

Maheshwar Sharon · Indrajit Mukhopadhyay
Susanta Ghosh

Photoelectrochemical laser imaging on anodically prepared α -PbO thin films

Received: 5 May 1998 / Accepted: 22 August 1998

Abstract The influence of various potential windows on the synthesis of α -PbO and the uniformity of its formation over the entire surface of the lead electrode has been studied by scanning a laser beam over the entire surface and measuring the corresponding photocurrent using the photoelectrochemical laser imaging technique. This technique revealed that a very uniformly distributed highly (110) plane oriented thin film of α -PbO is obtained by potentiodynamic anodization of the lead electrode in an alkaline medium at 80 °C in the potential range of -0.32 to $+0.08$ V vs SCE, giving the highest (73%) quantum yield at 480 nm, an open-circuit photopotential of 800 mV and a short-circuit photocurrent of 5.5 mA cm^{-2} . Gärtner analysis suggests that the highest photoactivity achieved with this material is due to the formation of a large space charge width ($0.63 \mu\text{m}$) and diffusion length ($0.36 \mu\text{m}$) of the minority carriers and absorption of almost 100% of the light (480 nm) within the space charge and diffusion regions.

Key words Photoelectrochemical laser imaging · Lead oxide · Gärtner analysis · Thin films

Introduction

The failure to achieve anywhere near the theoretical efficiency of solar to electrical energy conversion (15%) in a photoelectrochemical solar cell made out of α -PbO (band gap 1.92 eV) has kept interest alive in this material [1]. Veluchamy and Minoura [2] have reported that the (110) plane of the α -PbO seems to control the photoactivity. They could enhance the photoactivity by potentiostatic anodization of lead and achieved a short-circuit

photocurrent of 4.3 mA cm^{-2} , giving an efficiency of 1.53%. Mukhopadhyay et al. [3], on the other hand, tried to improve the efficiency by doping α -PbO with Sn and In. Though the resistivity of the α -PbO film decreased by doping, the growth of α -PbO, and in particular the (110) plane, was found to be suppressed considerably; as a result, the efficiency could not be increased further than that of pure α -PbO.

When a lead foil is anodized, it is assumed that anodization takes place uniformly over the entire surface of the lead foil. This may not be true; in fact, lead oxide formed over the entire surface may be composed of different stoichiometric compositions of lead oxide (i.e., PbO_n , where n could have any value from 0 to 1, because the potential range is set for obtaining PbO only). Moreover, to make the case worse, in addition to this, lead oxide formed over the entire surface may not be uniformly formed with the same intensity as that of plane (110). Both these factors will hamper obtaining the expected photocurrent from the anodized lead foil. The larger the size of the lead foil, the more pronounced would be the effect. Therefore, a non-destructive technique is needed which could give information about the uniformity of the formation of α -PbO (110) over the entire surface of the lead foil, so that anodization conditions could be altered to obtain the desired quality in the film. This can be done by illuminating the film with a laser beam and measuring the photocurrent developed by the spot illuminated with the laser beam diameter. Scanning of the laser beam over the entire surface and examining the distribution of the photocurrent produced will be able to give information about the uniform distribution of photoactive α -PbO (110) over the entire area of the lead foil.

The resolution of this technique will depend upon the magnitude of the current produced and the laser beam diameter. Since it would be very unlikely that anodization would be non-uniform within a diameter of about 1 mm, a simple laser (beam diameter around 1 mm) scanning technique may be quite sufficient for this purpose. Such a technique has been developed to con-

M. Sharon (✉) · I. Mukhopadhyay · S. Ghosh
Department of Chemistry, Indian Institute of Technology,
Bombay, Mumbai-400 076, India
e-mail: sharon@chem.iitb.ernet.in
Fax: +91-22-5783480

firm whether the various potential windows so far tried [1–3], including those used in this paper for the formation of α -PbO (110) by the anodization of pure lead, produce a uniform distribution of α -PbO over the entire surface area of 1 cm². This paper is an effort in this direction.

Experimental

The lead metal electrodes of area 1 cm² were cut from a lead foil (99.999%, BDH), soldered with Teflon-coated copper wire from the back side and insulated by acrylic paste, leaving the front face open towards the electrolyte. NaOH (0.1 M) prepared in 0.1 M Na₂SO₄ solution was used as an electrolytic bath to synthesize α -PbO. Before anodic oxidation, lead electrodes were etched with a mixture of methanol, glacial acetic acid and hydrogen peroxide (1 : 1 : 1) and washed with double-distilled water and then kept in the electrolyte at 80 °C. The electrochemical cell consisted of a three-electrode set-up. A platinum foil (4 cm²) and a normal Hg/HgO electrode were used as counter and reference electrodes, respectively. All potentials are converted to the SCE scale. After anodization (details of the potential range discussed later), the electrodes were washed thoroughly with double-distilled water and kept at 130 °C for 1 h in a vertical furnace fitted with an external temperature controller (Ulvac, HPC 7000).

The X-ray diffraction (XRD) patterns of the oxide films were recorded by using a diffractometer (Philips, model PW 1810) with Cu-K_α radiation. The surface morphology of the oxide films were observed using a scanning electron microscope (Cameca SU 30).

A photoelectrochemical (PEC) cell of configuration α -PbO (1 cm²)/0.1 M Fe(CN)₆^{4-/3-}/Pt (4 cm²) was used for these studies. For measuring photocurrent spectra, a stabilized 100 W tungsten-halogen lamp in conjunction with a microprocessor-controlled monochromator (Action Research Corporation, model 150), lock-in analyzer (PAR model 5204), potentiostat/galvanostat (PINE model AFRDE4) and a light chopper (PAR, model 197) were used. The action spectrum was normalized with the help of a calibrated silicon photovoltaic detector. The current-voltage characteristics of the PEC cell using a lead oxide electrode prepared under different potential ranges were measured to find out the corresponding short-circuit photocurrents and open-circuit photovoltages.

A self-explanatory simple photoelectrochemical laser imaging apparatus, as shown in Fig. 1, was used to measure the spatially resolved photocurrents. The output of a laser beam (3 mW, He/Ne laser, PMS Electro-optics, model LHGR-0050) was focused onto the working lead oxide electrode (prepared under various conditions). The PEC cell was mounted on a XYZ table (Newport, model

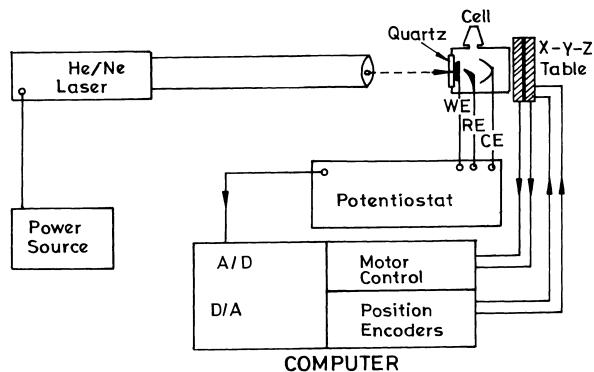


Fig. 1 A schematic diagram of the photoelectrochemical laser imaging system

PMC200P). The *X* and *Y* movements were controlled by the computer and the corresponding photocurrent during laser scanning was digitally recorded by a Keithley Metrabyte DAS-1600 I/O board. The magnitude of the photocurrent was determined and recorded as a function of the position of the laser beam focused on the surface of the film (surface area of the film, 1 cm²). The results of the photocurrent (*z*-axis) for various positions on the film (*x*, *y*) were plotted by software (Surfer, version 3.00), giving a 3-D view.

Results and discussion

Cyclic voltammetry

The characteristic cyclic voltammogram (CV) of the lead electrode in 0.1 M NaOH (prepared in 0.1 M Na₂SO₄) solution at 80 °C (Fig. 2) is similar to that reported earlier [1]. The anodic peaks *A*₁ and *A*₂ are due to the oxidation of Pb to PbO and PbO to PbO₂, respectively. In the reverse scan, peaks *C*₂ and *C*₁ correspond to the reduction of PbO₂ to PbO and PbO to Pb, respectively. The details of these reactions have been discussed elsewhere [1].

For the present experiment, the potentiodynamic anodization of the lead electrode was carried out in different potential ranges within *A*₁ and the foothill of *A*₂. Sharon et al. have shown that if anodization is carried out in potential region of -1.25 V to $+2.35$ V [1] or between -0.18 V and $+0.92$ V [4], many peaks appear in the XRD spectrum, and the intensity of the reflection from the plane responsible for the reflection of α -PbO₂ is greater than the reflection from the plane (110) (i.e., $d_{110} = 2.805$ Å) of α -PbO; when the potential range is maintained between -1.0 V and $+2.35$ V [5], or -0.35 V and $+0.75$ V [6], a reverse trend is observed. Interestingly, when an additional pulse potential at -0.65 V is applied during the sweep between -1.0 V and $+2.25$ V [7], the intensity of α -PbO increases manifold compared with the intensity of α -PbO₂. Though the intensity of α -

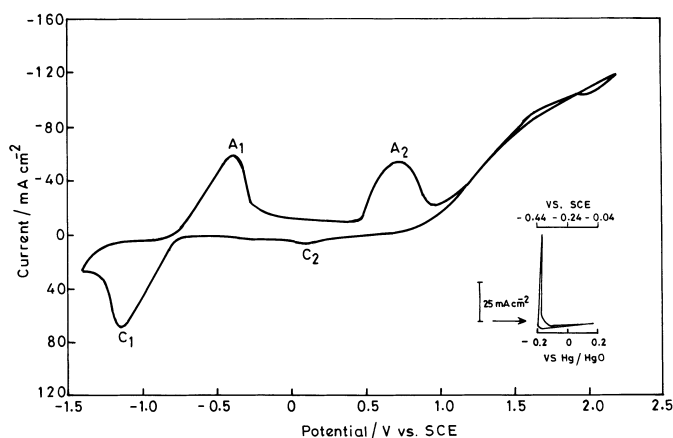


Fig. 2 The cyclic voltammogram for potentiodynamic anodization of a Pb electrode in 0.1 M NaOH with 0.1 M Na₂SO₄ solution at 80 °C in the potential range -1.25 to $+2.35$ V [-1.37 to $+2.23$ V (SCE)] and (inset) -0.32 V to $+0.08$ V; (sweep rate, $v = 100$ mV s⁻¹, electrode area 1 cm²)

PbO increases, many other XRD peaks appear. On the other hand, when Veluchamy and Minoura [2] applied a fixed potential +0.3 V they could obtain the highest peak for α -PbO with all other XRD peaks almost at the background level. This potential falls at the plateau between A_1 and A_2 , thus reducing the anodic current to an almost negligible amount. The low anodic current may perhaps be the reason for the need to anodize lead for more than 60 min to obtain a reasonable thickness of PbO [2]. Therefore, a potentiodynamic system with a potential range covering slightly negative potential to peak C_2 (Fig. 2), and slightly less positive to +0.3 V, may perhaps increase the anodic current without affecting the growth of α -PbO and also may tend to inhibit the growth of α -PbO₂. In the present work, various potential ranges falling within this limit have been tried.

After many trial experiments, it was found that a lead oxide photoanode, obtained in the potential range -0.32 V to +0.08 V (inset of Fig. 2), showed the best photoresponse. This result suggests that shifting the potential window from +0.3 V vs SCE (which is nearer to A_2) to the PbO growth potential side, i.e., nearer to A_1 (Fig. 2), gives a better result. The following discussions deal with the results obtained with lead oxide synthesized under this condition.

Structural aspect

The XRD pattern of the oxide thin film (Fig. 3) obtained after 20 min of potentiodynamic anodization was identified as α -PbO with unit cell parameters of 3.97 Å ($a = b$) and 5.01 Å (c), which matched well with the α -PbO phase [8]. One intense line for the (110) plane was observed at $d = 2.809$ Å for α -PbO. The XRD analysis shows one single high-intensity peak for the (110) plane of α -PbO with almost no peak corresponding to α -PbO₂. This is much better than the one obtained by performing a potential pulse at -0.65 V [7] and almost similar to the results of Veluchamy and Minoura [2]. The advantage

here is that we can obtain a similar film thickness in 20 min of anodization compared to 60 min of anodization needed by the potentiostatic method. It will be seen later that, though XRD of the film prepared in this potential window is similar to the film prepared by potentiostatic potential (+0.3 V vs SCE), the potentiodynamic method resulted in a more uniform film with a better light absorbing capacity and hence with improved photo-activity.

The crystal size was obtained from the full width half maximum of the XRD peak by using the following equation [9, 10]:

$$D = \frac{\lambda}{\beta \cos \theta} \quad (1)$$

where β is the full width half maximum, λ is the wavelength of the X-rays (1.5406 Å) and D is the average crystal size, calculated to be 660 Å in this case.

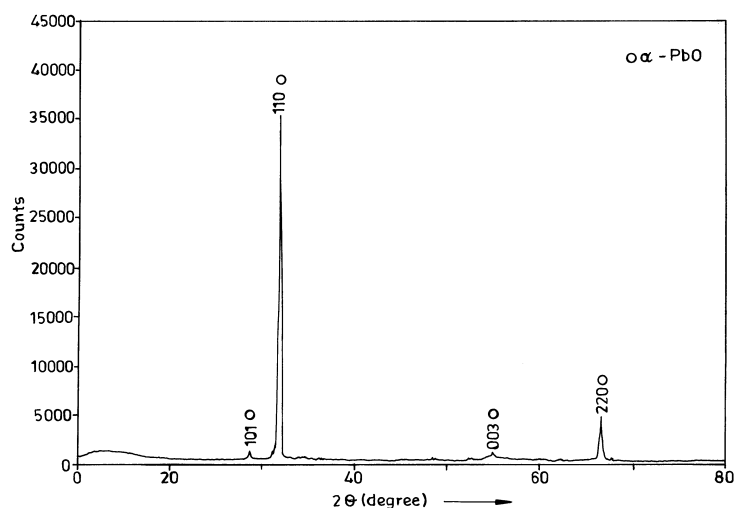
Surface morphology of anodic oxide thin films

The surface morphology of the oxide film (Fig. 4a) was similar to the film reported by Krishna et al. [11], showing the presence of some needle-shaped lead scattered over the homogeneous PbO film. This scanning electron micrograph also reveals that the crystallinity of the film obtained with the CV technique is quite good. From the cross-sectional view (Fig. 4b) of the thin film, its thickness was found to be 10 μ m.

Impedance studies

The flat-band potential and donor density of the oxide film were obtained by using the Mott-Schottky (M-S) relation [12], assuming that the surface state capacitance and space charge capacitance are in parallel [13, 14]. Typical M-S plots for the lead oxide electrode at frequencies of 1 kHz, 10 kHz and 30 kHz in 0.1 M

Fig. 3 The X-ray diffraction pattern of the lead oxide film obtained by potentiodynamic technique in the region -0.32 V to +0.08 V



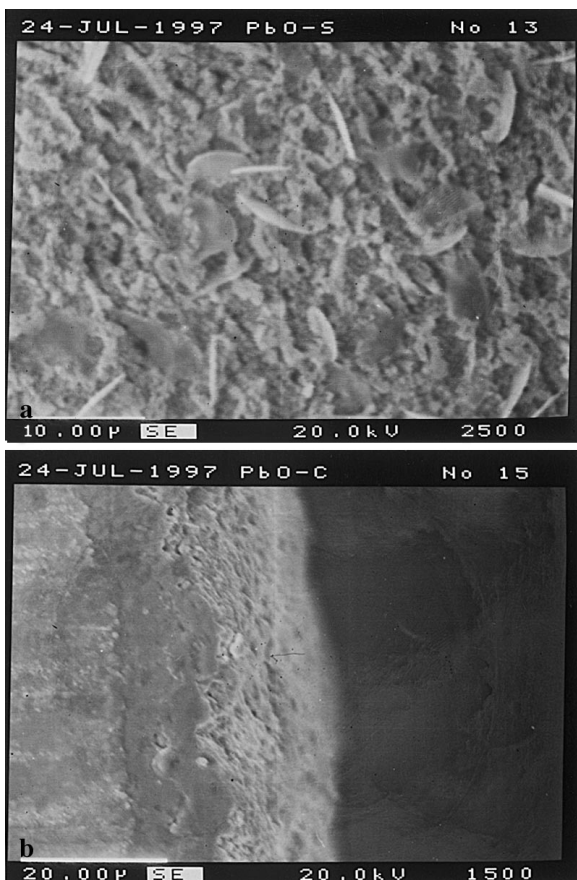


Fig. 4 Scanning electron microscope view of the oxide films showing **a** the surface morphology and **b** the cross-sectional view over the Pb electrode

$\text{Fe}(\text{CN})_6^{4-/3-}$ solution are presented in Fig. 5. The plots show two slopes which are typical for most of the oxide films [15]. Surface roughness and a non-uniform donor density distribution across the film may be the reason for such behavior [2]. Assuming that the M-S relation is valid near the flat-band region, the donor densities and the flat-band potentials were obtained from the slopes

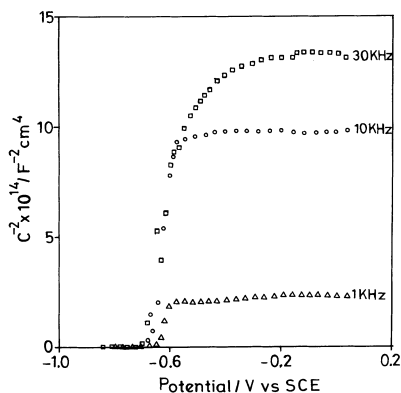


Fig. 5 Mott-Schottky plots of the oxide semiconductor over the Pb electrode in 0.1 M $\text{Fe}(\text{CN})_6^{4-/3-}$ solution (pH 9.2, buffer)

and the intercept on the X -axis, from the data obtained in the region of -0.7 V to -0.4 V respectively (Fig. 5). The average donor density was found to be $5.77 \times 10^{15}\text{ cm}^{-3}$ (Table 1), which is similar to the reported values [2, 16].

Photoelectrochemical studies

The band gap of this material was calculated from photoaction spectra and found to be 1.92 eV and 2.2 eV for indirect and direct transitions, respectively (graphs similar to those reported elsewhere [1]).

The quantum yields (ϕ) for the similar cell were calculated at different wavelengths by calibrating the photocurrent spectrum of the oxide film with respect to calibrated silicon diode. A maximum quantum yield of 73% at 480 nm (Fig. 6) is obtained. The quantum yield decreased after 480 nm owing to strong absorption of incident radiation in the redox electrolyte (inset of Fig. 6).

A typical power output curve of the PEC cell obtained with lead oxide formed by cyclic voltammetric anodization of lead in the potential range -0.32 V to $+0.08\text{ V}$ is shown in Fig. 7. This experiment was carried out with the films prepared under various other potential ranges; short-circuit photocurrents as well as open-circuit photopotentials were measured (Table 2). The highest short-circuit photocurrent (I_{sc} , 5.5 mA cm^{-2}) and open-circuit photovoltage (V_{oc} , 800 mV) were obtained with the film anodized for 20 min in the range -0.32 V to $+0.08\text{ V}$. The solar to electrical conversion efficiency of 1.84% was obtained with this film at 100 mW cm^{-2} white light. This is the highest photo-conversion efficiency reported for such a large area electrode of this material.

In order to understand the reasons for obtaining the highest photoactivity with films prepared under -0.32 V to $+0.08\text{ V}$, two approaches were adopted: (1) calculation of various junctions' characteristics by Gärtner's model and (2) the study of photocurrent distribution

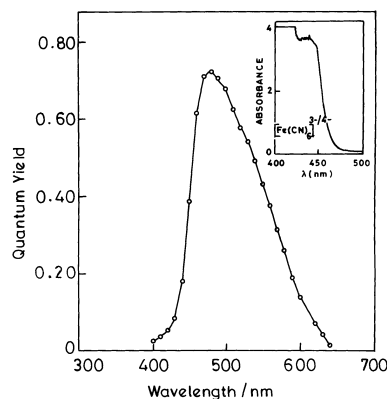
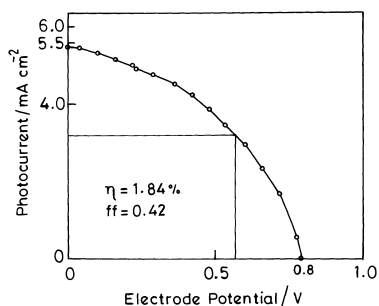
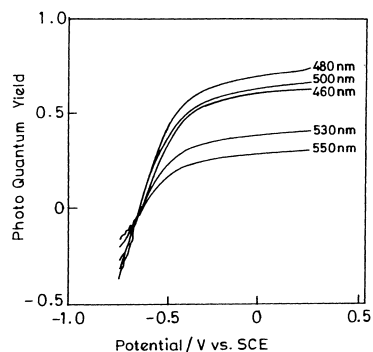


Fig. 6 A plot of the wavelength dependence of the quantum yield of the lead oxide photoanode after 20 min of anodization. *Inset:* the absorption spectrum of 0.1 M $\text{Fe}(\text{CN})_6^{4-/3-}$ (pH 9.2)

Table 1 Parameters related to the photoactivity of a lead oxide semiconductor in 0.1 M $\text{Fe}(\text{CN})_6^{4-/3-}$ solution

λ (nm)	V_{onset} (volts)	V_{fb} (volts)	$N_d \times 10^{15}$ (cm^{-3})	α (cm^{-1})	$1/\alpha$ (μm)	w (μm)	L (μm)	$w \times \alpha$
550	-0.63	-0.65	5.77	0.25	3.99	0.63	0.83	0.15
530	-0.63	-0.65	5.77	0.35	2.86	0.63	0.92	0.22
500	-0.64	-0.65	5.77	1.02	0.97	0.63	0.46	0.65
480	-0.64	-0.65	5.77	1.36	0.73	0.63	0.36	0.86
460	-0.63	-0.65	5.77	1.08	0.92	0.63	0.35	0.68

**Fig. 7** A typical power conversion curve for lead oxide (obtained from the potentiodynamic anodization of lead in the potential range -0.32 V to $+0.08$ V, in a photoelectrochemical cell of configuration: lead oxide (1 cm^2)|0.1 M $\text{Fe}(\text{CN})_6^{4-/3-}$ (pH 9.2)|Pt (4 cm^2))**Fig. 8** Variation of photocurrent quantum yield of lead oxide film with the applied bias under various monochromatic illuminations

over the entire surface of the film by the laser scanning technique. Their discussion follows.

Gärtner's analysis

A detailed description and method of calculations based on Gärtner's model is described by Mukhopadhyay et al. [16]. This model is valid for the region where recombination of the electron-hole pair is prevented (i.e., in the depletion region). For this region, a very useful relation has been derived by Gärtner [17, 18]:

$$-\ln(1 - \phi) = \alpha \left(\frac{2\epsilon\epsilon_0}{qN_d} \right)^{\frac{1}{2}} (V - V_{\text{fb}})^{\frac{1}{2}} + \ln(1 + \alpha L) \quad (2)$$

Using this equation, the values of the absorption coefficient (α) and diffusion length (L) can be obtained from the slope and intercept of a $-\ln(1 - \phi)$ vs $(V - V_{\text{fb}})^{\frac{1}{2}}$ plot, knowing the dielectric constant (25.9) [19] and the donor density of this material.

Table 2 Short-circuit photocurrent and open-circuit photo-potential of the oxide films obtained in different potential regions

Potential range (V vs SCE)	I_{sc} (mA cm^{-2})	V_{oc} (volts)	η (%)
-0.42 to 0.08	3.40	0.793	1.12
-0.32 to 0.08	5.50	0.800	1.84
-0.22 to 0.08	3.41	0.775	0.97
-0.32 to -0.02	5.01	0.734	1.16
-0.32 to 0.18	4.53	0.793	1.31
-0.32 to 0.28	4.08	0.750	1.05
-0.32 to 0.38	3.94	0.736	1.02

The quantum yield (ϕ) for the $\alpha\text{-PbO}|0.1 \text{ M Fe}(\text{CN})_6^{4-/3-}|\text{Pt}$ cell was calculated under bias at various monochromatic wavelengths (Fig. 8) by calibrating the photocurrent spectrum of the oxide film with respect to calibrated silicon diode. From the set of linear plots of $-\ln(1 - \phi)$ vs $(V - V_{\text{fb}})^{\frac{1}{2}}$ in the region where electron-hole pair recombination is expected to be a minimum (limitation of the Gärtner model) (Fig. 9), slopes and intercepts for each wavelength were calculated using the method of least squares fit to find α and L values (Table 1).

The space charge width (w) was calculated from the relation

$$w = \left[\frac{2\epsilon\epsilon_0(V - V_{\text{fb}})}{qN_d} \right]^{\frac{1}{2}} \quad (3)$$

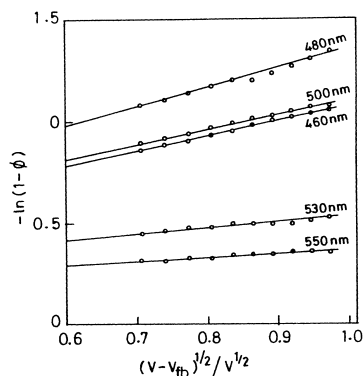
**Fig. 9** $-\ln(1 - \phi)$ vs $(V - V_{\text{fb}})^{\frac{1}{2}}$ plots for the determination of various parameters related to photoactivity

Table 3 Results of Gärtner's analysis of lead oxide prepared within different potential regions

Potential range (volts vs SCE)	w (μm)	L (μm)	$1/\alpha$ (μm)	% light (500 nm) absorbed		Reference
				(w)	($w + L$)	
-1.25 to 2.35	0.54	0.4	588.2	9	15	14
-0.75 to 1.25	0.37	0.24	140.8	26	43	18
-0.44 to -0.04	0.63	0.46	0.97	65	100	This work

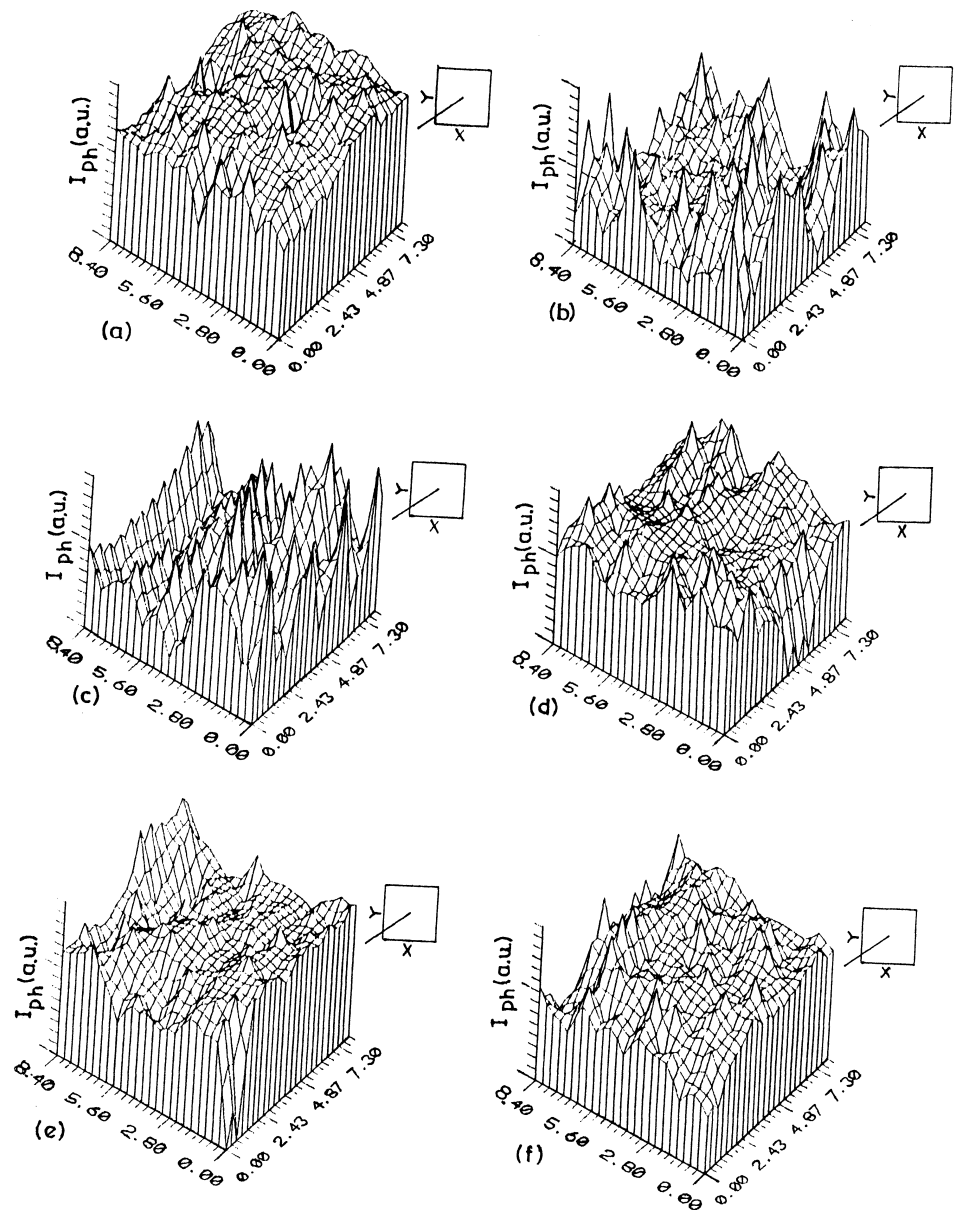
using donor densities and flat band potentials from ac impedance studies (Table 1).

It is clear from our results (Table 1) that the penetration depth ($1/\alpha = 0.73 \mu\text{m}$) with light of 480 nm is almost equal to the space charge width ($w = 0.63 \mu\text{m}$), suggesting that only about 13.8% of the total light of 480 nm wavelength is not absorbed in the space charge

region. Assuming ideal conditions, like the absence of any trapping centers, a high lifetime of carrier, etc., the quantum yield should have been about 86.2% compared to 73% observed experimentally for this material. Hence, there is still a scope to increase its photoactivity.

The results of the space charge width (w), diffusion length (L) and penetration depth ($1/\alpha$) of light of wave-

Fig. 10 3-D photocurrent map obtained with scanning of a He/Ne laser (3 mW) over the surface of a lead oxide electrode anodically prepared in the potential range **a** -0.32 V to +0.08 V, **b** -0.22 V to +0.08 V, **c** -0.42 V to +0.08 V, **d** -0.32 V to 0.18, **e** -0.32 V to +0.28 V and **f** -0.32 V to -0.02 V. The X length is 7.7 mm and the Y length is 8.4 mm. Step size is 0.7 mm; $h\nu$ is 2.33 eV



length 500 nm (because, for 480 nm, no more results are available in other published potential ranges) of the lead oxide film grown at (1) -0.32 V to $+0.08$ V, (2) -1.25 V to $+2.35$ V [16] and (3) -0.75 V to $+1.25$ V [20] are compared in Table 3. These calculations explicitly suggest that lead oxide thin film grown within -0.32 V to $+0.08$ V (i.e., in the present case) is not only able to absorb almost all light within its space charge width and the diffusion region, but also the space charge width is able to absorb 65% of the incident light and hence shows the highest photoresponse. Gärtner's analysis predicts the possibility of further improvement in the photoactivity of this material by improving the technique so as to obtain a larger space charge width. These results could not be compared with results of Veluchamy and Minoura [2] because Gärtner's analysis has not been shown in their paper.

Photoelectrochemical laser imaging studies

Though Gärtner's calculation explained the reasons for obtaining the highest photoactivity with the film obtained with cyclic voltammetric anodization of lead in the potential range -0.32 V to $+0.08$ V, it made us inquisitive to understand this behavior. For this purpose, a laser scanning technique was developed [21]. A laser beam was scanned over the entire surface of various lead oxide films obtained by CV using various combinations of potential ranges. Photoelectrochemical laser imaging maps of the potentiodynamically anodized oxide films in different potential ranges are shown in Fig. 10 (values shown are in arbitrary units, as they were normalized with respect to the highest photocurrent obtained in the experiment). From the 3-D map of photocurrent vs (x, y) , it is clear that lead oxide film obtained in the potential range -0.32 V to $+0.08$ V, shows the most uniform distribution of photocurrent over the entire 1 cm^2 area of the electrode, whereas with other potential ranges the uniformity of the photocurrent is not very good. This suggests that the kinetics of oxidation in the potential range -0.32 V to $+0.08$ V may be such that oxidation of lead over the entire surface becomes very uniform whereas with other potential ranges this may not be true. As a result of the uniform distribution of α -PbO over the entire surface, the 500 nm photons are able to be absorbed in the space charge width to the extent of 65% and the rest in the diffusion regions (Table 3).

Conclusions

A thin film of α -PbO prepared by potentiodynamic anodization of a lead electrode in the potential range

-0.32 V to $+0.08$ V (SCE) at a sweep rate of 100 mV s^{-1} in 0.1 M NaOH solution at 80°C shows the highest photoresponse for this material. The laser scanning studies revealed that this potential window is one of the best windows for obtaining a uniform surface of α -PbO over a large area electrode. Gärtner's analysis also suggests that 65% of the light (500 nm) is absorbed within the space charge width and rest in the diffusion region of α -PbO (produced under this experimental condition) and hence giving the highest photoactivity. This analysis also opens the possibility to increase the photoactivity of α -PbO further by improving the method of its preparation so that the remaining 35% of the light (500 nm) is also absorbed within the space charge width rather than in the diffusion region.

Acknowledgements One of the authors (S.G.) is grateful to the Indian Institute of Technology, Bombay, for the award of a senior research fellowship.

References

1. Veluchamy P, Sharon M, Minoura H, Ichilhashi Y, Basavaswaran K (1993) *J Electroanal Chem* 344: 73
2. Veluchamy P, Minoura H (1995) *J Electrochem Soc* 142: 1799
3. Mukhopadhyay I, Sharon M, Veluchamy P, Minoura H (1996) *J Electroanal Chem* 401: 139
4. Veluchamy P, Sharon M, Kumar D (1991) *J Electroanal Chem* 315: 293
5. Mukhopadhyay I, Ghosh S, Sharon M (1997) *Surf Sci* 384: 234
6. Veluchamy P, Sharon M, Shimizu M, Minoura H (1994) *J Electroanal Chem* 371: 205
7. Mukhopadhyay I, Raghavan MSS, Sharon M, Minoura H, Veluchamy P (1994) *J Electroanal Chem* 379: 531
8. JCPDS Power Diffraction File Cards (1987) 5-561 (α -PbO), 5-570 (β -PbO), 4-686 (Pb) and 37-517 (α -PbO₂). ASTM, Philadelphia, Pa
9. Chen S, Russak MA, Witzke H, Reichman J, Dep SK (1979) *US Pat* 4 172 925
10. Hodes G (1983) In: Gratzel M (ed) *Energy resources through photochemistry and catalysis*, chap 13. Academic Press, New York
11. Krishna KM, Sharon M, Mishra MK (1995) *J Electroanal Chem* 391: 93
12. Xia SJ, Zhou WF (1995) *Electrochim Acta* 40: 175
13. Bockris JO'M, Kang Y (1997) *J Solid State Electrochem* 1: 17
14. Nagasubramanian G, Wheller BL, Hope GA, Bard AJ (1983) *J Electrochem Soc* 130: 385
15. Nogami G, Ogawa Y, Nishiyama Y (1988) *J Electrochem Soc* 135: 3008
16. Mukhopadhyay I, Sharon M (1997) *Sol Energy Mater Sol Cells* 45: 141
17. Gärtner WW (1959) *Phys Rev* 116: 84
18. Butler MA (1977) *J Appl Phys* 48: 1914
19. Bullock KR (1987) *J Electroanal Chem* 222: 347
20. Mukhopadhyay I, Sharon M (1997) *Electrochim Acta* 42: 67
21. Preusser S, Stimming U, Tokunaga S (1995) *J Electrochem Soc* 142: 102