Chapter 7

Study on solid state Schottky junction Solar Cells

_A light on solid state devices of \( \text{PbO}_x \)_
7.1 Introduction

Over the years, the development in the field of energy conversion has been achieved through photoelectrochemical cells [177] to the third generation quantum dot solar cells [178, 179]. The researchers have always come up with new materials [180, 181] and new configurations of the devices [119, 182–184] for the efficient conversion of the solar energy. The low cost solution processed techniques [185, 186] have gained more attention in the fabrication of bulk as well as nanoscale materials. In this regard the nanocrystal excitonic solar cells [187–193] have gained a great interest due to their large exciton Bohr radii and low cost route of fabrication. One of the major concerns with the lead compounds is their lower V_{oc}. Joshua et al [194] reported the highest efficiency PbSe excitonic solar cell which exhibited very low V_{oc} due to interfacial recombination. Unlike the conventional p-n or Schottky junction solar cells, the V_{oc} of such excitonic solar cells mainly depends on the energy levels of nanocrystals which on contrary vary with their size. We would like to emphasize here that Pb compounds have only been extensively studied in nanocrystalline solar cells due to large exciton Bohr radii. Hence very few reports [195, 196] claim the bulk characteristic of the lead compounds as solid state power generating device.

Till date, lead oxide has been limitedly used in photoelectrochemical cells [19–23, 90, 170, 197–199] and batteries [17, 200]. In order to overcome the stability issue of such PEC solar cell based on nonstoichiometric lead oxide films, we have explored to fabricate a solid state Schottky junction out of this material. Higher work function metals such as Pt, Au and Pd are the most suitable candidates to realize a Schottky junction with n-PbO_x.

7.2 Experimental

The PbO_x photoanodes were prepared by two different electrochemical techniques namely potentiodynamic and potential pulse anodization. In the potentiodynamic
method[20], the potential was swept from -0.65 to 1.25 V at a sweep rate of 200 mV/s for 1200 s. Whereas, the potential pulse method as discussed in Chapter-3 was used to prepare nanostructured PbO$_x$ films. A high work function metal alloy of Au:Pd (60:40) was sputtered by a gold coater at a rate of 2.1 Å/s for making a suitable Schottky junction. The actual photograph of the gold coater (Leica EM ACE200) facility used for this study is shown in Fig.7.1. To avoid any shunting or shorting problem, the films were masked on the boundaries before Au-Pd coating. The actual photographs of PbO$_x$ photoanodes before and after Au-Pd coating are shown in Fig.7.2. Thicknesses of this metal alloy were varied from 1±0.2 to 70±1 nm for the photoanodes prepared from different techniques. A homemade probe station (Chapter-2, Fig.2.12) made using spring loaded copper probes with total series resistance less than 1Ω was used to make an external contact. The Schottky junction solar cells were characterized by I-V, C-V and ρ-T measurements. A homemade vacuum compatible high temperature probe station was used for the
temperature dependent I-V measurements.

### 7.3 Results and Discussion

#### 7.3.1 J-V characteristics

![Schematic Design of Schottky Junction Cells](image)

**Figure 7.3:** A schematic design of a Schottky junction cells made using anodized PbO$_x$ films.

As discussed in Chapter-3, the films prepared by potentiodynamic and potential pulse technique differ in crystallinity, morphology and optical properties. The films prepared via potentiodynamic technique contained unwanted impurity phases like
Pb$_x$O$_{1-x}$ and elemental lead. Whereas the films synthesized by potential pulse technique resulted having pure $\alpha$-PbO phase with trace of $\beta$-PbO. The overall film thicknesses calculated by Faraday’s equation in the case of potentiodynamic and potential pulse techniques were found to be 4.03 and 8.97 $\mu$m, respectively. The cell structures of both the films are shown in Fig.7.3. As the cell works under the illumination from the Au/Pd layer side, primary concern was to optimize the thickness of alloy such that the maximum transmittance is obtained maintaining its bulk characteristics. The J-V characteristics of the devices out of both the

![Graphs showing J-V characteristics](image)

**Figure 7.4:** J-V characteristics of the cells configured using PbO$_x$ electrodes prepared via (a) potentiodynamic and (b) potential pulse technique for different thicknesses of Au/Pd alloy.

PbO$_x$ films for different alloy thicknesses are given in Fig.7.4. It was found that the optimized thickness of Au/Pd alloy for potentiodynamic PbO$_x$ film is only 1 nm, whereas the potential pulse PbO$_x$ film required 10 nm thick alloy for its optimum performance. The transmittance data of 1 and 10 nm thick alloy are given in Fig.7.5. It is worth to mention here that we have chosen the fabrication conditions of PbO$_x$ films on the basis of their performance in photoelectrochemical cells. It was found that the optimizations for potentiodynamic PbO$_x$ films were exactly the same for their performance as solid state Schottky junction solar cell. However, the same were not applicable for the films prepared by potential pulse technique. Instead it was found that the films prepared for 400 s were better
Figure 7.5: Transmittance spectra of 1 and 10 nm thick Au-Pd alloy.

Table 7.1: Parameters obtained from J-V measurements

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Potentiodynamic</th>
<th>Potential Pulse</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_{oc}) (mV)</td>
<td>727</td>
<td>707</td>
</tr>
<tr>
<td>(J_{sc}) (mA/cm(^2))</td>
<td>0.574</td>
<td>2.04</td>
</tr>
<tr>
<td>FF (%)</td>
<td>49.16</td>
<td>26.74</td>
</tr>
<tr>
<td>(n) (%)</td>
<td>0.204</td>
<td>0.384</td>
</tr>
<tr>
<td>(R_s) (Ω)</td>
<td>314</td>
<td>686</td>
</tr>
<tr>
<td>(R_{sh}) (Ω)</td>
<td>8156</td>
<td>492</td>
</tr>
<tr>
<td>(J_0) (A/cm(^2))</td>
<td>6.67×10(^{-8})</td>
<td>1.43×10(^{-6})</td>
</tr>
<tr>
<td>(n)</td>
<td>6.04 ± 0.12</td>
<td>1.27 ± 0.03</td>
</tr>
<tr>
<td>(\phi_B) (eV)</td>
<td>0.91</td>
<td>0.77</td>
</tr>
</tbody>
</table>

performing compared to the films anodized for 800 s. The dark J-V characteristics [88] were used for the determination of the electrical parameters of the cells.

7.3.2 Electrical parameters

All the parameters of the cells made up with the PbO\(_x\) films prepared under different conditions are compared in Table-7.1. As it can be seen from the Fig.7.4(a)
that fill factor of the cell with potentiodynamic PbO$_x$ film is quite good compared to potential pulse PbO$_x$ film. This major difference may be due to the way in which PbO$_x$ films grown by different techniques. The potentiodynamic PbO$_x$ film is uniform all over the substrate as far as the material phase is concerned. However, in the case of potential pulse, the interface between PbO and PbO$_x$ nanowalls may offer high series resistance. The values of $R_s$ and $R_{sh}$ were derived from the illuminated J-V characteristics of both the cells. It can be seen that the series resistance of both the cells is higher but as expected, potential pulsed films exhibited comparatively high values. The major retarding factor in the low performance of potential pulsed films is their extremely low shunt resistances. The nature of J-V curve for potential pulsed films is a straight line with inward curve near the $V_{oc}$ values, which is due to the comparable series resistance to the shunt resistance of the cells. We also believe that change in material phases i.e. PbO and PbO$_x$ may have generated interface states in the bulk of the active region [88]. As seen in Chapter-4, the light generated interface states were playing a major role in the charge transport of PbO$_x$ photoelectrochemical cells. These light generated states in the case of potential pulse PbO$_x$ system facilitates the recombination phenomenon and hence lower the $V_{oc}$. However, the increased value of $J_{sc}$ can be ascribed to the high surface area nanowalls which favor the diffusion of majority carriers from the nanowalls to the bulk of PbO. To confirm the various recombination processes in both the cell configurations, the ideality factors of the films were calculated from the $d(V)/d(\ln(I))$ vs. I plots as shown in Fig.7.6. It was found that the cells of potentiodynamic PbO$_x$ films exhibit very high ideality factor of 6.04 ± 0.12 whereas the cells of potential pulsed PbO$_x$ films were performing as near to ideal diodes with the ideality factor of 1.27 ± 0.03. This suggests that the current transport mechanism in the potentiodynamic films cannot be totally understood as pure thermionic; instead the surface states are actively participating in the charge transport mechanism [201]. Though the ideality factor is near to 1 in the case of potential pulsed PbO$_x$ film, we believe that the slight variation from ideality is caused by trap assisted charge transport or recombination processes. The presence of surface trap states is quite common for metal oxide
semiconductors. In the present case, the surface states are more likely to generate at PbO/PbO$_x$ interface as well as on the nano walls with higher surface area. As we have observed a very poor fill factor for devices made out of potential pulsed PbO$_x$ film, the rate of recombination via trap states might be higher for such devices. To understand the role of interface states in the charge transport mechanisms of the cells, the activation energies were determined by the Arrhenius plots of resistivity (Fig.7.8). The values of activation energies were found to be 0.124 and 0.01 eV for potentiodynamic and potential pulsed PbO$_x$ films, respectively. These low values of activation energies in both the cases manifest the reason for
high ideality factor and active participation of traps in the transport mechanism especially at higher voltages. A complete band diagrams with the actual values of trap states on the energy axis for both the films are given in Fig.7.7.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7_8}
\caption{Arrhenius plots of resistivity for PbO$_x$ solar cells prepared via (a) potentiodynamic and (b) potential pulse technique.}
\end{figure}

\subsection{7.3.3 Impedance study}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7_9}
\caption{Mott-Schottky plots for PbO$_x$ solar cells prepared via (a) potentiodynamic and (b) potential pulse technique.}
\end{figure}
The C-V measurements were done in order to find the important parameters of the junction, i.e. built in potential \( V_{bi} \) and depletion width \( W_d \). The Mott-Schottky plots were studied for the frequency range 30 kHz to 3 kHz. It was found that the measurements done within the mentioned frequency range lead to the accurate C-V plots without any frequency dispersion phenomena. Typical Mott-Schottky plots at frequency of 3 kHz for both the cells are given in Fig.7.9. The calculated values of \( V_{bi} \), \( N_D \) and \( W_d \) for all the configurations are given in Table-7.2. The Nyquist plots for solar cells prepared by potentiodynamic and potential

<table>
<thead>
<tr>
<th>Anodization technique</th>
<th>( V_{bi} ) (V)</th>
<th>( N_D ) (cm(^{-3}))</th>
<th>( W_d ) ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potentiodynamic</td>
<td>0.85</td>
<td>5.33\times 10^{15}</td>
<td>0.701</td>
</tr>
<tr>
<td>Potential Pulse</td>
<td>0.72</td>
<td>9.29\times 10^{16}</td>
<td>0.149</td>
</tr>
</tbody>
</table>

**Figure 7.10:** Nyquist plots for potentiodynamically prepared cells under (a) forward bias and (b) reverse bias condition.

pulse PbO\(_x\) films are shown in Figs.7.10 and 7.11 for (a) forward and (b) reverse bias, respectively. As it can be seen from the figures that a single semicircle is obtained in both the techniques. However, the solar cells prepared by using potential pulse PbO\(_x\) films exhibited semicircle with almost ideal capacitive nature. In other case a compressed (in Y-direction) semicircle was obtained. To analyze the performance of these devices on the basis of their interfaces, a transmission line circuit as given in Fig.7.12 is made and an equivalent circuit as shown in Figs.7.13
Figure 7.11: Nyquist plots for potential pulse prepared cells under (a) forward bias and (b) reverse bias condition.

Figure 7.12: The equivalent circuit (transmission line model) of the Schottky junction solar cell in which $R_s$ is the series resistance, $R_{co}$ and $C_{jun}$ are the contact resistance capacitance occur at the interface of Pb/PbO$_x$. $R_{rec}$ represents the bulk or recombination resistance of the photoanode and $C_{jun}$ is the junction capacitance.

was fitted to all the experimental Nyquist plots. In the equivalent circuit $R_s$ is the series resistance, $R_{co}$ is the contact resistance between Pb and PbO$_x$, $R_{rec}$ is the bulk resistance, $C_{co}$ represents the contact/chemical capacitance that occurs at Pb/PbO$_x$ interface and $C_{jun}$ is the junction capacitance at PbO$_x$/Au-Pd Schottky contact. The variation in each element of the circuit is shown in the Figs.7.14 and 7.15 for cells made using (a) potentiodynamic and (b) potential pulse techniques, respectively. It was found that $R_s$ of the solar cells made by potentiodynamic
The reduced lumped equivalent circuit of the Schottky junction solar cell in which $R_s$ is the series resistance, $R_{co}$ and $C_{jun}$ are the contact resistance capacitance occur at the interface of Pb/PbO$_x$. $R_{rec}$ represents the bulk or recombination resistance of the photoanode and $C_{jun}$ is the junction capacitance.

The technique is much higher (34 $\Omega$) compared to potential pulse technique ($< 5\Omega$). This high value of $R_s$ lowers $J_{sc}$ of such cells. It was further observed that the bulk resistance of the PbO$_x$ films prepared by potentiodynamic technique is one order higher than the pulsed films. The higher bulk resistance lowers the recombination and hence increases $V_{oc}$ of the cells. It was observed earlier that the fill factor of potentiodynamically prepared cells is much higher than the potential pulse cells. This is due to the high shunt resistance of potentiodynamically prepared cells. The effect of $R_2$ was clearly seen on the obtained values of $J_{sc}$ by both the techniques. The lower the value of $R_2$ the higher is the $J_{sc}$. The value of $R_2$ in the case of potential pulse cells, near short circuit condition, was found to be 4.5 times less compared to potentiodynamic cells. This is the reason for obtained higher value of $J_{sc}$ (2.04 mA/cm$^2$) compared to 0.574 mA/cm$^2$ in potentiodynamically prepared cells. The junction capacitance ($C_{jun}$) of both the cells was found to be identical to capacitance of any Schottky junction solar cell. The maximum capacitance was found near open circuit voltage condition ($V_{oc}$). This is due to the increased number of accumulated charges which result in low or minimal flow of charge carriers in this condition. The values of $C_{jun}$ in reverse bias condition were found to be one order less for potential pulse cells compared to potentiodynamic cells. This is the reason for higher reverse saturation current density ($J_0$) in the case of potential pulse cells.
\section*{7.4 Conclusions}

In conclusion, we have fabricated solid state Schottky junction solar cells out of non stoichiometric PbO$_x$ films for the first time. It was found that the cells prepared from potential pulsed film result in efficiency of 0.384\%. The performance of both cells was compared and analyzed by dark and temperature dependent J-V characteristics. The high ideality factors were found to be the characteristic of trap assisted recombination process. The activation energies of such traps were calculated from the Arrhenius plot of resistivity. The calculated activation energies
were 124 and 10 meV for potentiodynamic and potential pulse films, respectively. Such low activation energy values suggest that the dominant charge transfer mechanism is transport via trap states. The Mott-Schottky plots confirmed the built in potential of 0.85 and 0.72 V for potentiodynamic and potential pulsed PbO$_x$ film cells respectively. Detailed impedance analysis by taking each and every interface into the account gave insight into the performance of solar cells.