Photoelectrochemical (PEC) Solar Cell with PbO_{2-x} Semiconducting Electrodes

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ABSTRACT

Lead dioxide, due to its attractive band gap (1.6 eV) and its prolonged use in lead acid batteries, may be a good choice as photoelectrode in PEC Solar Cells. Lead dioxide is a degenerate semiconductor and hence highly conducting. However, it can be made semiconducting and photoconducting on reduction. Therefore, electrochemically deposited PbO_2 films on nickel substrates are thermally reduced at different temperatures from 100°C to 450°C to get PbO_{2-x}. They are then characterised by resistivity, XRD, reflectance spectra and SEM studies. Finally, these films are used for PEC Cell studies.

1. INTRODUCTION

The Photoelectrochemical (PEC) Solar Cells have drawn much attention in recent years for their use in fabricating a solar rechargeable battery [1-7]. Efforts are being made [8-12] in the direction of developing an efficient PEC cell with stable photoanode or photocathode. In the earlier work [6] on n-Pb_3O_4 and the present investigations on PbO_{2-x} and α-PbO, we find that these oxides of lead may be suitable candidates for their use as photoelectrodes in PEC cells.

Lead dioxide, due to its attractive band gap (1.6 eV) and its prolonged use in lead acid batteries, seems to be useful choice for the PEC studies. Very few reports have been published for its use in the PEC-[13] and the photovoltaic [14] solar cells. The PbO_2 material, being highly conducting, is itself a degenerate [15] semiconductor. However, it can be made semiconducting and hence photoconducting on reduction [15-18].

In the present work, preparation, characterisation and some PEC studies of various non-stoichiometric films of the electrochemically deposited lead dioxide on suitable substrates have been carried out.

2. EXPERIMENTAL DETAILS

The dense films of PbO_2 were deposited from the perchlorate bath [19] with a constant current density 1 mA/cm^2. In the PEC studies, the photoelectrode was exposed to light through a window cut in platinum counter electrode, keeping them 0.5 cm apart from each other. The intensity of light was always maintained 100 mW/cm^2 at the electrodes with the help of a halogen quartz lamp (250 W). Analar grade of chemicals were used in all the experiments without any further purification. The thickness measurements were done by weight method using microbalance (Dhona Instruments). The scanning electron microscope (SEM) studies were carried out by the instrument "Siemens Autoscan".

3. RESULTS AND DISCUSSIONS

After selection of a suitable substrate, several PbO_2 films (4 cm^2 area) were deposited at the current density 1 mA/cm^2 for 2.5 hrs. Then the semiconducting and non-stoichiometric PbO_{2-x} films were obtained by annealing the As-deposited films for 24 hrs from 100°C to 450°C. These reduced films were then characterised by XRD, reflectance spectra, resistivity and SEM studies followed by PEC investigations.

3.1 Substrate Selection

An ohmic contact is always desirable between the semiconductor and its back metal contact to avoid any additional series resistance in the PEC Solar Cell. Therefore the current-voltage characteristics of lead dioxide films, deposited on nickel, platinum and tin dioxide substrates, were studied. The films on platinum and tin dioxide show highly non-ohmic behaviour, while nickel gives sufficiently low contact barrier.

However, the rough surface contact between semiconductor and metal usually gives barrierless contact because of the recombination conduction mechanism [20]. Therefore, the PbO_2 films were deposited particularly on scraped surface of nickel substrate. The current-voltage characteristics then proved it to be ohmic contact. The film was stable on substrate even after keeping it in ultrasonic vibrator for an hour. Hence, nickel was finally selected as suitable substrate for further work.

3.2 Rate of Deposition

The thickness of As-deposited films are plotted against the time of deposition as shown in Fig. 1. Based on the average rate of deposition (423.2 Å/min), the thickness of the film deposited for 2.5 hrs will be 6.3480 μm which is in good agreement with that of estimated by scanning electron micrograph 6.66 μm (Fig. 2).

3.3 X-ray Diffraction Studies

The X-ray diffraction pattern of the typical as deposited film (Fig. 3A)

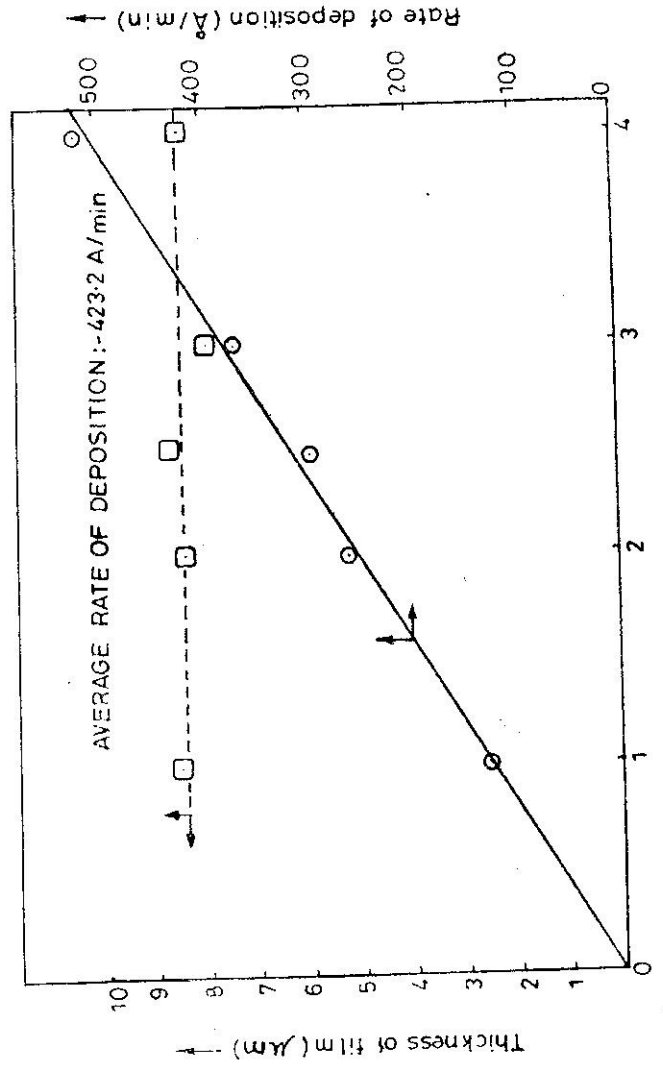

Fig. 1. The plot of time of deposition vs. thickness of the As-deposited PbO_2 films giving the average rate of deposition.

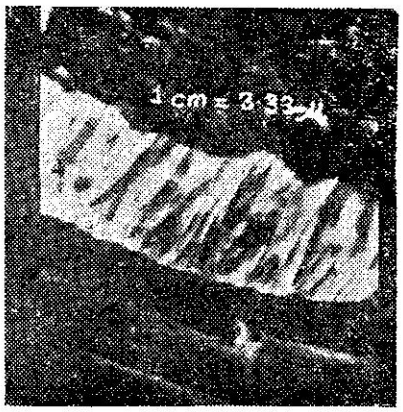

Fig. 2. Scanning electron micrograph of cross-sectional view of the thickness of film deposited for 2.5 hrs.

shows the formation of β-PbO_2 with highly preferred orientation ($hkl = 020$, $d = 2.48$ Å). On annealing, a marked change is observed only after 200° where some new peaks emerge (Fig. 3B). The nature of the pattern is same in both films annealed at 200°C and 250°C except that the relative intensities of new peaks are slightly higher in the latter. The relative intensities of these new peaks gradually increase with annealing temperature (Fig. 3C) and results in a pure new phase at 350°C (Fig. 3D). All the original peaks of Fig. 3A are absent here. The formation of Pb_3O_4 starts at 400°C (Fig. 3E) resulting in pure Pb_3O_4 at 450°C (Fig. 3F), which is also obvious by the colour change from black-brown to orange-red.

The pure intermediate phase (Fig. 3D) was identified and confirmed [21] to be $PbO_{1.57}$ by the comparison of its XRD pattern with that of β-PbO_2 powder annealed at 350°C for 24 hrs (Fig. 4).

The β-lead dioxide is always non-stoichiometric ($PbO_{1.94}$) at room temperature [22]. Various other intermediate oxides, e.g. $PbO_{1.71}$, $PbO_{1.63}$, $PbO_{1.57}$, $PbO_{1.44}$, $PbO_{1.33}$ (Pb_3O_4) and PbO can also be formed by the heat treatment of lead dioxide [23-27]. However, from our present XRD study it appears that only $PbO_{1.57}$ is a stable phase up to 350°C all other oxides between $PbO_{1.94}$ and $PbO_{1.57}$ seem to be the mixtures of the two in different ratios. This fact is also supported by the work of Anderson and Sterns [23], who found that the decomposition virtually stops at $PbO_{1.57}$ even after annealing PbO_2 for more than three days at 335°C.

3.4 SEM Studies

Scanning electron micrograph of As-deposited PbO_2 film shows the regular grain formation with average grain size 3.38 μm (Fig. 5). Besides this, some unusually big particles, as compared to the original grains, are formed at the edges (Fig. 6). However, the film at higher temperatures are found to loose their regular grain shapes and sizes, resulting into the complete distortion of

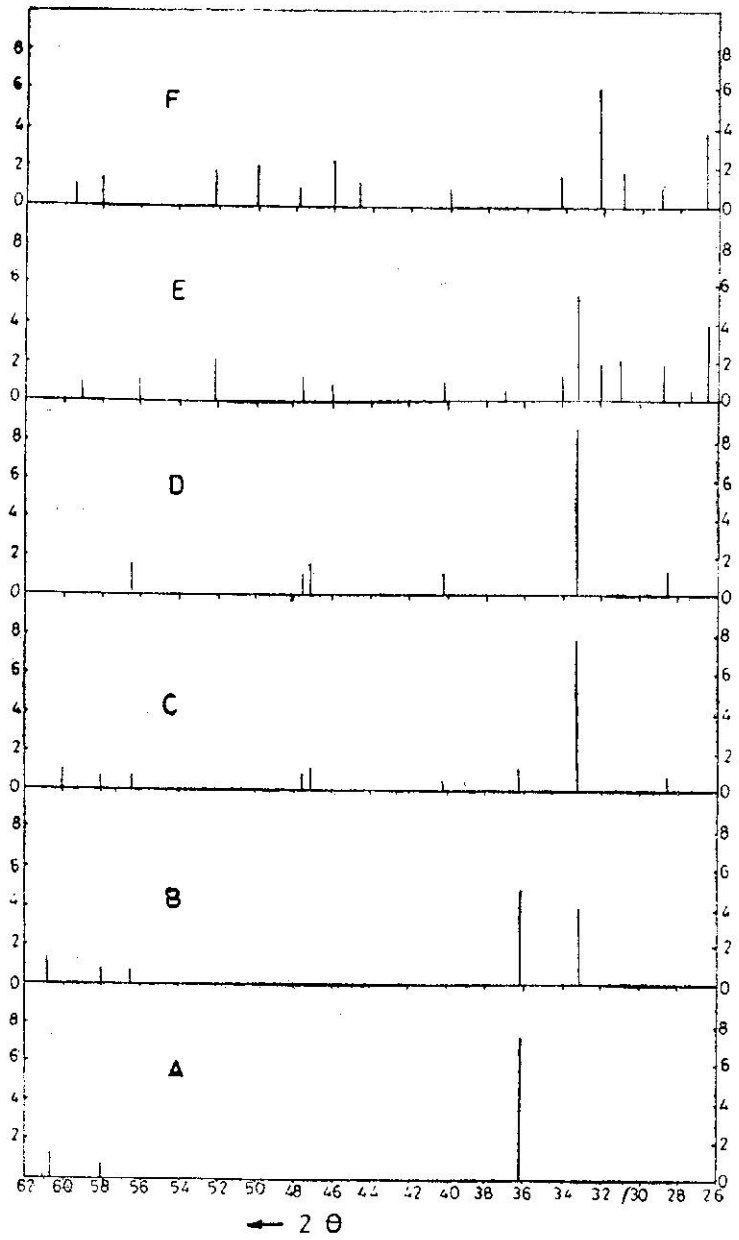

Fig. 3. A comparative X-ray diffraction patterns of the films annealed at different temperatures.
(A) As-deposited, 100°C, 150°C. (B) 200°C and 250°C.
(C) 300°C. (D) 350°C. (E) 400°C. (F) 450°C.

grains at 450°C (Fig. 7). The distortion of grains are probably responsible for the lack of preferred orientation in the films at 400°C and 450°C (Fig. 3).

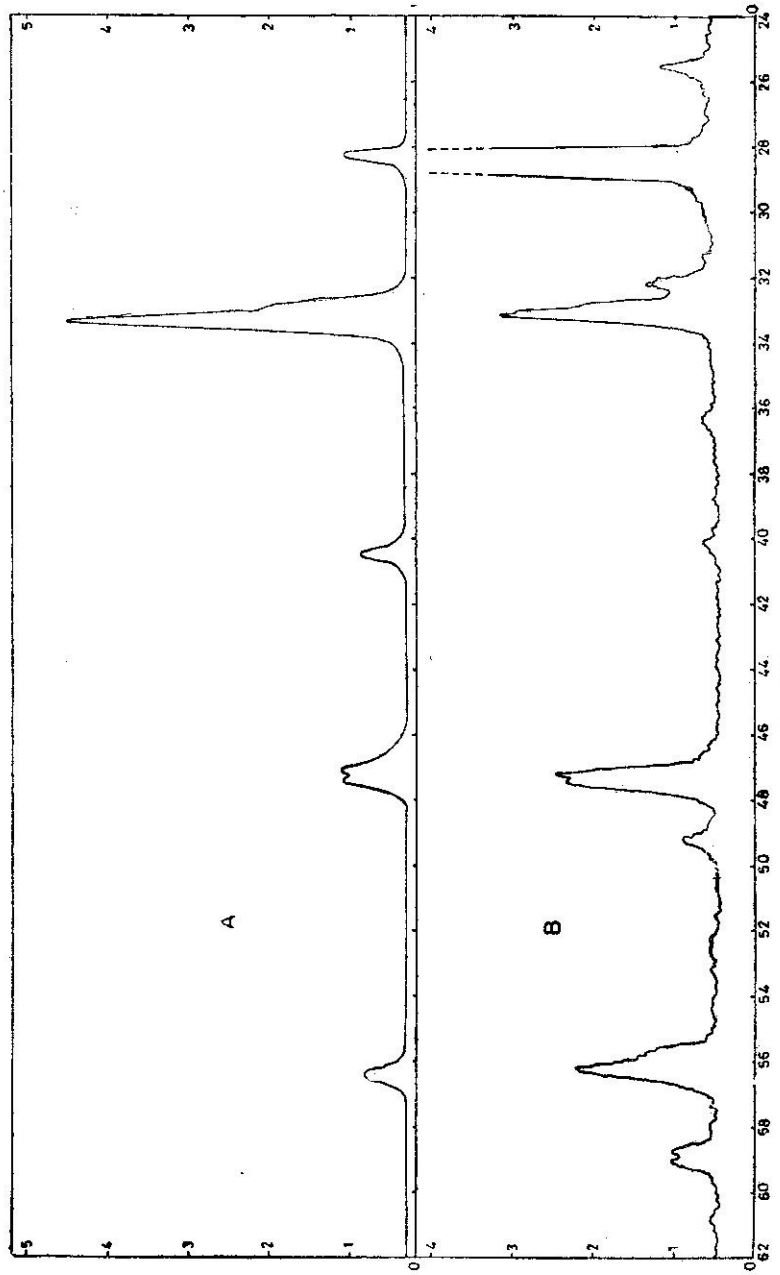

Fig. 4. Comparison of the XRD patterns of annealed PbO_x samples at 350°C for 24 hrs (a) film (b) powder.

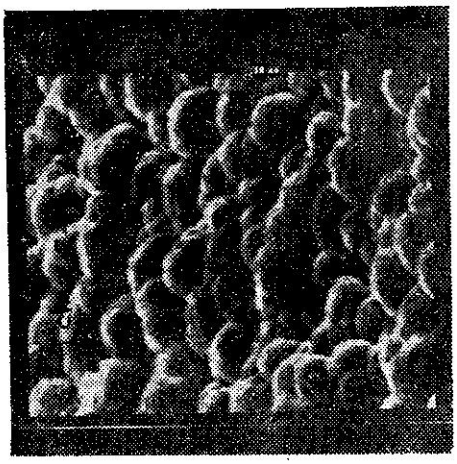

Fig. 5. Scanning electron micrograph of the surface of As-deposited PbO_2 films (1 cm = 2.94 μm).

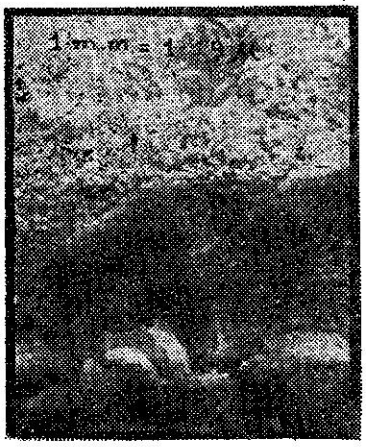

Fig. 6. Scanning electron micrograph of the As-deposited film of PbO_2 at the edge of substrate.

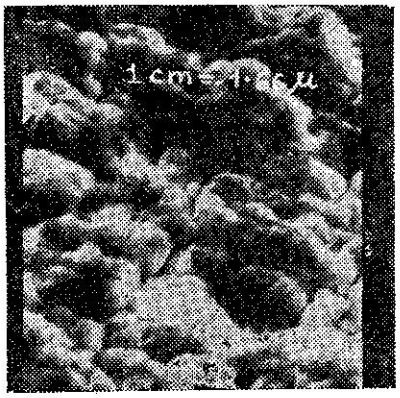

Fig. 7. Scanning electron micrograph of film annealed at 450°C.

3.5 Resistivity

The plot of log (resistivity) vs. the annealing temperatures of the films (Fig. 8) shows the drastic increase in resistivity from 5.4×10^{-3} ohm-cm to 3.95×10^{3} ohm-cm with the increase in annealing temperature. Initially up to 350°C, the increase is probably due to the formation of $PbO_{1.57}$ and then due to Pb_3O_4. The resistivity of the As-deposited film is in good agreement with that of reported by Mindt [28]). But the resistivity of Pb_3O_4 film is much less than that of powder (2.33×10^{10} ohm cm [29]). The electrochemical reduction of α-PbO_2 films also causes the increase in resistivity as reported by Peter [15, 16].

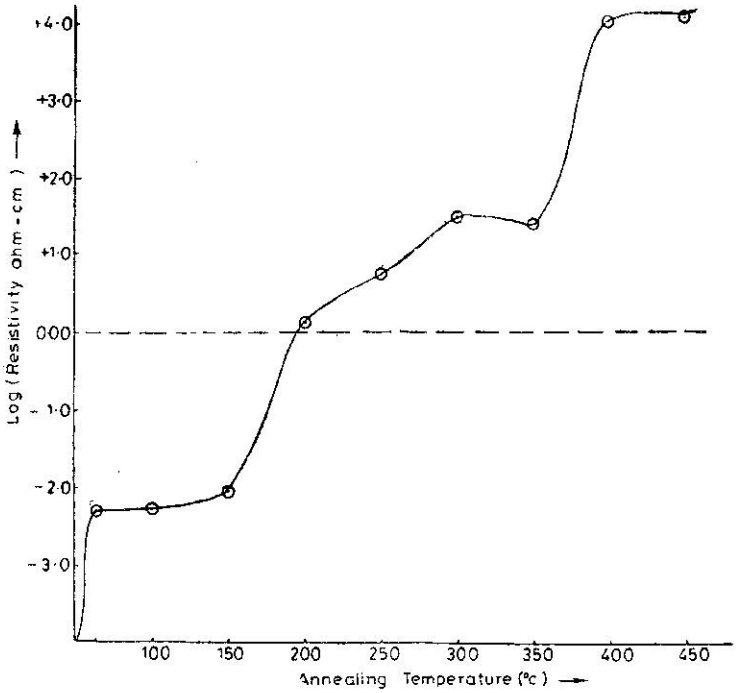

Fig. 8. The plot of log (resistivity) vs. annealing temperature of the films.

3.6 Reflectance Spectra

Reflectance spectra is an efficient tool for the determination of band gap of semiconductors [6, 30]. Galantseva and Shamba [31] have used the reflectance spectra for the study of the thermal decomposition of α-PbO_2. Recently the dynamic electrochemical growth of PbO_2 has been studied with this technique by Gale [32]. No report has been found on its use to study the thermal decomposition of β-PbO_2 films.

Out of the as-deposited and all annealed films, only those at 400°C and 450°C showed the characteristic inflection in reflectance spectra (Fig. 9e and 9d). The differential plot of these spectra gave the band gap 2.1 eV corresponding to Pb_3O_4, the presence of which is also confirmed by XRD studies (Fig. 3). However, the powder PbO_2 and $PbO_{1.57}$ (as obtained in section 3.3) shows some characteristic inflections (Fig. 9a and Fig. 9b) giving the value of band gap 1.67 eV and 1.47 eV respectively.

The band gap in the degenerate semiconductors (e.g. PbO_2) are always more due to already filled states in conduction band. The large variation in the reported [28, 33, 34] band gap values for PbO_2 from 1.45 to 2.0 eV seems to be due to variation in the extent of degeneracy from sample to sample.

The lack of reflection in all other films (i.e. from As-deposited to the annealed up to 350°C), appears to be a result of preferred orientation effect (Fig. 3A-3D), making very few scattering centres available for reflection. However, in powder, large number of scattering centres are available. This is obvious

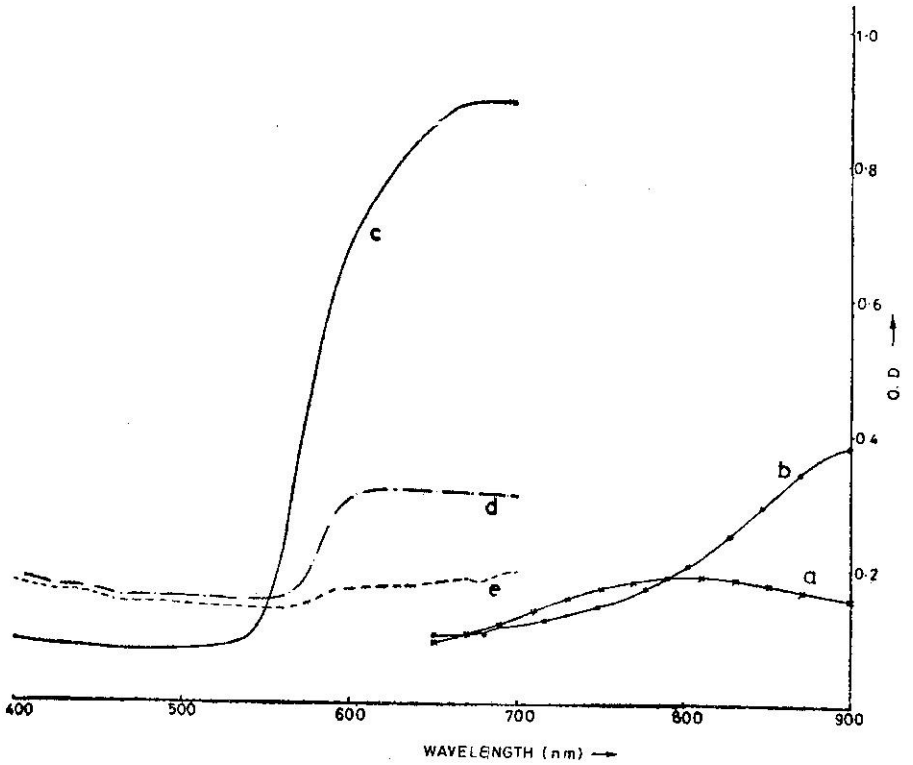

Fig. 9. The reflectance spectra of powder and films (a) $\beta-PbO_2$ powder. (b) $PbO_{1.67}$ powder. (c) Pb_3O_4 powder. (d) Annealed film at 450°C. (e) Annealed film at 400°C.

also from the difference in the extent of reflection in Pb_3O_4 powder (Fig. 9c) and its films (Fig. 9d and 9e). Peter [16] in the study of electrochemical reduction of α-PbO_2 films, has concluded that non-stoichiometric PbO_x phases are the mixtures of PbO_2 and PbO. Also, that PbO is responsible for the high resistivity of the reduced films. But according our combined XRD and reflectance spectra, there is no evidence of the presence of PbO in thermally reduced films. Hence, the pure intermediate phase $PbO_{1.57}$ becomes a matter of interest. Anderson and Sterns [23] have proposed a formula $Pb_{12}O_{19}$ for it.

3.7 PEC Studies

3.7.1 Chemical Stability

Besides having reasonable band gap and conductivity, the photoelectrode must be stable chemically in electrolytes. The effect of the treatment of the as-deposited films with 1 M acids and bases for 24 hrs was examined by XRD studies. The film dissolves in HCl and peels off from the substrate in HNO_3 and H_3PO_4. However, the surface is damaged severely in H_2SO_4 and slightly in $HClO_4$ (Fig. 10). The film was chemically unaffected by NaOH, KOH,

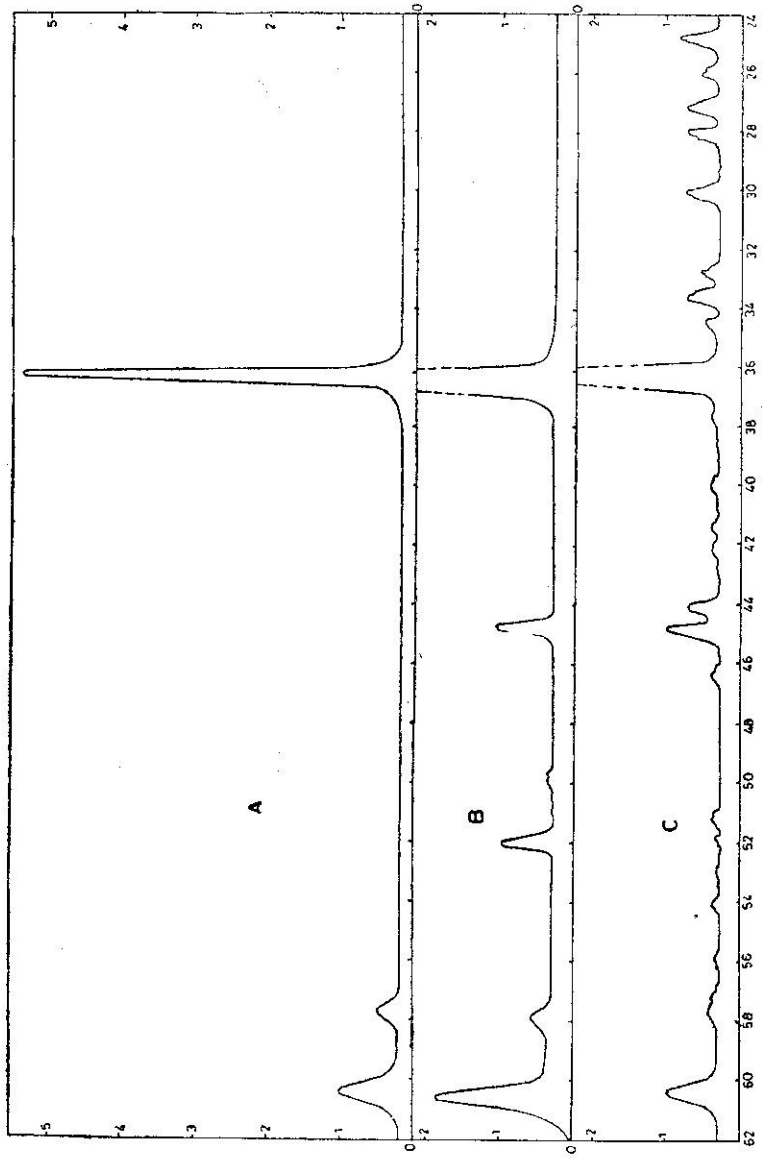

Fig. 10. The XRD pattern of As-deposited (A) $HClO_4$ treated (B) and H_2SO_4 treated (C) films.

NH_4OH and water. So we conclude that these electrodes should be used only in neutral or basic media.

3.7.2 Selection of Electrolyte

The valence band is approximately same in all oxides [35, 36]. Therefore, taking the valence band edge E_v at 6.56 eV and band gap 1.47 eV, the position of conduction band edge E_c becomes 5.09 eV. So the electrolytes having redox potential (E^0) around the conduction band edge, should be selected [37]. However, to our knowledge, only IO_3^-/I^- ($E^0 = 0.26$ V vs. standard Hydrogen electrode) is the redox couple in this range, which was found to be stable in neutral media. The electrodes dipped IO_3^-/I^- redox couple for 24 hrs did not show any chemical corrosion or surface damage.

3.7.3 Photoresponse

The photoresponse of intermediate lead oxides have been studied during the electrochemical oxidation of lead in H_2SO_4 [38-41]. Recently Peter [15,

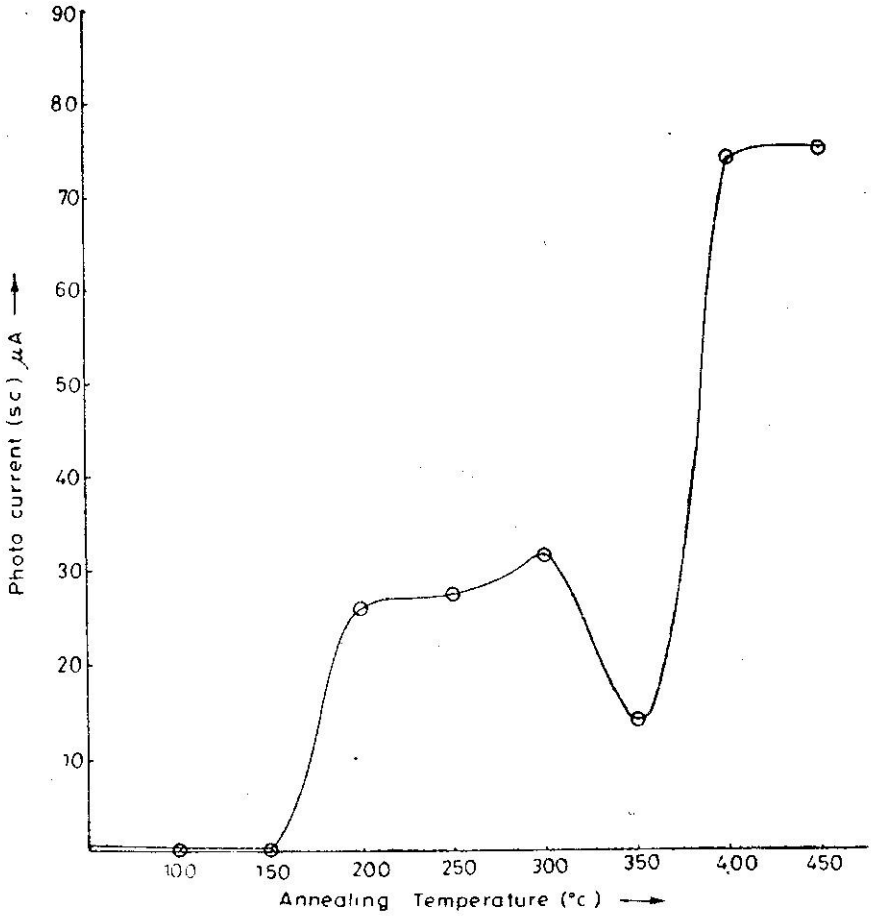

Fig. 11. A plot of short-circuit photocurrent vs. annealing temperatures of the films.

16] has used photocurrent spectra to study the electrochemical reduction of α-PbO_2. Vigneron [13] has done PEC study on sputtered film of PbO_2 in alkaline solution.

In the present work, the PEC Cell of the type PbO_x/IO_3^-, I^-/Pt is made. The short-circuit photocurrent, $I_{ph\ (sc)}$, and open circuit photovoltage, $V_{ph\ (oc)}$ were measured for all the annealed films and were plotted against the annealing temperature (Figs. 11 and 12). These plots show the increase in photoresponse with annealing temperature except at 350°C. On comparison with Fig. 8 we find that the photoresponse increases with resistivity. However, a slight decrease in resistivity at 350°C causes marked decrease in photoresponse. The sharp increase in photoresponse at 400°C is due to the

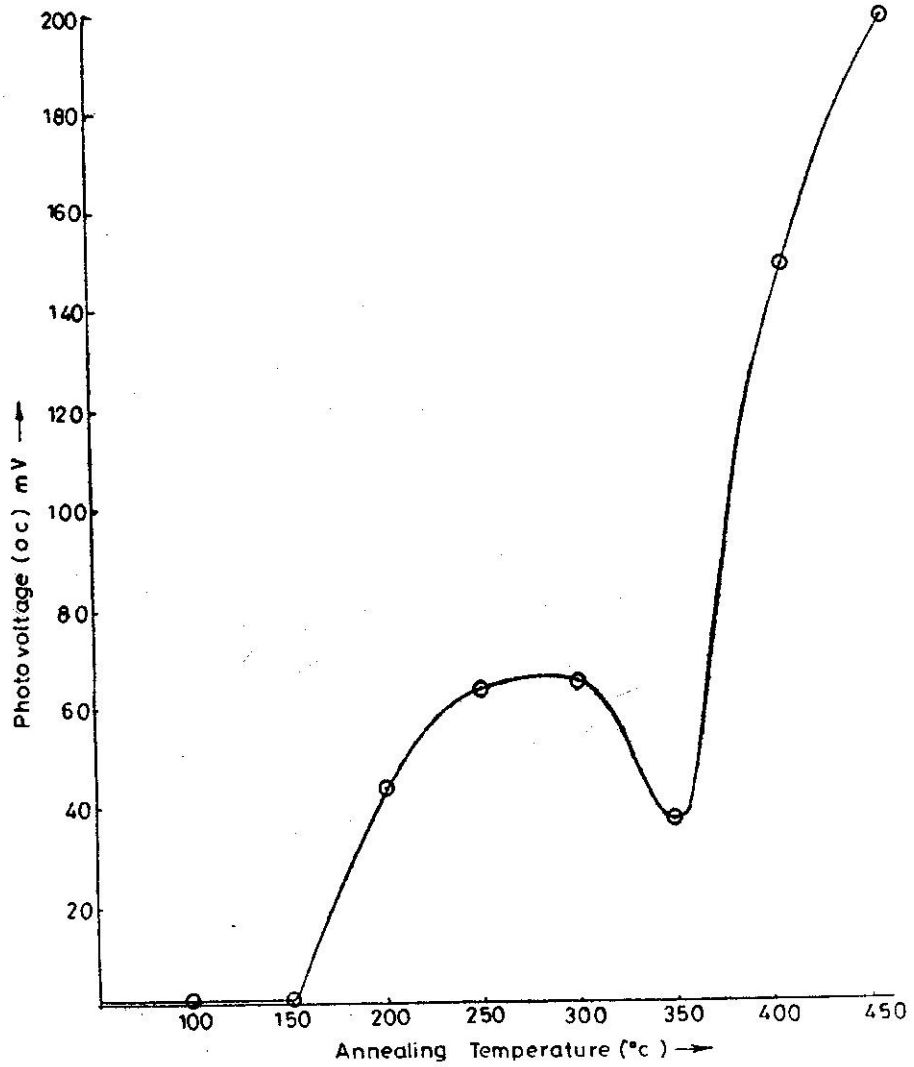

Fig. 12. A plot of open circuit photovoltage vs. annealing temperatures of the films.

formation of Pb_3O_4, which has already been found to be photoconducting [6]. The exact cause of the behaviour of these plots can be given only after detailed study which is in progress at present. The Photocurrent maxima, as reported by Peter [16], is observed at the stoichiometry $PbO_{1.50}$ and then falls to zero. But in our work, the photocurrent is found to increase even up to $PbO_{1.33}$ (Pb_3O_4).

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