JUNCTION FORMATION AND CURRNET TRANSPORT MECHANISMS IN TIN-DOPED CADMIUM OXIDE FILMS FOR TCO-Si BASED PHOTOVOLTAIC DEVICES APPLICATION

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Abstract

Junction formation and current transport mechanisms of transparent conducting Sn doped CdO thin films on silicon (Si) substrate have been studied as a function of Sn doping concentration (0.15wt%, 0.20wt% and 0.25wt%). The samples have been investigated using current-voltage (I-V) and capacitance voltage (C-V) measurements in order to define the transport mechanisms in heterostructure and basic electronic parameters. From the current density - voltage, illuminated J-V measurement as well as the photovoltaic response extracted the solar cell parameters. The built-in potential, photo and dark saturation current at Sn doped CdO on p-Si interface are monitored varying Sn doping concentration. It is observed that a high built-in potential form at the Sn 0.25wt% doped CdO/p-Si junction. The current voltage characteristics were analyzed using Schottky and abrupt p-n junction models. The open circuit voltage \( V_{oc} \) and saturation current density \( J_o \) extracted from the illuminated and dark J-V curves as well as calculated assuming a Schottky junction and an abrupt p-n junction for different Sn doping density \( N_D \).

Keywords: Sn doped CdO films, Schottky junction, The open circuit voltage \( V_{oc} \)

Introduction

Transparent conducting oxides (TCOs) have been widely used in different areas due to their high optical transparency, low resistivity and wide energy band gap. Hence there has been great deal of work on investigating their preparation process and optimizing their properties [Jeyadheepan K et al 2010]. Among the various TCO materials available, cadmium stannate is one of the potential candidates for solar cell application [Hani Khallaf et al 2012]. Cadmium tin oxide is an n-type semiconductor and has great technological interest due to their high quality electrical and optical properties superior to the conventional transparent conducting oxide materials. In addition, these films have wide applications in photogalvanic cell, liquid crystal displays, heat mirrors, transparent electrode and solar cells [Wu X and Sheldon P et al 1997, Britt J and Ferekides C 1993].

SnO\(_2\) semiconducting transparent thin films have various appealing features for technical applications in solar energy conversion, flat panel displays, electro-chromic devices, invisible security circuits, LEDs etc. The SnO\(_2\) films close to stoichiometric condition have low free carrier concentration and high resistivity, but non-stoichiometric SnO\(_2\) films have high carrier concentration, high conductivity and high transparency [Ginlley D S and Bright C 2000 and Mostafa M et al 2012].

Solar cell is the basic unit of solar energy generation system where electrical energy is extracted directly from light energy without any intermediate process. The working of a solar cell solely depends upon its photovoltaic effect, hence a solar cell also known as photovoltaic cell. A

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solar cell is basically a semiconductor p-n junction device. It is formed by joining p-type (high concentration of hole or deficiency of electron) and n-type (high concentration of electron) semiconductor material at the junction excess electrons from n-type try to diffuse to p-side and vice-versa.

In the present study the junction and the device performance of Sn doped CdO thin film on p-Si photovoltaic cell are investigated in great detail. Investigation of junction transport in these devices is essential for understanding the photovoltaic loss mechanism and achieving higher efficiency.

**Experimental**

The films were deposited on silicon substrates by sol-gel spin coating method. Appropriate proportions of highly pure (99.99%) CdO and SnO$_2$ powders were ground by agate mortar. Mixture of CdO and SnO$_2$ have been used to prepare $(\text{CdO})_{1-x}(\text{SnO}_2)_x$ with $(x = 0.15, 0.20$ and $0.25 \text{ wt }\%)$. To increase complete mixing, the mixtures were ground for at least three hours. The mixed powders were annealed at 800°C for 3 hours. After that, 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH) is added to the mixture and then stirred and heated upon 100°C for 30 min. The homogeneous precursor solution or coating solution was obtained and these solutions were used to depose on Si substrates using spin coating technique. After the coating all the films were dried at the room temperature for 1 day in order to diffuse the solvent. Before the spin coating deposition, the silicon substrate was cleaned by standard semiconductor cleaning method.

The cleaning sequences are:

- **General clean:** The wafer was cleaned by using mixture of Sulfuric Acid and Hydrogen Peroxide for 10 minutes to remove organic and inorganic contamination from the silicon wafer.
- **Particle removal:** They were cleaned in a ratio of (5:1:1) DI water, Ammonium Hydroxide, Hydrogen Peroxide for 2 minutes to remove silica and silicon particle from the wafer, as well as certain organic and metal surface contamination.
- **Oxide removal:** The wafer were dipped in (1:20) Hydrofluoric acid, DI water for 60 seconds to remove the native oxide from the wafer surface.
- **Metal contamination removal:** The wafer were cleaned in a (6:1:1) ratio mixture of DI water, Hydrochloric acid, Hydrogen Peroxide for 10 minutes to remove certain ionic and metal surface contamination. The silicon wafers were rinsed in distilled water for all steps.

Finally the resulting thin films were annealed at 500°C for 3 hours.

The extract junction parameters and solar cell characteristics of TCO devices based on silicon substrates with different doping concentrations. To extract the solar cell parameters, used current density-voltage (dark J-V & illuminated J-V) and small signal capacitance- voltage (C-V) measurements.

Measurement of current- voltage curve, by using Digital multi meter DT 9205 as a voltmeter and DT 9208 A as an ammeter. For illumination, 150 watt Halogen lamp (220V, 50Hz) as a light source and Easy View Digital Light Meter Model EA 30 was used to count the light...
intensity. Capacitance-voltage characteristics were measured using G\textsuperscript{W}\textsuperscript{InSTEK}(LCR-8110G) at 1kHz and various applied voltage.

**Results and Discussion**

There are two approaches to describe the junction between Sn doped CdO thin film and p-Si layer. One is based on the Schottky junction theory that explains the interface of semiconductors to a metal. The other is the description of a one-sided abrupt junction between a moderately doped n-type thin film semiconductor region and a highly doped p-type semiconductor region. For both cases the current density - voltage characteristics of such a photovoltaic junction is in the simplest form described by the ideal diode equation under illumination (Equation 1). Rewriting Equation 1 at open circuit conditions (J=0) shows that the open circuit voltage \( V_{oc} \) of a solar cell mainly depends on the dark saturation current density \( J_0 \) and short circuit current density \( J_{sc} \) shown in Equation 2.

\[
J = J_0 \left( \exp \left( \frac{qV}{kT} \right) - 1 \right) - J_{sc}
\]

\[
V_{oc} \approx \frac{kT}{q} \ln \left( \frac{J_{sc}}{J_0} \right)
\]

At a Schottky junction between a metal and high-mobility semiconductor like silicon, the dominating transport mechanism is the thermionic emission of majority carrier over the potential barrier \( \Phi_b \) that forms at the interface. The \( J_0 \) for a Schottky junction described in Equation 3,

\[
J_0 = A^{**} T^2 \exp \left( \frac{-q \phi_b}{kT} \right)
\]

\( A^{**} \) denotes the reduced effective Richardson constant including effects of tunneling and scattering of majority carriers at phonons as well as a correction factor for a small contribution of majority carrier diffusion for moderately doped silicon. At room temperature, in a reasonably small applied field, \( A^{**} \) is about 110 A/(cmK)\(^2\).

If the doping of the p-type semiconductor is substantially larger than that of the n-type semiconductor, the dark saturation current density \( J_0 \) of the so called one-sided abrupt p+n junction is defined by Equation 4.

\[
J_0 = n_i^3 \mu_p kT \frac{L_p N_A}{L_p N_A}
\]

where, \( \mu_p \) = the mobility, \( L_p \) = the diffusion length of the minority carriers (electron for p-Si) and \( n_i \) = the intrinsic carrier concentration.

Mott-Schottky analysis probes the depletion capacitance at a Schottky or p-n junction which is determined by the width of the bias dependent depletion region. Hence the depletion capacitance \( C \) is also bias dependent and can be expressed as in equation 5, where, \( V \) is the applied bias voltage and \( V_{bi} \) is the built-in voltage.

\[
\frac{1}{C^2} = \frac{2(V_{bi} - V)}{A^2 q \varepsilon \varepsilon_0 N_A}
\]
Figure 1(a ~ c) depicts the characteristics $1/C^2$ versus $V$ plots for Sn doped CdO thin films on Si substrate at frequency range 10 kHz. The so-called Mott-Schottky plot of $1/C^2$ versus applied DC voltage yields a straight line, whose slope yields the doping density and whose extrapolated intersection with the voltage axis yields the built-in voltage. The doping density is given by equation 6.

$$N_a = -\frac{2}{q\varepsilon_0 A^2} \left( \frac{dV}{dC^2} \right)^{-1}$$  \hspace{1cm} (6)

The main parameters obtained from Mott-Schottky analysis for Sn doped CdO/p-Si thin films devices collected in Table 1. The current density - voltage (J-V) curve for dark and under illumination conditions are shown in Figure 2 (a ~ c ) and Figure (3). All relevant solar cell parameters extracted from the illumination J-V curves are collected in Table (1).

The open circuit voltage $V_{oc}$ and saturation current density $J_o$ extracted from the illuminated and dark J-V curve, as well as calculated assuming a Schottky junction (Equation 3) and an abrupt junction (Equation 4) for different doping density ($N_A$). The extracted values are summarized in Table (2).

**Table 1 Summary of Sn doped CdO/p-Si thin films devices interface, solar cell parameters for all differently doped Sn concentration from C-V and I-V measurements**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_A$ (cm$^3$)</th>
<th>$V_{bi}$ (V)</th>
<th>$\Phi_0$(eV)</th>
<th>$V_{oc}$(V)</th>
<th>$J_{sc}$ ((\mu A/cm^2))</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(0.15wt%) doped CdO/p-Si</td>
<td>$6.44 \times 10^{13}$</td>
<td>0.083</td>
<td>0.42</td>
<td>3.367</td>
<td>9.60</td>
<td>0.419</td>
<td>1.028</td>
</tr>
<tr>
<td>Sn(0.20wt%) doped CdO/p-Si</td>
<td>$8.20 \times 10^{12}$</td>
<td>0.148</td>
<td>0.54</td>
<td>4.042</td>
<td>11.1</td>
<td>0.487</td>
<td>1.657</td>
</tr>
<tr>
<td>Sn(0.25wt%) doped CdO/p-Si</td>
<td>$6.79 \times 10^{11}$</td>
<td>0.156</td>
<td>0.61</td>
<td>4.729</td>
<td>10.8</td>
<td>0.592</td>
<td>2.295</td>
</tr>
</tbody>
</table>

**Table 2 Summary of open circuit voltage $V_{oc}$ and saturation current density $J_o$ extracted from the J-V curve (dark & illumination), calculated Schottky junction and abrupt junction equations**

<table>
<thead>
<tr>
<th>$N_A$[cm$^{-3}$]</th>
<th>J-V curves</th>
<th>Schottky junction</th>
<th>p*\text{n-junction}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J_o$[(\mu A/cm^2)]</td>
<td>$V_{oc}$ [V]</td>
<td>$J_o$[(\mu A/cm^2)]</td>
</tr>
<tr>
<td>$6.44 \times 10^{13}$</td>
<td>8.79 x 10$^{-1}$</td>
<td>3.367</td>
<td>8.75 x 10$^{-1}$</td>
</tr>
<tr>
<td>$8.20 \times 10^{12}$</td>
<td>8.36 x 10$^{-1}$</td>
<td>4.042</td>
<td>8.40 x 10$^{-3}$</td>
</tr>
<tr>
<td>$6.79 \times 10^{11}$</td>
<td>9.24 x 10$^{-1}$</td>
<td>4.729</td>
<td>5.60 x 10$^{-4}$</td>
</tr>
</tbody>
</table>
Conclusion

Tin doped CdO thin films were prepared by sol-gel spin coating method on Si substrate. The effect of junction formation and current transport mechanisms of Sn doped CdO/p-Si thin films were investigated by capacitance-voltage and current voltage characteristics under dark and illumination. The doping density obtained from C-V characteristics in the range of \((6.79 \times 10^{11} \text{ cm}^{-3} - 6.44 \times 10^{13} \text{ cm}^{-3})\). The barrier height is in the range of \((0.42\text{eV} - 0.61\text{eV})\). The built in voltage range are \((0.083\text{V} - 0.156\text{V})\) respectively. From the Schottky junction observation, Schottky junction \(J_0\) mainly depends on the Schottky barrier height \(\Phi_b\). From the abrupt \(p^+n\)-junction observation, \(J_0\) solely depends on properties of the moderately doped \(p\)-type semiconductor and is inversely proportional to its doping concentration \(N_A\). Therefore, it is obvious that the \(V_{oc}\) in a \(p^+n\)-junction increased with larger \(N_A\). By measuring and modeling, the dark and illuminated current-voltage characteristics, and comparing the extracted open-circuit voltage and dark saturation current density, with value calculated from transport equations based on different junction models. In general, the results corroborate that Sn doped CdO/p-Si thin film devices hetero-interfaces can be great charge carrier selective contacts for photovoltaic and other optoelectronic devices.

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![Figure 1 (a)](image-url)
Figure 1(b) $1/C^2$ versus V plots for Sn 0.20 wt% doped CdO/p-Si thin film device

Figure 1(c) $1/C^2$ versus V plots for Sn 0.25 wt% doped CdO/p-Si thin film device
Figure 2(a) The dark J-V plots for Sn 0.15 wt% doped CdO/p-Si thin film device

Figure 2 (b) The dark J-V plots for Sn 0.20 wt% doped CdO/p-Si thin film device
Figure 2(c) The dark J-V plots for Sn 0.25 wt% doped CdO/p-Si thin film device

Figure 3 Photovoltaic properties of Sn doped CdO/p-Si thin film device with differently doping density ($N_A$)
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