

OBTAINING THIN FILMS OF LEAD OXIDES BY REACTIVE CATHODIC SPUTTERING

BY A. CZAPLA, M. JACHIMOWSKI AND E. KUSIOR

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

(Received April 8, 1971)

Thin films of lead oxides have been obtained by reactive cathodic sputtering in an argon-oxygen mixture. Sputtering carried out in a 96%Ar + 4%O₂ atmosphere yielded PbO films of tetragonal and orthorhombic structure and PbO_x solid solutions of pseudocubic structure. The effect of sputtering conditions: pressure, power and substrate-cathode distance on the structure of the produced films has been examined. Certain selected conditions of films formation allow a pure orthorhombic or pure tetragonal phase to be achieved.

1. Introduction

Reactive cathodic sputtering may be used as a method of obtaining thin films of chemical compounds. Many materials submitted to sputtering may form with the same reactive gas several chemical compounds which, in addition, may appear in several crystallographic versions. Among others, lead is such a material. Combining with oxygen lead forms well-defined compounds: PbO₂ of orthorhombic and tetragonal structure. In addition, it is possible to acquire solid solutions PbO_x with $1.33 < x < 1.66$ of pseudocubic structure, among which different authors isolate various definite compounds. Most often the compound Pb₁₂O₁₉ is specified [1]. Because of the multitude of different compounds and structures of lead oxides, lead is suitable for examining the process of reactive cathodic sputtering. Work which had been done heretofore on obtaining lead oxides by this method yielded PbO of tetragonal structure [2, 3], PbO₂ of both structures [2] and Pb₁₂O₁₉ [4].

2. Equipment

For obtaining films of lead oxides by reactive cathodic sputtering use was made of the two-electrode apparatus described in Ref. [5]. The cathode was a disc 9.2 cm in diameter made of 5N pure polycrystalline lead pressed on to a metal block cooled by water. Sputtering was accomplished in a mixture of argon and oxygen. Before introducing the

* Address: Instytut Metalurgii AGH, Kraków, Mickiewicza 30, Poland.

reactive gas into the apparatus, it was pumped off to a pressure of the order of 10^{-5} torr. Gas dosing and pressure was controlled by means of a needle valve. Sputtering was carried out at pressures ranging from 5 to 12×10^{-2} torr. The cathode voltages were from 600 to 1200 V.

Effect of oxygen partial pressure on sputtering process

In order to examine the effect of the partial pressure of oxygen on the sputtering process, sputtering was carried out for the lead at various percentage compositions of the argon-oxygen mixture. Films were deposited onto uncooled substrates, causing the temperature of the substrate block to rise during sputtering up to about 100°C . Measured rates of film growth and specific conductivities of films obtained at a cathode potential of 1100 V, pressure of 1×10^{-1} torr and for two substrate-to-cathode distances of 18 and 38 mm are shown in Figs 1 and 2.

Any change in the oxygen content in the sputtering atmosphere causes a change in both the sputtering rate and the specific conductivity of the deposited films of lead oxides. A comparison of the dependence $\sigma = f(\%O_2)$ with the data of Ref. [2] obtained for films deposited under similar conditions shows up large discrepancies.

The films grown at various oxygen contents in the sputtering atmosphere but constant substrate-to-cathode distance of 18 mm varied in colour from black at the lowest oxygen concentration, through yellow characteristic of the orthorhombic PbO , various shades of red of the lead-oxygen solid solutions of different degrees of oxidation [6], up to the brown lead dioxide at the highest oxygen concentration.

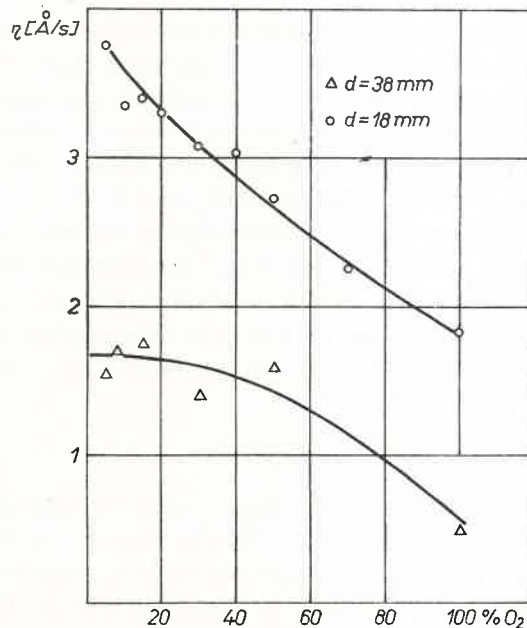


Fig. 1. Rate of growth of lead oxide films versus oxygen content (per cent) in sputtering atmosphere, d - substrate-to-cathode distance, $p = 10^{-1}$ torr, $P = 60$ watts

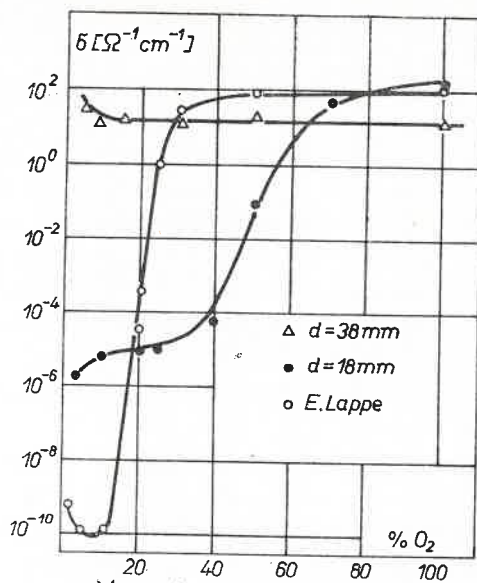


Fig. 2. Conductivity of lead oxides versus oxygen content (per cent) in sputtering atmosphere, d - substrate to-cathode distance, $p = 10^{-1}$ torr, $P = 60$ watts

The measured values of film conductivity vary between the limits established by the conductivity of PbO_2 , *i. e.* $\sigma \approx 10^3 (\Omega \text{ cm})^{-1}$ [7], and single-crystalline PbO , *i. e.* $\sigma \approx 10^{-12} (\Omega \text{ cm})^{-1}$ [8]. Films produced at substrate-to-cathode distance $d = 38$ mm exhibit practically unchanged conductivity when the oxygen content in the sputtering atmosphere is altered. The rate of film deposition is low under these conditions.

In the process of reactive sputtering oxidation may occur at the cathode surface, during the transport of the sputtered material, or at the substrate itself. At high oxygen concentrations in the sputtering atmosphere and small applied sputtering energies the oxidation of the cathode surface may cause a pronounced decrease in its active area, thereby reducing the rate of sputtering. A similar effect has been observed when sputtering Ta in an $\text{Ar} + \text{O}_2$ atmosphere [9]. At the pressures we used the mean free path of sputtered lead atoms does not exceed several millimeters. Hence, it is much smaller than the substrate-to-cathode distance. The probability of oxidation during transport is high, what with oxidation at the substrate gives a lead oxide film of a high degree of oxidation. The greatest possibilities of changing the degree of oxidation by altering sputtering parameters are had, as convincing evidence showed, when the oxygen content in the sputtering atmosphere is several per cent. Therefore, such mixture compositions were used in subsequent researches.

Obtaining PbO of various crystallographic structures

Reactive cathodic sputtering was carried out in a 96% $\text{Ar} + 4\% \text{O}_2$ atmosphere. Applied pressures ranged from 5 to 12×10^{-2} torr. The temperature of the substrate block was maintained constant throughout sputtering within 90 and 120°C . The sputtering

process was accomplished at powers varying between 30 to 65 watts. Structural analysis was by X-ray diffraction, while the composition with respect to crystallographic phases was estimated from the relative intensities of diffraction peaks. In order to ensure a continuous change of the substrate-to-cathode distance at fixed power and pressure, the substrate was set at an angle of about 17° with respect to the cathode surface.

The rate of film deposition as a function of substrate-to-cathode distance, at various powers and fixed pressure and *vice versa*, is illustrated in Figs 3 and 4. At a fixed pressure the rate of film deposition increases considerably with increasing powers. After exceeding approximately 65 watts, a sponge-like layer of unoxidized amorphous lead becomes deposited on the substrate. Likewise, a drop in pressure at a fixed power caused unoxidized layers to become formed.

The temperature of the substrate block may differ considerably from that of the substrate surface reacting with the oxygen. Figure 5 presents the temperature measured by a thermocouple directly at the substrate surface as a function of applied power at a fixed pressure, but various substrate-to-cathode distances.

It was ascertained that the chemical composition and crystallographical structure of the obtained lead oxide films are sensitive to changes in such parameters as the substrate-to-cathode distance, power, and pressure of the sputtering atmosphere. Diagrams of structural

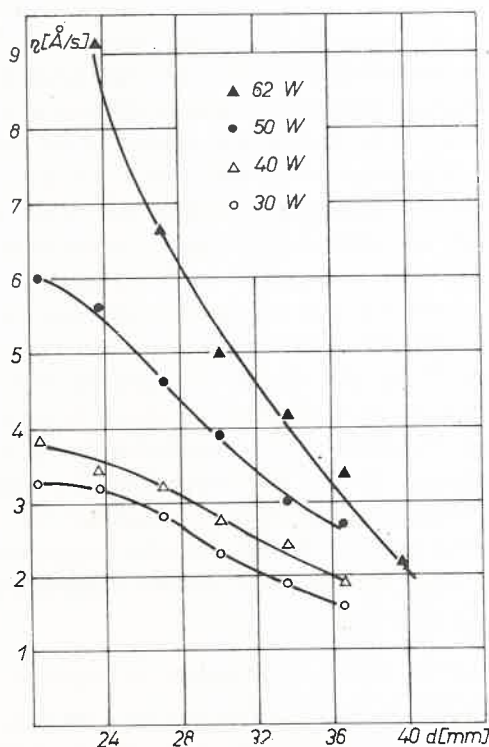


Fig. 3. Rate of growth of lead oxide films *versus* substrate-to-cathode distance d , $p = 12 \times 10^{-2}$ torr

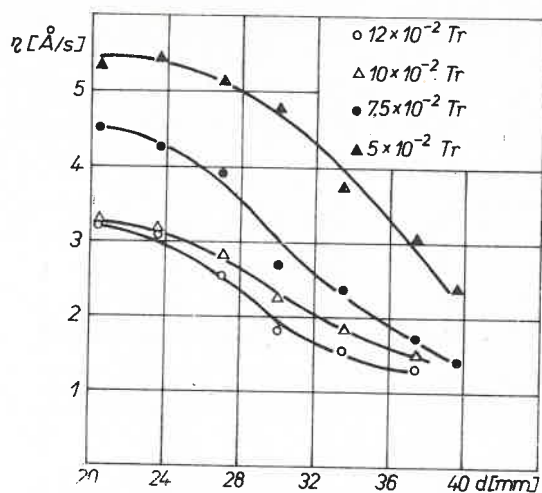


Fig. 4. Rate of growth of lead oxide films versus substrate-to-cathode distance d , $P = 30 \text{ W}$

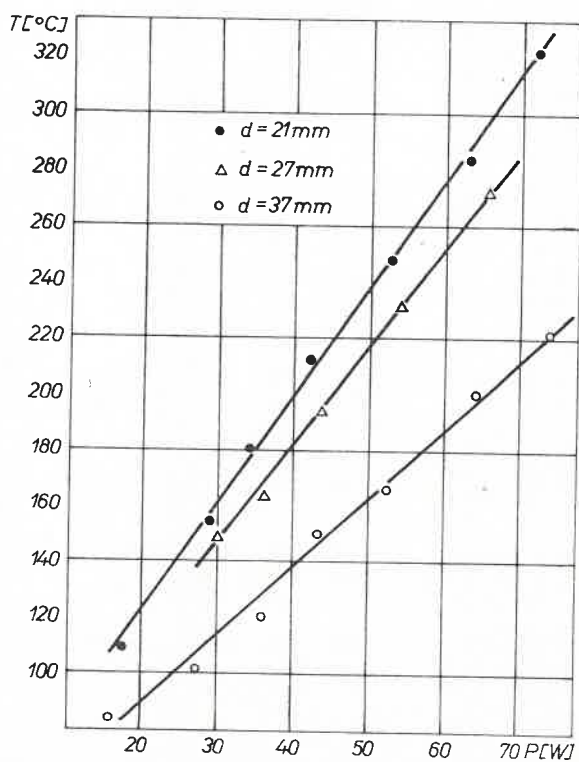


Fig. 5. Dependence of substrate surface temperature T on power P , $p = 12 \times 10^{-2} \text{ torr}$

changes as a function of these parameters are shown in Figs 6 and 7. It is seen in Fig. 6 that the PbO orthorhombic structure arises at lower pressures and small substrate-to-cathode distances, hence, at a condensation of plasma of higher temperature. The PbO tetragonal structure forms at large distances and not too low pressures, hence, at a condensation of plasma of lower temperature. When the oxygen concentration is increased (that is, pressure is lowered), lead oxides of a higher degree of oxidation and pseudocubic structure are formed.

Conditions favourable for obtaining PbO of orthorhombic structure are achieved by lowering pressure at a fixed power or by increasing power at a fixed pressure (Fig. 7). The feasibility of such changes are limited, however. When the pressure is lowered the amount of unoxidized lead increases, giving a strongly non-stoichiometric composition of the film. A similar effect prevails when power is increased too much.

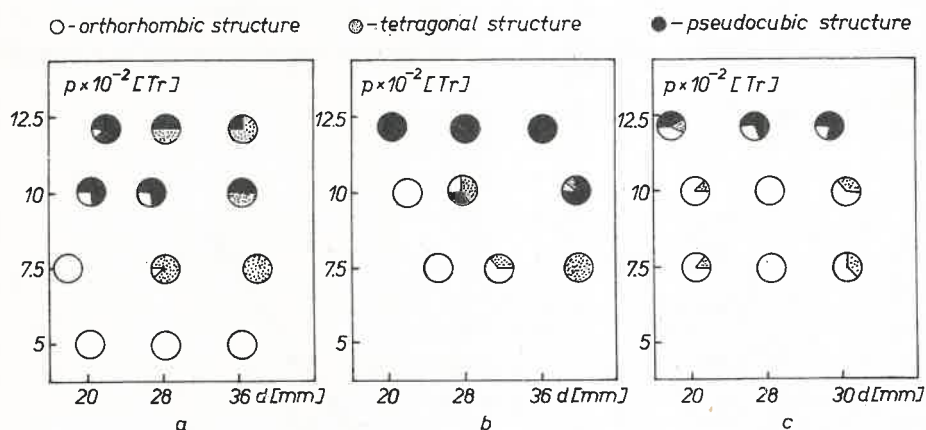


Fig. 6. Changes in structure of lead oxide films as a function of substrate-to-cathode distance d and sputtering atmosphere pressure p for powers P of: a) 30, b) 40 and c) 50 watts

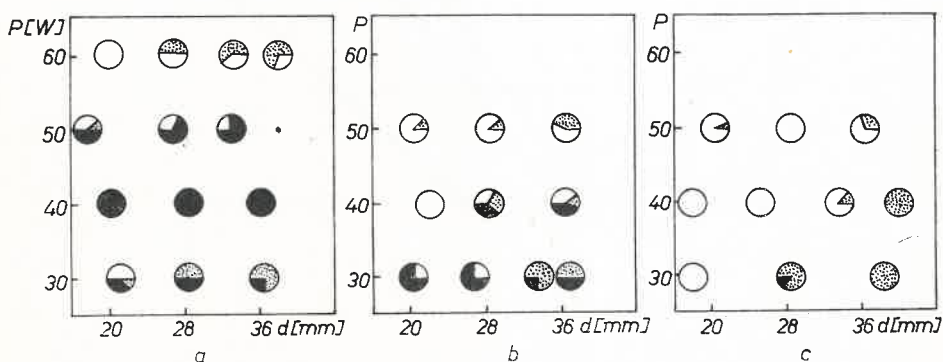


Fig. 7. Changes in structure of lead oxide films as a function of substrate-to-cathode distance d and power P for pressures p of a) 12×10^{-2} , b) 10×10^{-2} and c) 7.5×10^{-2} torr. Notation as in Fig. 6

The conditions for obtaining PbO of tetragonal structure are rather critical. They are determined by the ratio of oxygen concentration to sputtering rate and the temperature of the condensing plasma.

The possibility of choosing sputtering parameters in order to get PbO of tetragonal or orthorhombic structure may be assessed on the basis of the diagrams in Fig. 7. It is easiest to get either of the PbO phases at a pressure of 7.5×10^{-2} torr (Fig. 7c). The tetragonal phase becomes formed at powers between 30 and 40 watts and substrate-to-cathode spacings greater than about 33 mm. The orthorhombic phase forms at the same powers at smaller substrate-to-cathode distances. With increasing power the region occupied by the orthorhombic phase shifts towards the larger substrate-to-cathode spacings.

At a pressure of 12×10^{-2} torr and power of 40 watts the obtained lead oxides had a higher degree of oxidation and pseudocubic structure. The fact that they appeared in the region of medium powers may stem from a superposition of two effects. With increasing power the plasma temperature rises, hence, oxidation of lead is more probable. At the same time, owing to the enhanced rate of sputtering, there is a drop in the number of oxygen atoms per atom of sputtered lead. In effect, maximum oxidation occurs at the medium powers.

3. Conclusions

In the process of reactive cathodic sputtering it is possible to obtain lead oxides of compositions ranging from PbO to PbO₂. At high oxygen concentrations in the sputtering atmosphere (Ar + O₂) the chemical composition of the deposited layer is determined by the oxidation of the cathode surface. In this case the sputtering product is PbO₂. At low oxygen contents in the sputtering atmosphere it is possible to obtain PbO of tetragonal and orthorhombic structures or PbO_x solid solutions of pseudocubic structure. By appropriately selecting the sputtering parameters, *i.e.* the pressure, power and substrate-to-cathode distance, PbO of pure tetragonal or orthorhombic structure may be obtained. The orthorhombic structure forms at low pressures, high powers and small substrate-to-cathode spacing (that is, at higher plasma temperatures), whereas the tetragonal structure forms at higher pressures, lower powers and larger substrate-to-cathode distances (that is, at lower plasma temperatures). Under favourable conditions of pressure and power both phases may become oxidized, forming PbO_x solid solutions of pseudocubic structure.

Results of a study of the electrical and optical properties of PbO films obtained by reactive cathodic sputtering will be published in future papers.

The authors thank Professor T. Piech for his interest in this work, fruitful discussions and aid in editing this article.

REFERENCES

- [1] W. B. White, R. Roy, *J. Amer. Ceram. Soc.*, **47**, 242 (1969).
- [2] F. Lappe, *J. Phys. Chem. Solids*, **23**, 1563 (1962).
- [3] K. Wasa, S. Hayakawa, *Japan J. Appl. Phys.*, **8**, 276 (1969).

- [4] M. L. Lieberman, R. C. Medrud, *J. Electrochem. Soc.*, **116**, 242 (1969).
- [5] E. Leja, *Acta Phys. Polon.*, **A38**, 165 (1970).
- [6] T. Katz, *Ann. Chem.*, **5**, 5 (1950).
- [7] I. A. Aguf, A. I. Rusyan, M. A. Dasoyan, *Zashchitnye metalicheskie i oksidnye pokrytiya*, Moscow 1965.
- [8] L. Heijne, *Philips Res. Rep. Suppl.*, **4**, 2 (1961).
- [9] E. Hollands, D. S. Campbell, *J. Math. Sci.*, **3**, 544 (1968).