PREPARATION OF A THIN FILM OF Pb_3O_4 BY THERMAL TREATMENT OF PbO_2 FILM

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β-PbO_2 films were deposited onto a nickel substrate by an electrochemical process. They were thermally treated in air for 24 h at different temperatures (100–650 °C). Then, these films were characterized in terms of their structure, band gap, film morphology, room temperature resistivity and photoresponse. It was observed that β-PbO_2 can be converted to $PbO_{1.57}$ or Pb_3O_4 and β-PbO by thermal treatment at 350 °C, 450 °C and 650 °C respectively, and Pb_3O_4 seems to be a better material for developing photoelectrochemical solar cells.

1. INTRODUCTION

Lead forms many oxides, of which Pb_3O_4 is a photosemiconductor with a band gap of 2.14 eV. In the absence of any method available for the preparation of thin films of Pb_3O_4, we have tried to explore this preparation by thermally removing one oxygen atom per three PbO_2 molecules because Pb_3O_4 is expected to be formed according to the following reaction

$$2PbO_2 + PbO \rightarrow Pb_3O_4$$

and because there is an electrochemical method available for the preparation of PbO_2 film. In the present work, a study has been made to find out the best conditions under which electrochemically deposited β-PbO_2 from a lead perchlorate bath[1] could be converted by thermal treatment to obtain a thin film of Pb_3O_4.

2. EXPERIMENTAL TECHNIQUES AND RESULTS

Analytical grade chemicals and doubly distilled water were used in our experiments. Thin films of PbO_2 were prepared by electrochemical oxidation of a lead perchlorate bath over a nickel substrate, a constant current density of 1 mA cm^{-2} was used. All films were deposited to a thickness of about 6 μm.

For conversion of PbO_2 to Pb_3O_4, a thermal treatment was used[2–4] for which lead dioxide films were kept in a furnace under a closed air atmosphere for 24 h at

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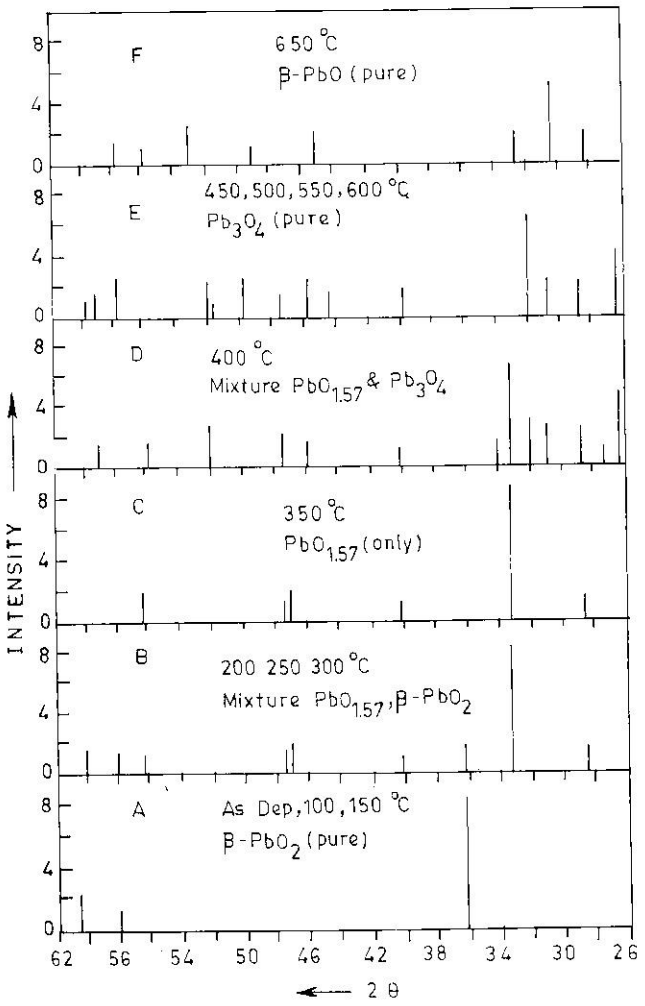

Fig. 1. XRD patterns of thermally treated films.

different temperatures ranging from 100 to 650 °C in steps of 50 °C. Films were heated and cooled at the rate of 10 °C min^{-1} and 5 °C min^{-1} respectively. A nickel substrate was used because its work function is close to the value of the conduction band of Pb_3O_4 and thus it can give an ohmic contact at the back of the film. It is possible that the nickel substrate could form its oxide during the thermal treatment, but its impact on the physical properties of Pb_3O_4 was not studied.

Each thermally treated film was analysed by X-ray diffraction (XRD) and the observed d spacings were compared with those given in the ASTM[5] chart (these values are not given because it would increase the length of the paper) to confirm the type of oxide formed (Fig. 1). The XRD results were obtained with a Phillips diffractometer (model PW 1140) using a Cu Kα source. Scanning was done at 2° min^{-1} in the 2θ range 26–62 °C.

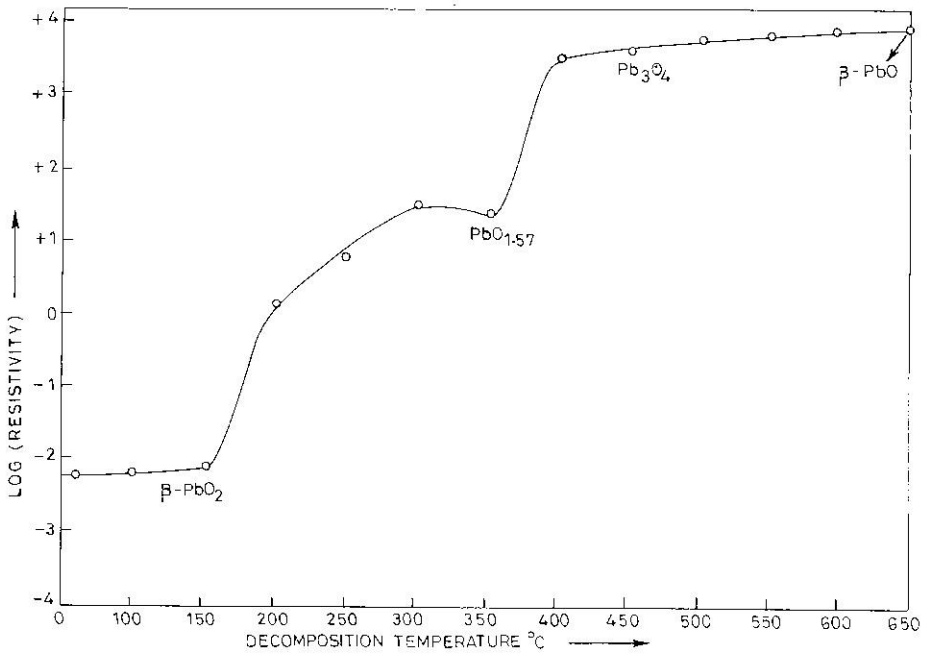

Fig. 2. Room temperature resistivity of thermally treated films. The temperatures on the axis are those at which the films were prepared.

The electrical resistivity (d.c.) of each film was measured with a Solatron digital multimeter, model 7151 (which can measure eight and a half digits), at room temperature by making a front contact on the film. The contact was made by evaporating 1 μm of lead under vacuum over the lead oxide film. For d.c. conductivity measurements, contact was made between the lead film and the nickel substrate. Typical results of the room temperature resistivity of films obtained by thermal treatment at different temperatures are shown in Fig. 2. Here the temperature on the x-axis is the temperature at which the films were thermally treated.

The morphology of the films was studied by scanning electron microscopy (SEM) at magnifications of $300\times - 3000\times$. Scanning electron micrographs of as-deposited film of β-PbO_2 are shown in Figs. 3 and 4. Figure 3 shows the bulk surface morphology of the film. Figure 4 shows the distorted surface of the film near the edges (which is expected in electrochemical deposits if the corners of the surfaces of substrates are not very uniform).

Scanning electron micrographs of films thermally treated at 450 °C (*i.e.* the temperature where Pb_3O_4 was formed) show that there is some difference in the morphology of the film due to thermal conversion of PbO_2 into Pb_3O_4; this may also be expected owing to change in the structure of film from PbO_2 to Pb_3O_4 (Fig. 5). On the basis of SEM observations it can be concluded that thermal treatment does affect the surface morphology of the film and some pin holes were formed.

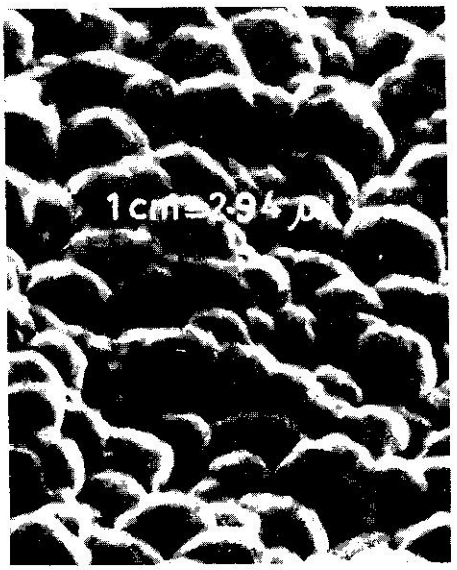

Fig. 3. Scanning electron micrograph of a deposited film of PbO_2.

Fig. 4. Scanning electron micrograph of the edge of the PbO_2 film.

Fig. 5. Scanning electron micrograph of PbO_2 film thermally treated at 450 °C for 24 h in air.

In order to measure the band gap of the material formed at different temperatures, diffuse reflectance spectra (Varian Superscan-3) of each film were taken in the range 200–800 nm. The derivative of the reflectance was also plotted *vs.* wavelength to produce accurate values of the band gap[7] (Fig. 6).

A photoelectrochemical cell[4] of the type lead-oxide/iodate, iodide ions/Pt was

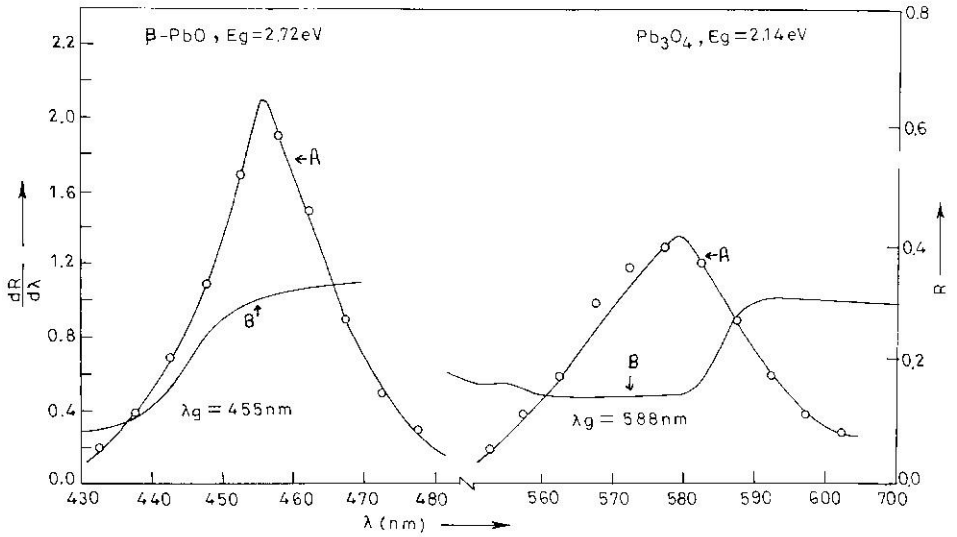

Fig. 6. (A) Reflectance spectra of Pb_3O_4 and β-PbO; (B) differential plots of reflectance spectra.

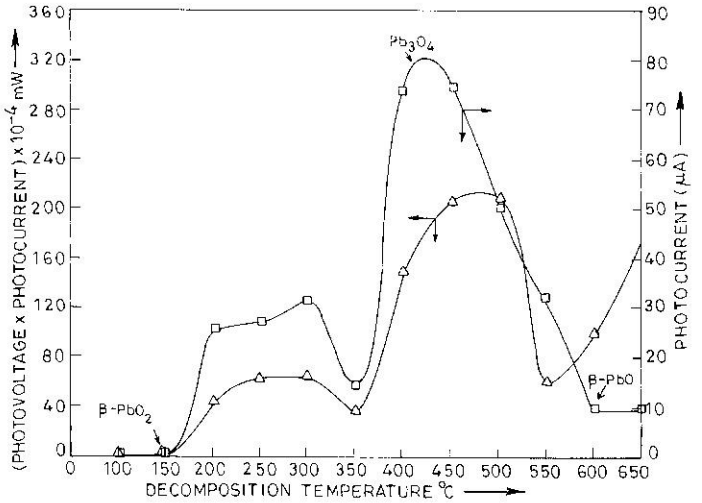

Fig. 7. Photoresponse of thermally treated films in a $PbO_x/IO_3^-, I^-/Pt$ photoelectrochemical cell. The temperatures on the axis indicates the temperatures at which these films were prepared. The photoresponse was measured at room temperature.

fabricated. The short-circuit photocurrent and open-circuit photopotential were measured on each film obtained after different thermal treatments. The variation in photocurrent *vs.* temperature at which films were thermally treated (of the films whose resistivity values are plotted in Fig. 2) is shown in Fig. 7. This figure also includes a graph showing the variation in power (*i.e.* the product of the open-circuit photopotential and short-circuit photocurrent) *vs.* the different temperatures at which the films were thermally treated. This experiment was done to find out the

relative photoresponse of the different oxides formed during the thermal treatment of PbO_2 films.

3. DISCUSSION

Electrochemically deposited thin film PbO_2 converts to $PbO_{1.57}$, Pb_3O_4 and β-PbO after annealing for 24 h in air at 350 °C, 450 °C and 650 °C respectively. Annealing of the film gives a mixture of different oxides when thermally treated at any other temperatures (Fig. 1). It is also observed that the room temperature d.c. electrical resistivity shows a sharp change for materials formed at different temperatures (Fig. 2). The band gaps of films annealed at the above three temperatures were determined by reflectance spectrometry and the band gaps for β-PbO and Pb_3O_4 were found to be 2.72 and 2.14 eV respectively. The intensity of the reflectance peak for $PbO_{1.57}$ was too low to be recorded. Hence the reflectance data of this film are not shown in Fig. 6. The morphology of thin films of β-PbO_2 and Pb_3O_4 suggests that during thermal annealing of the PbO_2 film, surface morphology is not the same (Figs. 4 and 5). This change in the surface morphology of these two films is due to the structural changes (from β-PbO_2 to Pb_3O_4) occurring in the film. Scanning electron micrographs of PbO_2 film also show that if the substrate is not uniformly cleaned, a non-uniform growth of the materials can occur at the edges of the substrate. This behaviour however is very common in electrochemical deposition (Fig. 3).

It can therefore be concluded that electrochemically deposited thin film PbO_2 can be thermally converted to thin film Pb_3O_4. Among the various oxides formed, Pb_3O_4 seems to be the best photosemiconductor material[6] for developing a photoelectrochemical cell (Fig. 7). The high resistivity of Pb_3O_4 also suggests the material to be near the required stoichiometry.

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