OPTICAL ABSORPTION IN THIN FILMS OF LEAD OXIDES

By M. Jachimowski and J. Szczyrbowski

Department of Solid State Physics, Institute of Metallurgy, Academy of Mining and Metallurgy, Cracow*

Experiments were performed on thin PbO films prepared by reactive cathodic sputtering of lead of 5 N purity. The films deposited in substrates of optical quartz were polycrystalline of tetragonal or orthorhombic structure. Transmission was measured in the range from 1.9 eV to 3.5 eV. McLean's analysis, employed in the elaboration of absorption coefficient data, showed that the optical absorption edge in PbOα is 3.18 eV and in PbOβ 3.36 eV. Optical transitions at energies of 3.11 eV and 2.62 eV were also discovered in PbOβ, interpreted as transitions from the acceptor levels to the conduction band.

1. Introduction

Lead oxide occurs in two polymorphic modifications, tetragonal PbOα and orthorhombic PbOβ. There are many published papers dealing with the optical properties of these oxides. It is commonly acknowledged that the optical absorption edge for PbOα is approx. 2.0 eV, whereas for PbOβ about 2.7 eV. The data quoted in literature are the results of measurements performed by various authors on samples obtained by different techniques. They are highly divergent as regards both the values of energies quoted and the character of the transitions (Table I).

The mentioned substances exhibit photoconduction, the magnitude of which depends on the sample preparation procedure, as this bears an effect on the character and degree of imperfection. A detailed analysis of the trap levels for PbOβ on the basis of measurements of photoelectric and thermostimulated currents was carried out by Heijne [1]. He found the following values of energy for the various kinds of traps:

$A \quad -E_1 = 0.23$ eV relative to the valence band,

$B' \quad -E_2 = 0.33$ eV relative to the valence band,

$C \quad -E_3 = 0.26$ eV relative to the conduction band,

$D \quad -E_4 = 0.5$ eV,

$E \quad -E_5 = 0.38$ eV relative to the valence band.

---

* Address: Zakład Fizyki Ciała Stałego, Instytut Metalurgii AGH, Kraków, al. Mickiewicza 30, Poland.

TABLE I

E(eV) PbOα	Transition	Ref.	E(eV) PbOβ	Transition	Ref.
—	—	—	3.0	—	[11]
2.92 2.06	—	[12]	2.78	—	[12]
2.0	—	[13]	2.7	—	[13]
2.0	for $n = 1$	[15]	2.7	allowed direct	[15]
2.18	forbidden direct	[15]	2.5 1.9	allowed indirect	[15]
2.0	—	[14]	2.72	—	[14]
2.75 1.70 1.90	allowed direct allowed indirect forbidden direct	[16]	2.67	forbidden direct	[16]
2.0	—	[17]	2.6	—	[17]
3.18	allowed direct	[10]	3.36	allowed direct	[10]

Studies on the temperature-dependence of the conductivity of pure and doped PbO are described in Refs [2−5]. The values of activation energy for pure PbOβ quoted in them are 2.3 eV, 2.89 eV and 3.2 eV. The authors of papers [4] and [5] also found that in doped PbOβ there are a number of acceptor levels whose activation energies are contained within the interval 2.1 eV to 2.5 eV.

Our investigation concerns optical absorption in thin films of PbOα and PbOβ formed by cathodic sputtering. A detailed analysis of the results obtained is made for the PbOβ modification.

2. Sample preparation

Experiments were carried out on samples obtained by reactive sputtering of Pb target with 5N purity. Closer details concerning the procurement of films of both PbOα and PbOβ are given in Refs [6] and [7].

Samples were procured by sputtering cathodes of Pb of 5N purity. Transmission measurements were performed on samples of various thicknesses ranging between 0.05 μm to 4 μm deposited on substrates of optical quartz. The thickness of the films was found by the method of single- or multi-ray interference. Crystallographic structure was determined by the Debye-Scherrer method of X-ray analysis.

The films used in measurements were polycrystalline and textured, the degree of which was higher in the thinner films.

3. Measuring techniques and analysis of results

Transmission measurements were carried out on a Specord UV VIS spectrophotometer (Carl Zeiss Jena). The experiments were made with unpolarized light perpendicularly incident on the sample at room temperature. Two measuring techniques were used. The first was based on measurements of transmissions T_1 and T_2 for a pair of films of different thicknesses. With an appropriate choice of thickness difference the error
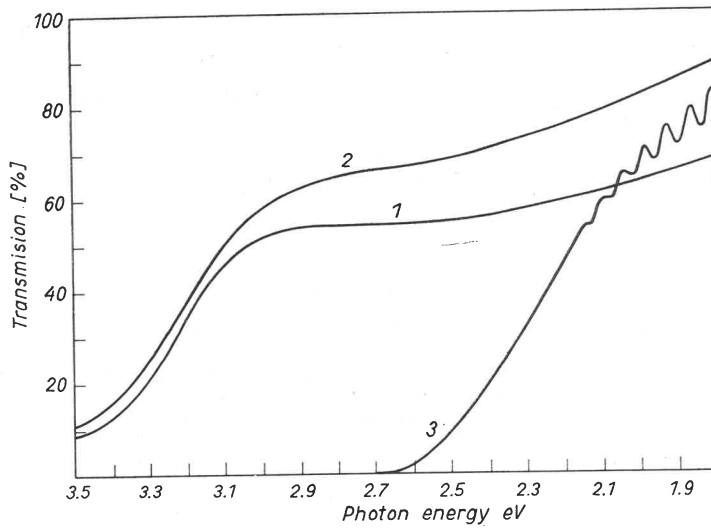
Fig. 1. Transmission curves for typical lead oxide films; curve *1* – tetragonal modification, curve *2* – orthorhombic modification, curve *3* – orthorhombic modification
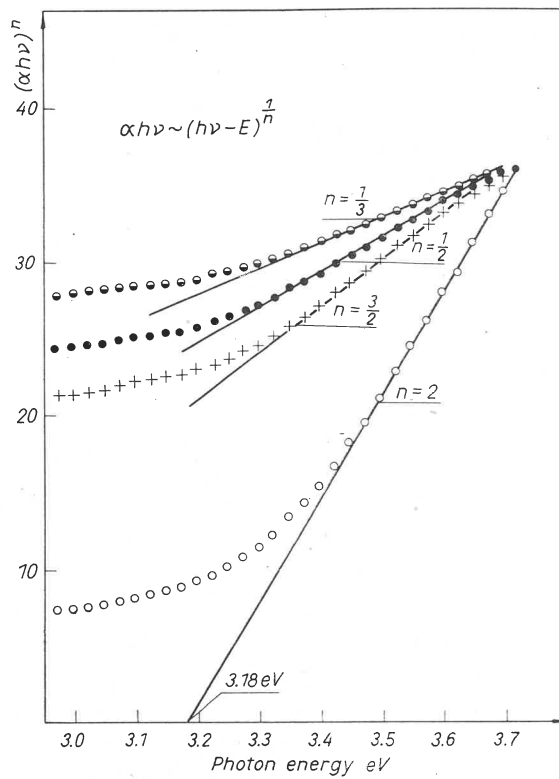

Fig. 2. McLean analysis of absorption for sample 1 of tetragonal PbO

of the absorption coefficient measurement by this method is not greater than one per cent [8]. The second technique was based on measurements of the transmission T_1 of the layer deposited on the substrate and the transmission T_2 of the substrate itself. Under our experimental conditions the error of both techniques is almost the same. A proper choice of sample thickness ensured that the character of the transmission curve was related directly with the given transition.

Figure 1 shows two typical transmission curves for thin films of thicknesses of the order 0.05 to 0.1 μm (curve *1* — tetragonal; curve *2* — orthorhombic) and a curve for a thickness of 4 μm (sample *3*, orthorhombic).
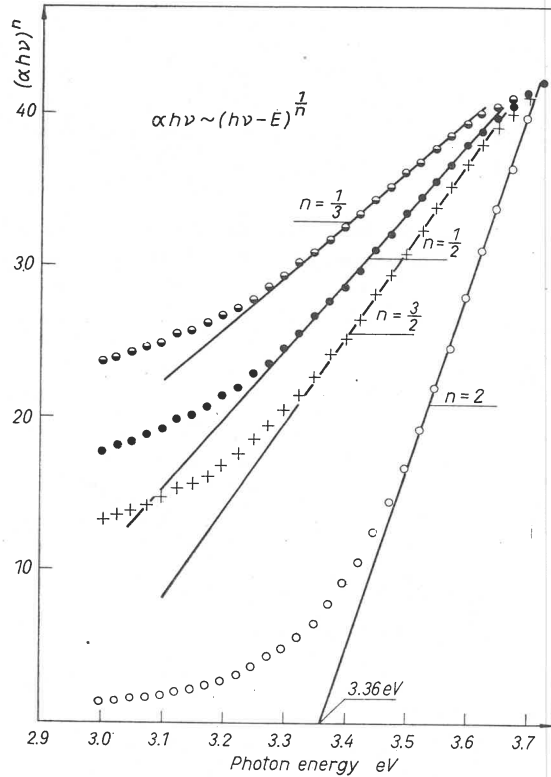

Fig. 3. McLean analysis of absorption for sample 2 of orthorhombic PbO

The analysis of the experimental data was made on the basis of the Mc Lean method [9]. This analysis makes use of the assumption that the absorption coefficient satisfies the relation $\alpha h\nu \sim (h\nu - E_g)^{1/n}$. By extrapolating α to zero we get that the appropriate transition energy E_g is equal to the photon energy $h\nu$. When $n = 2$ the transitions are allowed direct ones, when $n = 2/3$ they are forbidden direct ones, whereas when $n = 1/2$ they are allowed indirect and when $n = 1/3$ forbidden indirect ones.

The necessary numerical computations were carried out on the ODRA 1013 computer at the Institute of Physics of the Polish Academy of Sciences in Warsaw. The program

elaborated in the Department of Spectroscopy of Solids at this Institute for the McLean method linearized the results by the least squares method.

The results of the analysis are presented in Figs 2, 3 and 4. As is seen in Figs 2 and 3, the respective absorption edges (direct transitions) for the tetragonal and orthorhombic modifications are 3.18 eV and 3.36 eV. These results are in good agreement with those quoted earlier in Ref. [10].

A number of samples of the $PbO\beta$ modification of various thicknesses have been examined. It was found that there are additional energy transitions, $E_1 = 3.11$ eV and
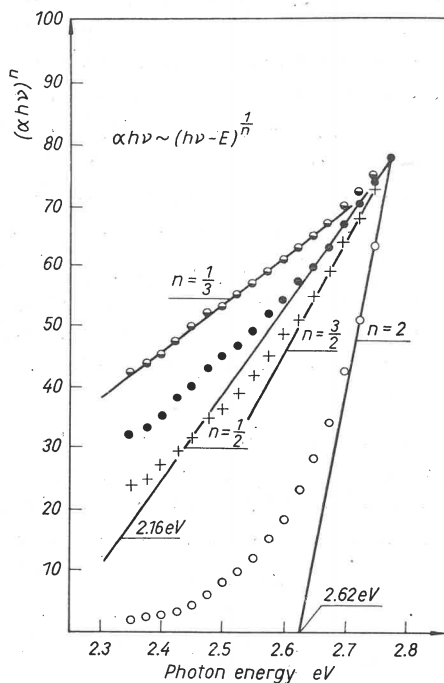

Fig. 4. McLean analysis of absorption for sample 3 of orthorhombic PbO

$E_2 = 2.62$ eV ($E_2' = 2.16$ eV). Transition E_1 found from studies on thin films can be explained well by the model of allowed direct transitions. Transition E_2 (E_2') determined from measurements on thick samples cannot be unambiquously described by the transition model. The value of energy $E_2 = 2.62$ eV corresponds to the model of allowed direct transitions, whereas $E_2' = 2.16$ eV to the model of allowed indirect transitions. The McLean analysis for one of the samples is shown in Fig. 4.

4. Discussion of results

PbO is a AIV — BVI compound. For most compounds of this group the theoretical band model has been calculated. Up to now, however, there is no such model for lead oxides. It appears on the basis of papers [10] and [5] and our measurements that the energies of the optical absorption edges for $PbO\alpha$ and $PbO\beta$ are 3.18 eV and 3.36 eV,

respectively. These energies presumably correspond to the smallest distance between the valence band and the conduction band. Owing to the possible occurrence of exciton levels these values may be slightly too low. The obtained transition of 3.11 eV for some of our samples is in good agreement with the results of Heijne — a transition from the trap level with $E_1 = 0.23$ eV to the conduction band. The used technology of thin films ensured high perfection of structure in the case of the very thin films. Hence the good fit of the E_g transitions to the given model.

For the thick samples (2 to 4 μm) absorption appeared at much lower energies. The transitions occuring in them are hard to describe even approximately with the use of any of the models considered (Fig. 4). By approximating them to allowed direct transitions an energy of about 2.62 eV is obtained, close to the values quoted in a number of papers as the absorption edge [11–17]. Approximation by means of the allowed indirect transitions gives an energy of about 2.16 eV.

Considering that the formation of a number of discrete acceptor levels in PbO β is an established fact, the transition $E_2 = 2.62$ eV ($E_2' = 2.16$ eV) observed by us is a transition from these levels to the conduction band. The difficulties encountered when trying to describe them on the basis of any of the theoretical models may stem from the fact that the experimental absorption curve is conditioned by transitions from two or more acceptor levels, the density of which additionally depends on the purity and/or the perfection of the material.

REFERENCES

[1] L. Heijne, *Philips Res. Rept. Suppl.*, **4**, 2 (1961).

[2] A. Kalb, V. Leute, *Phys. Status Solidi*, (a) **2**, K27 (1970).

[3] A. V. Panfilov, E. G. Ivanchieva, P. V. Drogomiterskii, *J. Phys. Chem.*, **41**, 1072 (1967).

[4] H. Ritschel, G. Schmidt, *Phys. Status Solidi*, **3**, 294 (1963).

[5] H. Ritschel, G. Schmidt, *Phys. Status Solidi*, **3**, 303 (1963).

[6] M. Jachimowski, *Thesis*, AGH, Kraków 1968.

[7] A. Czapla, M. Jachimowski, E. Kusior, *Acta Phys. Polon.*, to be published.

[8] L. Gibson, *Proc. Phys. Soc.*, **63**, 756 (1950).

[9] T. P. McLean, in *Progress in Semiconductors*, Meywood and Company Ltd., London 1960, Vol. 5, p. 55.

[10] N. L. Kramarenko, N. K. Miloslavskii, J. V. Naboikin, *Optika i Spektrosk.*, **6**, 971 (1968).

[11] F. Lappe, *J. Phys. Chem. Solids*, **20**, 173 (1961).

[12] V. A. Izvozkchikov, *Fiz. Tverdogo Tela*, **4**, 2746 (1962).

[13] E. F. Haan, A. Drift, P. P. M. Schampers, *Philips Tech. Rev.*, **8**, 251 (1963/64).

[14] V. A. Izvozkchikov, *Izv. VUZ, Fiz.*, **4**, 128 (1963).

[15] V. A. Izvozkchikov, *Zh. Prikl. Spektrosk.*, **4**, 282 (1966).

[16] R. C. Keezer, D. L. Bowman, J. H. Becker, *J. Appl. Phys.*, **39**, 2062 (1968).

[17] J. C. Schottmiller, *J. Appl. Phys.*, **37**, 3505 (1966).