory with a relationship^{6,8}

$$w = Aw_0 |T - T_0|^{1/2} = Aw_0(T_0 - T)^{1/2} \quad (1)$$

where T is the temperature, A is a constant, and w_0 is the mode frequency at the transition temperature T_0 . The second equality is valid for T between 80 and 300 K because the T_0 of PbTiO₃ is near 500°C.¹ Therefore, the frequency of the E(1TO) soft mode increases in wavenumber with a decrease of T from 300 K to 80 K, which is also true for other non-silent modes.

The observed PbTiO₃ Raman-line frequencies also vary with respect to the values of bulk PbTiO₃ depending on the particular substrates.

CONCLUSIONS

In summary, we have successfully grown lead titanate (PT) thin films on a variety of substrates including: the important semiconductors Si and GaAs, widely-used oxides of MgO, fused quartz and sapphire, and another perovskite oxide KTaO₃. The films were characterized by Raman spectroscopy and exhibited all of the PbTiO₃ characteristic modes. Comparative Raman spectra indicate that the film quality is better for PbTiO₃ grown on GaAs than on Si, and is better on MgO than on quartz. The “difference-Raman” technique was used to successfully distinguish the contributions of the PbTiO₃ film and the KTaO₃ single-crystal substrate. The temperature behavior of the PbTiO₃ Raman lines was explained by soft-mode theory. The success of the growth of the PbTiO₃ and other complex-ferroelectric films on technologically important materials by the MOCVD growth technique that is well-established in the semiconductor industry may enhance the future development and application of ferroelectric thin films and stimulate efforts in combining integrated electronics and ferroelectric devices.

ACKNOWLEDGMENT

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FIGURE CAPTIONS

Fig. 1. Raman spectra of MOCVD grown PbTiO_3/Si taken at 300 and 80 K under excitation of 501.7 nm and 100 mW.

Fig. 2. Raman spectra of MOCVD-grown $\text{PbTiO}_3/\text{GaAs}$ taken at 300 and 80 K under 457.9 nm and 100 mW.

Fig. 3. Raman spectra for a MOCVD-grown PbTiO_3 on MgO . The rising backgrounds with increasing the wavenumber in the figure are due to the MgO substrate.

Fig. 4. Three Raman spectra: (a) MOCVD-grown PbTiO_3 on quartz (a) the bare quartz substrate, and (c), the difference spectrum, which also clearly shows all of the PbTiO_3 characteristic bands.

Fig. 5. Raman spectra of (a) MOCVD-grown $\text{PbTiO}_3/\text{sapphire}$ taken at 300 K (b), 80 K, (c) and bare $\alpha\text{-Al}_2\text{O}_3$ under excitation of 501.7 nm and 100 mW, in the range of 40–470 cm^{-1} .

Fig. 6. Raman spectra of (a) MOCVD-grown $\text{PbTiO}_3/\text{sapphire}$ taken at 300 K, (b) 80 K, and (c) bare $\alpha\text{-Al}_2\text{O}_3$ under excitation of 457.9 nm/100 mW (150–900 cm^{-1}). Asterisks mark the features for $\alpha\text{-Al}_2\text{O}_3$.

Fig. 7. Raman spectra from (a) MOCVD-grown $\text{PbTiO}_3/\text{KTaO}_3$ (b) the bare KTaO_3 substrate taken at 300 K under excitation at 488.0 nm and 100 mW with >5000 accumulations, and (c) their difference.

Fig. 1 MRS 93 Fall

PT-SiR.sp5 from E411-444-423-435.PT (4-92)
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PT-GAR.sp5 from E721-726-734.PT (6-92)
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Fig.2 MRS 93 Fall

PT-MgOR.sp5 from E524-535-509-389.PT (5-92)
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Fig.3 MRS 93 Fall

PT-QZR.sp5 from D836, 837, 836-7.PTO (6-91)
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Fig.4 MRS 93 Fall

PT-SAR1.sp5 from E609-690-589.PZT (5-92)
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Fig. 6 MRS 93 Fall

PT-KT.sp5 from D824-825-824-5.PTO (6-91)
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Fig. 5

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