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Optical Characterization of Lead Monoxide Films Grown by Laser-Assisted Deposition

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The Raman spectra of PbO films, grown by laser-assisted deposition (LAD) at different substrate temperatures are investigated. The spectra of the films, deposited on amorphous, single crystal quartz and polycrystal PbTe substrates, are compared with the Raman spectra of tetragonal and orthorhombic powder samples. The phonon frequencies determined in our experiment with powder samples coincide fairly well with those obtained by Adams and Stevens, *J. Chem. Soc., Dalton Trans.*, 1096 (1977). Thus the Raman spectra of the powder samples presented in this paper can be considered as unambiguous characteristics of the two different PbO crystal phases. It was concluded that the Raman scattering may serve as a tool for identification of PbO films and their crystal modifications. On the basis of this investigation it was concluded that the film structure changes from orthorhombic to tetragonal with increased substrate temperature, and that the nature of the substrate influences the crystal structure of the films. On the basis of the Raman spectra of the β-PbO films with prevailing (001) orientation of crystallization, an assignment of the modes is proposed.

INTRODUCTION

PbO exists in two polymorphic forms: a tetragonal phase of red color, α-PbO, space group D_{4h}^{7}, and an orthorhombic phase of yellow color, β-PbO, space group D_{2h}^{11} (1). PbO in both phases possesses a broad range of applications of industrial importance (2). In the form of thin films, PbO can be used as a protective coating for lead salt devices and gas sensors in particular. Using the laser-assisted deposition (LAD) technique we have grown PbO films on different types of substrates, maintained at different temperatures (3). Structural investigations show that the crystal structure of the films depends on the substrate temperature (4). In our attempts to find a method for optical characterization of PbO film crystal modifications we have investigated the transmittance and reflectance spectra in the energy range of the absorption edge. It turns out that the absorption edges of neither modification are clearly defined because of the large number of direct and indirect transitions taking place in a narrow energy range in the vicinity of the gap energy. Thus it is difficult to identify the PbO modifications from transmittance and reflectance measurements.

This work aims to demonstrate that the PbO crystal phases can be identified by Raman scattering investigations and thus by the crystal structures of films grown on different substrates and at different substrate temperatures.

Up to now there have been only two significant attempts at a full phonon mode assignment on the experimental basis. Donaldson *et al.* (1974) (5) have studied Raman and infrared spectra of powders, and Adams and Stevens (1977) (6) have reported Raman and infrared spectra of α-PbO single crystals and β-PbO thin plates. As the mode frequencies and assignments reported by these authors show some disagreements we have investigated the Raman spectra of the tetragonal and orthorhombic PbO powder samples as well.

EXPERIMENTAL

Samples

A. α-PbO and β-PbO powders. The α-PbO and β-PbO powders were obtained as a sediment of water-soluble lead acetate in a highly alkaline medium,

$$\mathrm{PbO(OOCCH_3)_2 \cdot 3H_2O + KOH \rightarrow PbO},$$

in the facilities of the Faculty of Chemistry at Sofia University. The lattice constants of α-PbO and β-PbO determined from X-ray diffractograms are $a = b = 3.98$ Å, $c = 5.03$ Å for α-PbO, and $a = 5.91$ Å, $b = 5.49$ Å, $c = 4.77$ Å for β-PbO. These values coincide with the corresponding values reported in the literature (1, 7, 8).

The Raman spectra were recorded using powder samples prepared in the form of tablets with a diameter $d = 12$ mm. The α-PbO tablets were obtained at a pressure about 10^8 Pa from α-PbO powder. As the mechanical treatment of β-PbO at room temperature induces the $\alpha \rightarrow \beta$ transition, the β-PbO tablets were obtained by heating the α-PbO tablets at 500°C under atmospheric

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TABLE 1
PbO Film Characteristics

Sample	T_s (°C)	*d* (nm)	*Crystal structure* (RHEED)
Q25	165	120	(001) direction
Q05	298	150	(100) direction
C3	160	200	—
C4	250	290	—
G8	160	200	—
G13	250	290	—
PT1	187	120	—
PT2	298	150	—

Note. Q, quartz; C, ceramic; G, glass; PT, polycrystal PbTe substrate.

pressure. The transition temperature of the $\alpha \rightarrow \beta$ phase transition at atmospheric pressure is 489°C (2).

B. PbO films. PbO films are grown by LAD on different types of substrates: amorphous substrates—ceramic and glass, single crystal quartz (AT-cut), and polycrystal PbTe at different substrate temperatures. The technological parameters which can be varied in LAD technique are (a) the distance between the target and the substrate, (b) the substrate temperature, T_s, and (c) the energy of the laser pulses. The films were grown at different substrate temperatures in the range between 20 and 300°C, with the remaining parameters equal. The film thicknesses, *d*, varied with the number of the laser pulses, were determined from the extrema of the transmittance and reflectance spectra using the method described by Ohlidal *et al.* (9). The surface structure of the films grown on quartz substrates is studied by reflectance high-energy electron diffraction (RHEED). The data about the films whose Raman spectra are studied here are given in Table 1.

Raman Spectra

The room-temperature Raman spectra were obtained by a SPEX 1404 double monochromator in a backscattering geometry using an Ar^+ 514.5-nm exciting laser line with intensity about 30 mW. The samples are placed in a vacuum chamber. The Raman spectra, of α-PbO and β-PbO taken with spectral resolution 0.5 cm^{-1} are shown in Figs. 1 and 2, respectively. Clearly resolved peaks appear at 81, 145.5, and 337 cm^{-1} in the spectrum of α-PbO (Fig. 1). The Raman spectrum of β-PbO shown in Fig. 2 (curve 2 is curve 1 magnified about 10 times) consists of intense peaks at 71.5, 87.5, 143, 289.5, and 384.5 cm^{-1} seen in curve 1, less intense peaks at 52.5, 99.5, and 424 cm^{-1}, and shoulders at 171, 194, and 250 cm^{-1}, which can be seen in curve 2. It is worth noting that the intensity of the strongest peak in the β-PbO spectrum is about one order of magnitude higher than the intensity of the strongest peak in the α-PbO spectrum. The values of Raman active mode frequencies are given in Tables 2 and 3 for α-PbO and β-PbO, respectively.

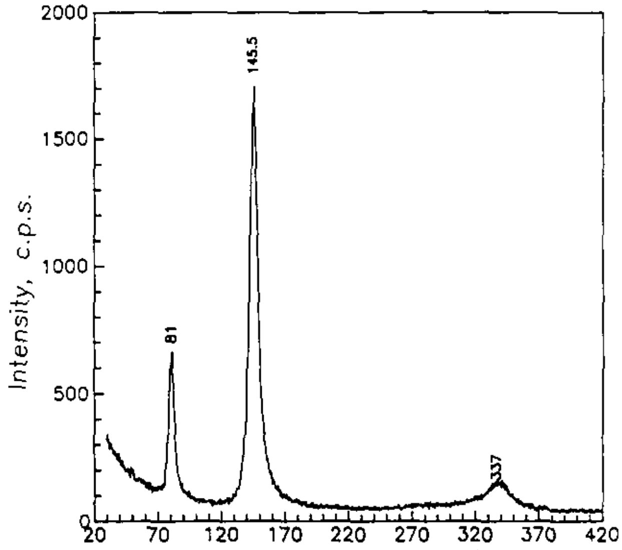

FIG. 1. The Raman spectrum of the α-PbO powder sample.

The Raman spectra of films grown on quartz substrates at different substrate temperatures T_s are shown in Figs. 3a (Sample Q25) and 3b (Sample Q05) with thick lines. In the same figures the spectrum of the quartz substrate with intensity divided by a factor of about 10 is shown by a dashed line. The spectrum of the film deposited at lower T_s, shown in Fig. 3a, is compared with the Raman

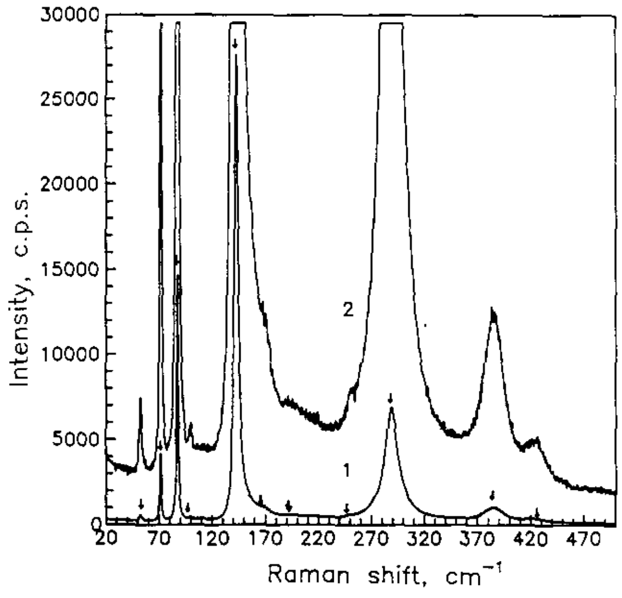

FIG. 2. The Raman spectrum of the β-PbO powder sample: curve 2 is curve 1, magnified about 10 times.

TABLE 2
Phonon Frequencies in Tetragonal PbO

Mode assignment	Theoretical (13) (ω, cm^{-1})	Experimental (6) (ω, cm^{-1})	Our experiment (ω, cm^{-1})
B_{1g}	338.5	338.7	337
E_g	306.4	321.5	—
A_{1g}	144.8	146.5	145.5
E_g	80.1	81	81

spectrum of the β-PbO powder sample (thin line), whose intensity is divided by a factor of about 10^3. In Fig. 3b the spectrum of the film deposited at a higher T_s (Q05) is compared with the Raman spectrum of the α-PbO powder sample (thin line) divided by a factor of about 10.

Figure 4 shows the Raman spectra of two films deposited on amorphous ceramic substrates at T_s = 160°C (a) and at T_s = 250°C (b).

In Fig. 5 the Raman spectra of two films deposited on glass substrates at two different substrate temperatures are shown: (a) T_s = 160°C and (b) T_s = 250°C.

The Raman spectra of two films deposited on polycrystal PbTe substrates at different substrate temperatures are shown in Fig. 6: (a) T_s = 187°C and (b) T_s = 298°C. The fcc PbTe substrate does not have first-order Raman active modes, so the features seen in the spectra are due to the PbO films.

DISCUSSION

Raman Spectra of Powder Samples

The crystal structures of lead monoxide are well known (1, 8). Both modifications have layer structures. The α-PbO layer represents a planar-square grid formed by oxygen atoms with lead atoms placed alternatively on both sides of the grid. The layers are stacked along the c-axis. The β-PbO layer consists of two zig-zag chains with 2[PbO] repeat parallel to b-axis and stacked along the c-axis. The layers are stacked along the a-axis. The unit cell of both monoxides contains one layer.

α-PbO. The stable phase of lead monoxide crystallizes in the tetragonal system of D_{4h}^7 symmetry with two formula units per unit cell ($Z = 2$). The factor-group analysis (fga) (10) as well as the site symmetry analysis (11, 12) gives the representation Γ_{opt} for the optical vibration modes of α-PbO,

$$\Gamma_{\text{opt}} = A_{1g} + B_{1g} + 2E_g + A_{2u} + E_u,$$

where A_{1g}, B_{1g}, and E_g are Raman-active modes, and A_{2u} and E_u are infrared-active modes. Hence, four peaks have to be observed in the Raman spectrum of α-PbO.

The Raman spectrum of the α-PbO powder sample presented in Fig. 1 reveals three prominent peaks of the four predicted by fga, which are centered at 81, 145.5, and 337 cm^{-1}. Adams and Stevens (6) have detected a very weak peak at 321.5 cm^{-1} which is not seen in our spectrum. The mode frequencies determined from our experiment coincide fairly well with those obtained by Adams and Stevens (6). The assignment of these peaks made by Adams and Stevens (6) on the grounds of single-crystal polarized measurements is not in doubt. The most intense peak, centered at 145.5 cm^{-1}, is assigned as the A_{1g} mode resulting from the motion of the lead atoms parallel to the c-axis. It is reasonable to assume that the motion of the lighter oxygen atoms parallel to the c-axis, the B_{1g} mode,

TABLE 3
Phonon Frequencies in Orthorhombic PbO

Theoretical (12)		Experimental (6)		Our experiment	
Mode assignment	ω, cm^{-1}	ω, cm^{-1}	Mode assignment	ω, cm^{-1}	Mode assignment
A_g	390	385	B_{1g}	384.5	B_{1g}
B_{1g}	345	349[1]	A_g	—	
B_{1g}	288	289	A_g	289.5	A_g
A_g	255	250	B_{1g}	250	B_{1g}
B_{2g}	217	217	B_{1g}	198	B_{2g}
B_{3g}	216			—	
A_g	167	171	B_{3g}	171	B_{3g}
B_{1g}	147	144	A_g	143	A_g
B_{2g}	91	87		99.5	B_{2g}
A_g	89			87.5	A_g
B_{1g}	71	72	lattice modes	71.5	B_{1g}
B_{3g}	57	52		52.5	B_{3g}
		424	B_{1g}	424	

[1] Seen in Raman spectrum at 100 K.

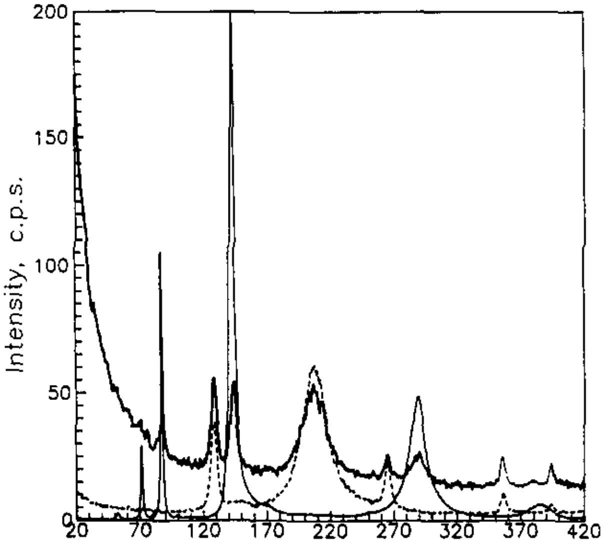

FIG. 3a. The Raman spectrum of film grown on quartz substrate at T_s = 165°C (thick line), Raman spectrum of quartz substrate (dashed line), and Raman spectrum of the β-PbO powder sample (thin line).

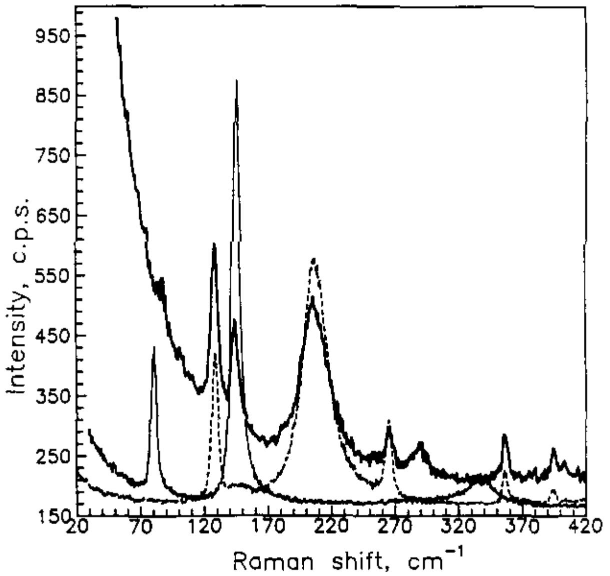

FIG. 3b. The Raman spectrum of film grown on quartz substrate at T_s = 298°C (thick line), Raman spectrum of quartz substrate (dashed line), and Raman spectrum of the α-PbO powder sample (thin line).

results in the peak which appears at 337 cm^{-1}. The remaining peak observed at 81 cm^{-1} is attributed to the E_g mode. In Table 2 our experimental data are compared with results of other authors.

β-PbO. The high-temperature phase of the lead oxide crystallizes in the orthorhombic system of D_{3h}^{11} symmetry with 4 formula units per unit cell ($Z = 4$). The symmetry of the β-PbO phase is lower than that of α-PbO, and the number of phonon modes in the β-PbO phase is greater. The fga gives the representation for β-PbO optical vibration modes

$$\Gamma_{\text{opt}} = 4A_g + 4B_{1g} + 2B_{3g} + 2B_{3g} + 2A_u + B_{1u} + 3B_{3u} + 3B_{3u},$$

where the first four irreducible representations correspond to Raman-active modes, A_u is an inactive mode, and the remaining modes are infrared active. Hence, β-PbO has 12 Raman-active modes and 7 infrared-active modes. In our experimental Raman spectrum (Fig. 2) 11 peaks are seen. The values of mode frequencies obtained in our experiment coincide fairly well with those obtained by Adams and Stevens (6). The difference between our results and those of Adams and Stevens (6) is that they have reported a very weak peak at 217 cm^{-1}, which is not seen in our spectrum; we have detected a shoulder at 194 cm^{-1}. On the other hand, they have not seen the peak at 99.5 cm^{-1}, which is weak but clearly resolved in our spectrum. The assignment of the β-PbO modes given by Adams *et al.* (6) is contradictory to one given by Vigouroux *et al.* (13) on the basis of theoretical considerations and is subject to doubt because their spectra are not polarized. The most intense mode at 143 cm^{-1}, like the one at 145.5 cm^{-1} in α-PbO, is due to the motion of the lead atoms, whose distance in the β-PbO phase is larger and is obviously of A_g symmetry. The intense peaks at 87.5 and 289.5 cm^{-1} can be related to modes of A_g symmetry as well. The assignment of the remaining modes derived from the analysis of our film spectra with predominant crystal orientation is given in Table 3.

As the mode frequencies determined in our experiment coincide fairly well with those obtained by Adams and Stevens (6), the Raman spectra of powder samples, presented in this paper, may be considered as unambiguous characteristics of the two different PbO crystal phases.

Raman Scattering of PbO Films

The RHEED investigations along the surfaces of the films deposited on single-crystal quartz substrates show the following. (i) The films grown at $T_s < 200°\text{C}$ consist of an orthorhombic phase solely; the films are polycrystal with predominant growth in the (001) direction of crystallization. (ii) The films grown at $T_s \geq 200°\text{C}$ are polycrystal and consist of both phases; the films grow predominantly in the (100) direction; the quantity of the tetragonal phase increases with increasing of the substrate temperature. The predominant orientation of the films on the quartz substrate makes clear the reduction of some peaks and the different ratios of the peak intensities in the film spectra in comparison with the powder ones. The spectrum of a film

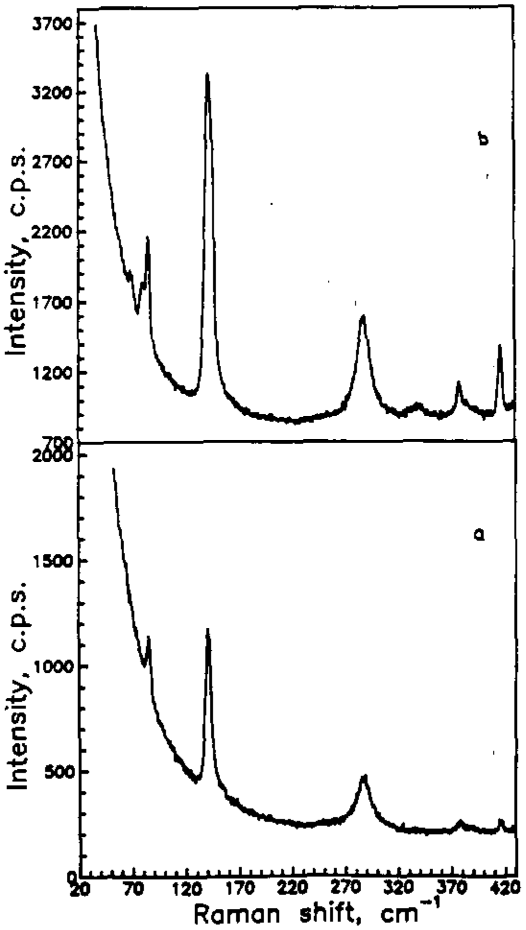

FIG. 4. The Raman spectra of films deposited on ceramic substrates at two different temperatures: (a) T_s = 160°C and (b) T_s = 250°C.

grown at T_s = 165°C (Fig. 3a) indicates only an orthorhombic phase. The frequencies of the six modes, 71.5, 87.5, 143, 250, 289.5, and 384 cm^{-1}, seen in the spectrum coincide with those seen in the orthorhombic powder spectrum. In a backscattering geometry and (001) crystal orientation the modes of A_g and B_{1g} symmetry are seen. The ratio of the A_g and B_{1g} mode intensities in the (001) oriented sample spectrum has to be smaller than that of a powder (randomly oriented) sample spectrum. Then the peaks at 87.5, 143, and 289.5 cm^{-1} are obviously due to modes of A_g symmetry, and the peaks at 71.5, 250, and 384.5 cm^{-1} are due to modes of B_{1g} symmetry. It is visible that in the film spectrum the intensities of the B_{1g} peaks at 71.5, 250, and 384.5 cm^{-1} is much higher than it is in the powder sample spectrum, in contrast to the A_g mode peaks. The peaks at 52.5, 99.5, 171, and 194 cm^{-1}, which are not seen in the film spectrum, have to be attributed to modes of B_{2g} or B_{3g} symmetry not allowed in this geometry.

As it concerns the tetragonal phase in backscattering geometry and (100) crystal orientation, all of the modes of A_{1g}, B_{1g}, and E_g symmetry are seen with lower intensities. The latter fact, along with the fact that the Raman peaks of the orthorhombic phase, which are always present in the films, are very intense, makes the detection of the tetragonal phase difficult. The presence of the tetragonal phase in the film whose spectrum is shown in Fig. 3b is indicated only by the slight shift of the most intense peak from 143 to 145.5 cm^{-1}.

So the most intense peak in the Raman spectra of PbO appears at nearly the same frequency for both crystal phases: 143 cm^{-1} for the orthorhombic phase and 145.5 cm^{-1} for the tetragonal phase. The frequency difference of the less intense peaks at 87.5 and 81 cm^{-1} in the orthorhombic and tetragonal powder, respectively, is more significant, and these peaks may serve as a criterion for the identification of the phases. The appearance of the peak at 289.5 cm^{-1}, which can be seen only in the spectrum of orthorhombic powder, may also be an indication of the presence of the orthorhombic phase.

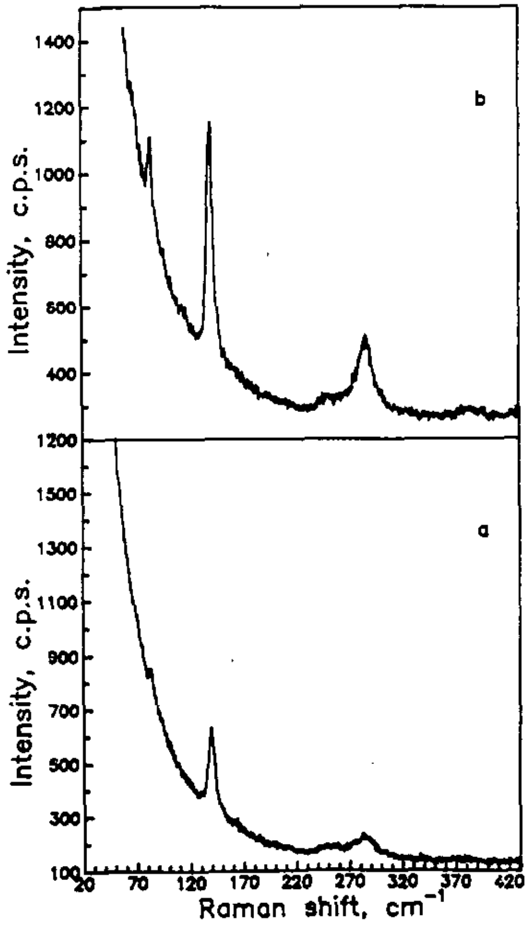

FIG. 5. The Raman spectra of films deposited on glass substrates at two different temperatures: (a) T_s = 160°C and (b) T_s = 250°C.

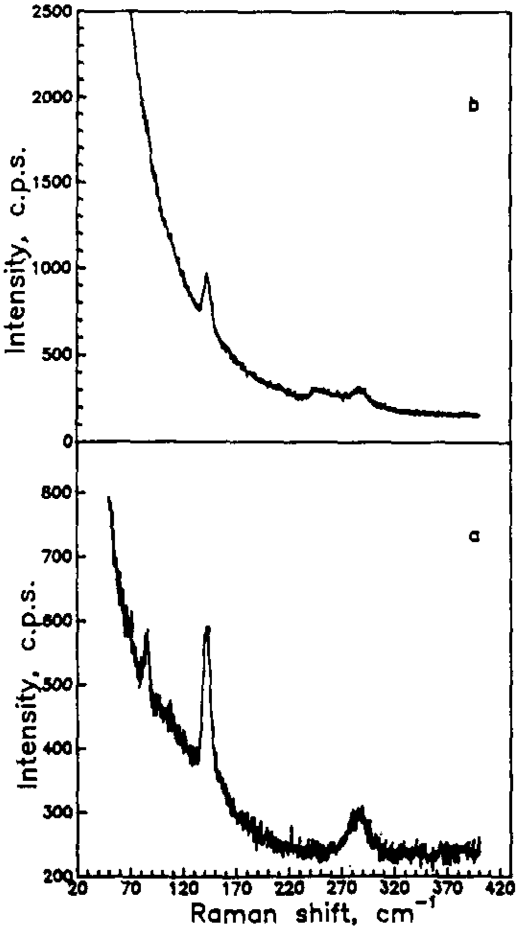

FIG. 6. The Raman spectra of films deposited on polycrystal PbTe substrates at two different temperatures: (a) T_s = 187°C and (b) T_s = 298°C.

The comparison of the Raman spectra of the powder samples with the spectra of the films deposited on amorphous ceramic substrates indicates that the film grown at T_s = 160°C (Fig. 4a) is in the orthorhombic phase. The peaks at 87.5, 143, and 289.5 cm^{-1}, which are the most intense peaks in the orthorhombic powder sample spectrum (Fig. 1), are clearly resolved in the spectrum of the film. In a Raman spectrum of a film deposited at a higher substrate temperature, T_s = 250°C (Fig. 4b), the most intense peak is at 145 cm^{-1}. This is the most intense peak in the spectrum of the α-PbO powder (Fig. 1). The peaks at 81 and 337 cm^{-1}, proper to the tetragonal phase, are seen as well. Along with the tetragonal phase peaks, the peaks at 71.5, 87.5, 289, 384, and 424 cm^{-1} are well resolved in the film spectrum as well. Thus it can be concluded that the film grown at T_s = 250°C consists of both phases—tetragonal and orthorhombic. The same holds for the films grown on glass and PbTe substrates. The Raman spectra of the films deposited at lower substrate temperatures (Sample G8, Fig. 5a and Sample PT1, Fig. 6a) indicate an orthorhombic phase—the peaks at 87.5, 143, and 289.5 cm^{-1} are seen in the spectra. The Raman spectra of the films grown at higher substrate temperatures (Sample G13, Fig. 5b and sample PT2, Fig. 6b) indicate again the presence of both phases. The presence of the tetragonal phase is indicated by the small, but observable shift of the most intense peak to higher frequency as compared with the peak in the orthorhombic powder spectrum.

The investigation of the Raman scattering of PbO films grown on amorphous, quartz, and polycrystal PbTe substrates showed that (i) the presence of lead monoxide films of both phases can be identified by the peak at 143–145.5 cm^{-1}, which is the most intense peak in the Raman spectrum of both PbO crystal modifications, and (ii) the crystal modification of the lead monoxide can be identified by the comparatively intense peaks at 87.5 and 289.5 cm^{-1}. The presence of these peaks, along with the most intense peak at 143–145.5 cm^{-1}, indicates the orthorhombic phase.

It is worth noting that the intensity of the modes of B_{1g} symmetry (71.5, 250, and 384.5 cm^{-1}) in the films grown on amorphous and polycrystal substrates (Figs. 4a, 5a, and 6a) is much lower than the intensity of those in the β-PbO film grown on quartz substrate. The ratio of the B_{1g} and A_g mode intensities in the films grown on amorphous and polycrystal substrate is the same as in β-PbO powder sample spectrum. The peaks due to B_{1g} modes in the powder sample spectrum (Fig. 2) are too weak as well. Thus the films grown on amorphous and polycrystal substrates do not seem to have a predominating orientation of crystallization.

CONCLUSION

The Raman scattering investigations of PbO films deposited on different types of substrates lead us to the following conclusions: 1. The Raman spectra may serve as a tool for identifying the PbO film crystal modifications and directions of crystallization.

2. The results of the RHEED investigations concerning the crystal structure of the PbO films grown by LAD are confirmed by other means. It is evident that the PbO films consisting solely of a tetragonal phase cannot be grown by LAD at substrate temperatures lower than 300°C, which is the highest T_s in our experiment.

3. The nature of the substrate influences the crystal structure of the films. The films grown on single-crystal quartz substrates show a prevailing orientation of crystallization, while those deposited on amorphous and polycrystal substrates do not seem to show such an orientation.

4. The investigation of the Raman spectra of the β-PbO films with predominant (001) crystal orientation contri-

butes to a more correct, in our point of view, assignment of the phonon modes in this phase, which can hardly be grown in a form of a single crystal.

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