Electrical and photovoltaic characteristics of indium phthalocyanine chloride/p-Si solar cell

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\textbf{A B S T R A C T}

Hybrid (organic/inorganic) heterojunction solar cell based on indium phthalocyanine chloride derivative (InPcCl-D) deposited by thermal evaporation technique onto p-type silicon single crystal wafer has been fabricated. The cell was characterized by current–voltage and capacitance–voltage measurements. The dark current–voltage characteristics of Au/InPcCl-D/p-Si/Al heterojunction device were measured at different temperatures. The device showed rectification behavior with a rectification ratio of 102 at ±1 V determined at room temperature. The dominant conduction mechanisms operating consequently are the thermionic emission and the single-trap space-charge limited current. The junction parameters such as diode ideality factor, potential barrier height and series resistance are estimated as a function of temperature. The device is non ideal in showing ideality factor of 3.28 at room temperature. The temperature dependence of the ideality factor, barrier height and series resistance indicates the formation of non homogenous barrier height in the junction. The space charge limited current conduction mechanism showed that the trap concentration is 1.53 \times 10^{25} \text{m}^{-3} and it lies at 0.11 eV above the valence band edge. Capacitance–voltage measurements showed the abrupt nature of the junction and the built-in potential is determined. The value of the built in potential and carrier concentration are estimated as 0.85 V and 3.31 \times 10^{22} \text{m}^{-3}, respectively. Under illumination intensity of 100 \text{W/m}^2, the device showed photovoltaic behavior with open circuit voltage, $V_{oc}$, and short circuit current density, $J_{sc}$, of 0.352 V and 7.6 mA/cm$^2$, respectively. The values of filling factor, FF, and photo-electrical conversion efficiency, $\eta$, are estimated as 0.31 and 2.96%, respectively.

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1. Introduction

Phthalocyanines (Pcs) and metallophthalocyanines (MPcs) have interesting properties such as photochemical properties, semi-conductivity, photoconductivity, thermal and chemical stability, very high coloring properties and chemical inertness. Therefore, they find many technological applications such as: solar cells [1,2], light emitting diodes [3], gas sensors [4] and rectifiers [5]. Phthalocyanines (Pcs) have also medical applications especially in photodynamic therapy [6].

Phthalocyanines and MPcs have highly conjugated delocalized $\pi$-electrons system and large flexibility in the structure of the phthalocyanines that enables to modify their structure by different substitution groups in the peripheral position of Pc ring or inserting different transition metals.

In device fabrication, it was found that bilayer devices based on organic/inorganic layers, have overcome the disadvantages of single-layer devices. The type of conduction in organic thin films controls the Schottky barrier height, which could be increased or decreased [7]. P-type increases the barrier height and n-type decreases it [7]. Choice of organic molecule, the interlayer thickness and reducing optical filter effects control the fundamental device parameters [8].

Heterojunction devices of p-MgPc/n-Si studied by Raid [9] in dark and under illumination showed that these junctions exhibit rectifying and strong photovoltaic characteristics with power conversion efficiency of 1.05%. Yanagi et al. [10] investigated AlPcCl/n-Si heterojunctions diode. They controlled thickness of deposited AlPcCl and changed substrate temperature of n-Si. They found that the thickness and morphology of the deposited AlPcCl have an important role in increasing the photovoltaic efficiency of theAu/AlPcCl/n-Si cells. Placia et al. [11] created organic photovoltaic cells (OPV) with good near-IR photo activity from highly textured titanylphthalocyanine...
From voltaic devices subject Cl-AlPc fundamental absorption structure. TiOPc seemingly Al/OPVs structure Axially (**fi**) donating current along structure (**et**) (TiOPc)/C60 heterojunctions. Incident photon current efficiency (IPCE) plots confirmed the enhanced near-IR OPV activity, with maximum IPCE values of ca. 30% for devices using IpPhase II only of TiOPc films. Chauhan et al. [12] explored the structure-function relationship of organic photovoltaic (OPV) cells based on the (CIAIPc)/fullerene (C60) planar heterojunction. Optimization is achieved with the use of a molybdenum oxide (MoOx) and an underlying 3, 4, 9, 10-pyrenyle tetracarboxylic acid (PTCDA) interlayer at the hole extracting electrode, the latter is acting as a structural template for the subsequent growth of the CIAIPc donor layer. OPV cells demonstrate power conversion efficiencies of 3.0% under simulated AM1.5G (air mass 1.5 global) illumination, with the short-circuit current (**jc**) showing an ~25% improvement relative to a device without a templating layer. The effect of the MoOx, interlayer is to minimize losses in the open-circuit voltage and fill factor caused by significant band bending and pinning of the highest occupied molecular orbital levels of organic layer adjacent to nonstoichiometric defect states in the near fermi level region of MoOx. Lessard et al. [13] fabricated preliminary planar heterojunction (PHJ) organic photovoltaic (OPV) devices using F-AlIPc as an electron donating material paired with C60 and a ternary device including a Cl-AlIPc interlayer. Additionally, an all AlPc device where F-AlIPc functioned as the electron donor and Cl-AlIPc as the electron acceptor was fabricated. The EQE plots of the resulting PHJ OPV devices illustrate that an exciton-rectifying layer is present between the CI-AlIPc and F-AlIPc layers in the ternary devices as well as the all AlPc device. These results further exemplify that the seemingly minor change from chloride to fluoride in the AlPc structure has significant implications in optoelectronic properties and functionality of AlPc in PHJ OPV devices. Lessard et al. [14] have assessed the potential application of dichloro silicon phthalocyanine (Cl2-SiPc) and dichloro germanium phthalocyanine (Cl2-GePc) in modern planar heterojunction organic photovoltaic (PHJ OPV) devices. The results established the potential for the application of SiPc and GePc in PHJ OPV devices.

The search for new materials with good performance characteristics as well as the improvement in device fabrication has been a subject of importance. The application for solar cells calls for specific organic compound structure with excellent absorption in the visible region of spectra. The phthalocyanines exhibit absorption spectra with two strong absorption regions, one of them is in the ultraviolet region at about 300–350 nm (B-band) and the other one is in the visible region at 600–700 nm (Q-band). Axially substituted indium phthalocyanine chloride InPcCl-D of ABAB type has been recently synthesized with the molecular structure given in Fig. 1 [15]. Its films have a nanocrystalline structure and showed excellent absorption in the visible region of spectra with absorption coefficient > 105 cm−1. The optical and fundamental energy gaps are 1.51 and 2.9 eV, respectively [15].

In this work, we report on the rectifying contact characteristics and photovoltaic properties of thermally evaporated InPcCl-D thin films deposited onto silicon single crystal substrates. The properties of this rectifying junction are studied with the help of current–voltage characteristics at different temperatures and capacitance–voltage characteristics at constant frequency of 1 MHz. The photovoltaic properties of InPcCl-D/p-Si device have been also estimated.

2. Experimental

The used substrate in the fabrication of the device is a p-type Si wafer oriented at [100] with a thickness of 0.45 mm and a resistivity of 150 Ω cm. The cleaning procedure of the Si substrate was performed by boiling it for 10 min in NH4OH + H2O2 + 6H2O solution to remove the surface damaged layer and undesirable impurities, followed by immersing it in a solution consisting of HF: H2O (1:10) to remove the native oxide on its surface. Then, the wafer was rinsed in extra-pure ethyl alcohol, dried and inserted into the deposition chamber. An electrode was made by evaporating a thick pure aluminum film on the back surface of a Si wafer substrate. InPcCl-D thin film with a thickness of about 100 nm was deposited on the front surface of p-Si substrate. To reduce the optical filter effect of Au on InPcCl-D a mesh gold electrode was deposited through a special mask on the surface of the organic thin film instead of a continuous Au thin film electrode. Au also makes an Ohmic contact with InPcCl-D. Thus, an Au/InPcCl-D/p-Si/Al heterojunction solar cell was designed. The effective area of the solar cell is 0.28 cm2.

InPcCl-D films and metal electrodes were thermally deposited under vacuum by using a high vacuum coating unit (Edwards Co., Model E306 A, England). The pressure inside the working chamber was pumped down to 6 × 10−4 Pa before starting the evaporation process. A mechanical shutter is applied to prevent any probable contamination to reach the film in the first stage of the evaporation process and also control to the film thickness. InPcCl-D was sublimated under vacuum using quartz crucible that was subjected to induction heating from molybdenum heater. Quartz crystal thickness monitor (Maxtek. Inc., model, TM-350, USA) controls the rate of deposition and film thickness during the deposition process. The deposition rate is controlled at about 2.5 Å/sec. Gold and aluminum electrodes were thermally evaporated directly from boat-shaped molybdenum and basket-shaped tungsten filaments, respectively.

The hot probe method [16] specified the type of the semiconductor and showed that InPcCl-D is a p-type semiconductor. The experiment is performed by connecting a sample from one end with a hot probe such as a heated soldering iron and the other end is connected to a cold probe. Charge carriers will diffuse through the sample from hot end to cold one causing a current to flow. The net current will depend on the majority carriers within the sample, electrons or holes. Since electrons and holes have opposite charges and cold terminal is connected to positive terminal of galvanometer. The type of charge carriers can be determined directly by the sign of the current. The electrical and photovoltaic properties of the heterojunction device were investigated by **I–V** measurements using source-meter (Keithly
type 2635A). The measurements were performed at different temperatures in dark/light conditions. The intensity of incident light from tungsten filament lamp was recorded by a calibrated digital light meter (Lutron-Model LX-107) situated at the same level position of the device and is calculated as 100 W m\(^{-2}\). The capacitance versus voltage (C–V) measurements of the device in air and at dark conditions was achieved at 1 MHz by using computerized C–V meter (Model 4108, solid-state measurements, Inc., Pittsburgh, UK).

3. Results and discussion

3.1. Dark current–voltage characteristics

Fig. 2 illustrates the typical forward and reverse current–voltage (I–V) characteristics of Au/InPcCl-D/p-Si/Al heterojunction device at different temperatures, ranged from 300 to 375 K in dark condition. The results show that the curves have the same I–V behavior. For a constant applied voltage, current increases with increasing temperature, indicating a negative temperature coefficient for the resistivity. Fig. 3 shows the I–V behavior of the same heterojunction in forward and reverse bias directions at room temperature. The results also show existence of leakage current in the reverse bias direction. The results prove the good rectification performance for the junction diode and the rectification ratio has been estimated to be 102 at bias potential of ±1 V. From Table 1 it can be seen that the rectification ratio decreases with increasing temperature; this is due to the increased leakage current with increasing temperature.

Fig. 4 illustrates the natural logarithm of the forward current plotted versus the applied voltage at fixed temperature. At applied potentials less than 0.45 V, the logarithm of the current increases linearly with increasing applied voltage; this indicates that thermionic emission conduction is the predominant conduction mechanism in such a potential range. Sze [17] relates the current to the applied bias in this region by:

\[ I = I_0 \exp \left( \frac{e(V - I R_s)}{m k T} - 1 \right) \left[ 1 - \exp \left( -\frac{e(V - I R_s)}{k T} \right) \right] \]  

(1)

where \( e \) is the electron charge, \( m \) refers to the ideality factor, \( k \) stands for the Boltzmann constant, \( T \) denotes the absolute temperature, \( V \) is the applied potential, the term \( I R_s \) represents the potential drop across the series resistance \( R_s \) and \( I_0 \) denotes the reverse saturation current, which is given as [17]:

\[ I_s = A A^* T^2 \exp \left( \frac{-e\phi_{bi}}{k T} \right) \]  

(2)

\( A \) is the diode area (0.28 cm\(^2\)), \( A^* \) is the effective Richardson constant (32A cm\(^{-2}\) K\(^{-2}\) for p-type Si[17]), \( \phi_{bi} \) is the zero-bias barrier height. The diode ideality factor \( m \) and the built-in potential \( \phi_{bi} \) can be deduced from Eqs. (1) and (2) as:

\[ m = \frac{e}{k T} \frac{d(V - I R_s)}{d \ln (I)} \]  

(3)

and

\[ \phi_{bi} = k T \frac{AA^* T^2}{e I_s} \]  

(4)

### Table 1

Electronic parameters of Au/InPcCl-D/p-Si/Al heterojunction diode at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>RR</th>
<th>( I_s ) (A)</th>
<th>( m )</th>
<th>( \psi ) (eV) ( (I-V) )</th>
<th>( R_s (k\Omega) )</th>
<th>( \psi ) (eV) Norde</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>102</td>
<td>1.86 × 10(^{-9})</td>
<td>3.28</td>
<td>0.84</td>
<td>141.14</td>
<td>0.87</td>
</tr>
<tr>
<td>325</td>
<td>101</td>
<td>3.87 × 10(^{-9})</td>
<td>3.17</td>
<td>0.89</td>
<td>113.63</td>
<td>0.92</td>
</tr>
<tr>
<td>350</td>
<td>70</td>
<td>7.41 × 10(^{-9})</td>
<td>3.07</td>
<td>0.95</td>
<td>99.78</td>
<td>0.96</td>
</tr>
<tr>
<td>375</td>
<td>43</td>
<td>1.18 × 10(^{-9})</td>
<td>2.95</td>
<td>1.01</td>
<td>9.08</td>
<td>1.05</td>
</tr>
</tbody>
</table>
The values of the diode ideality factor $m$ and the reverse saturation current $I_0$ are determined at different temperatures from the slope and the intercept of semi-logarithmic forward bias $I$-$V$ plots for $V > 3kT/\varepsilon$, respectively. Once the reverse saturation current is known, the barrier height can be calculated by using Eq. (2). The change of $m$ and $\phi$ with temperature is presented in Table 1. It can be observed, the values of $m$ and $\phi$ are functions of temperature. The high values of the ideality factor are probably caused by various effects such as inhomogeneities of organic film thickness, non-uniformity of the interfacial charges and the effect of series resistance. The deviation of $m$ from unity indicates that the device is not ideal. Probably, there is an insulating oxide layer at the InPcCl-D-Si interface. The interface oxide layers can be formed by water or vapor adsorbed onto the surface of Si substrate before the deposition of the organic layer. For a sufficiently thick interface layer, the interface states are in equilibrium with the p-Si substrate and they cannot interact effectively with the organic semiconductor [18].

At relatively higher voltages $>0.45$, the current as a function of applied potential, at different temperatures is plotted on double natural logarithmic scale as shown in Fig. 5. The relation is linear with slope equal to $2.1 \pm 0.02$. This indicates that the space charge limited current, dominated by a single energy trap level [19], is the dominant conduction mechanism in that voltage range, the current density in this region is given by [19]:

$$ J = \frac{9}{8} \varepsilon \mu \frac{V^2}{d^2} $$  \hspace{1cm}(5)

where $\varepsilon$ is the permittivity of organic film, $\mu$ is the hole mobility, $d$ is the thickness of organic layer and $\theta$ is the trapping factor given by:

$$ \theta = \frac{N_e}{N_i} \exp\left(-\frac{E_t}{k_B T}\right) $$  \hspace{1cm}(6)

where $N_e$ and $N_i$ are the effective density of states in the valence band and the total trap concentration situated at energy level $E_t$ above the valence band edge. From the above expressions, it is evident that $\ln J$ versus inverse of temperature should be a straight line as shown in Fig. 6. The slope and intercept with the ordinate axis are used for estimating the $E_t$ and $N_i$ values, respectively. Using values of $\varepsilon = 3.53 \, [15], \mu = 10^{-7} \, m^2 \, V^{-1} \, s^{-1} \, [20]$, and $N_e \approx 10^{25} \, m^{-3} \, [21]$, the $E_t$ and $N_i$ values are found to be 0.11 eV and $1.53 \times 10^{23} \, m^{-3}$, respectively. The value of $N_i$ is comparable with those observed on cobalt phthalocyanine [22], nickel phthalocyanine [23] and PbPc [24] i.e., $1.5 \times 10^{25} \, m^{-3}$, $7.8 \times 10^{25} \, m^{-3}$ and $5.18 \times 10^{25} \, m^{-3}$, respectively.

The series resistance, $R_s$, is an important parameter since it affects the electrical characteristics of the rectifying contacts. $R_s$ in solar cells arises from the contact resistance between metal-semiconductor interface, Ohmic resistance in metal contacts and Ohmic resistance in the semiconductor material. The forward bias $I$-$V$ characteristics are usually linear in the semi-logarithmic scale at low voltages and deviate from linearity due to effect of the series resistance, when the applied voltage is sufficiently large. In the present study, the junction with its structure is influenced by the presence of the interface layer between the organic layer and the inorganic semiconductor and leads to non-ideal forward bias $I$-$V$ characteristics. The series resistance is calculated according to the modified Norde’s method [25], which is applicable all over the applied potential range. The Norde function is given by:

$$ F(V) = \frac{V}{\gamma} - \frac{k_B T}{\varepsilon} \ln \left( \frac{I(V)}{AA' T^\gamma} \right) $$  \hspace{1cm}(7)

where $\gamma$ is a first integer greater than the ideality factor. $I(V)$ is the current obtained from the $I$-$V$ curve. Fig. 6 represents the variation of $F(V)$ with the applied voltage of the junction. From Norde’s function, the value of series resistance, $R_s$, is determined as:
\[
R_s = \left( \frac{kT}{e} \right) \left( \frac{1}{f(V_o)} \right) 
\] (8)

where \( I(V_o) \) is the current corresponding to the minimum point of the \( F(V) \) relationship. The series resistance of the heterojunction device in the investigated temperature range is given in Table 1. The high series resistance values may be ascribed to a decrease of the exponentially increasing rate in current due to space-charge injection into the InPcCl-D thin film at high forward bias voltage. The series resistance decreases with increasing temperature. The variation of \( R_s \) with temperature may be due to the factors responsible for the high values of ideality factor \( m \) and lack of sufficient free carrier concentration at low temperatures. On the other hand, the barrier height can also be determined in the framework of Norde’s method. The barrier height is given by:

\[
\phi = F(V_o) + \frac{V_o}{e} - \frac{kT}{e} 
\] (9)

where \( F(V_o) \) is the minimum point of \( F(V) \), and \( V_o \) is the corresponding voltage. From Table 1, it can be seen that there is a good agreement between the values of the \( \phi \) obtained from Norde function and those deduced by thermionic emission theory.

The reverse biased \( I-V-T \) characteristics of Au/p-InPcCl-D/p-Si/Al device, as illustrated in Fig. 8, shows temperature rather than voltage dependence, this indicates that it is a thermally activated process and is controlled by [26]:

\[
I_R \propto \exp \left( \frac{-\Delta E}{kT} \right) 
\] (10)

where \( \Delta E \) is the carrier activation energy. The temperature dependence of \( I_{R} \) for the device, in reverse bias direction, is shown in Fig. 7. The calculated average activation energy is 0.56 eV which is approximately one half of the band gap of Si \( (E_g = 1.12 \text{ eV}) \). This suggests that the dark current originates in Si substrate and is controlled by generation and recombination of carriers [27].

### 3.2. Capacitance–voltage characteristics

The capacitance–voltage \( (C-V) \) measurements are one of the most regular electrical measurement techniques used to determine some important parameters of the heterojunction devices, such as impurity concentrations and barrier height. For this purpose the \( C-V \) characteristic of the structure at a fixed frequency of 1 MHz was investigated. Fig. 9 illustrates the reverse bias \( C-V \) relation plotted on double natural logarithm scale. The relation is linear with a slope of 0.53 implying that the junction has abrupt nature [28]. The relation \( C^{-2} - V \) measured at room temperature in reverse bias direction is shown in Fig. 10. The relation indicates that the behavior of the device resembles a Schottky diode behavior. According to Schottky theory, the depletion layer capacitance is given by [17]:

\[
\frac{1}{C^2} = \frac{2}{\varepsilon e A^2 N_a} (V_{in} + V) 
\] (11)

where \( V_{in} \) is the built-in potential at zero bias, \( A \) is the effective area of the diode and \( \varepsilon \) is the dielectric constant of the semiconductor, \( \varepsilon_o \) is the dielectric constant of free space and \( N_a \) is the carriers concentration. The value of \( V_{in} \) and \( N_a \) could be estimated from the intercept with abscissa axis and the slope of the straight line. The value of \( V_{in} \) and \( N_a \) are estimated as 0.85 V and \( 3.31 \times 10^{22} \text{ m}^{-3} \), respectively. The value of \( V_{in} \) is comparable with the value of \( \phi \) obtained from \( I-V \) characteristics as shown in Table 1.

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**Fig. 7.** Norde’s function of Au/InPcCl-D/p-Si/Al heterojunction diode at different temperatures.

**Fig. 8.** Plot of \( \ln I_R \) versus reciprocal temperature for Au/InPcCl-D/p-Si/Al heterojunction diode at different voltages.

**Fig. 9.** Variation of \( \ln C \) versus \( \ln V \) at reverse biasing potential.
3.3. The energy band diagram for InPcCl/p-Si heterojunction device

Electron affinity, $\chi$, is defined as the energy required to remove an electron from the bottom of inorganic semiconductor's conduction band or bottom of HOMO band in organic semiconductor to the vacuum level. Electron affinity (EA) and the band gap ($E_g$) are intrinsic properties of semiconductor materials and are independent of doping. The presence of different substituents on the Pc ring [i.e., sulfonate (electron withdrawing group) versus butoxy (electron donating group) versus no substituents] has little effect on the EA that centers around 3.7 eV for all the compounds [29]. Yuen et al. [30] determined the electron affinity and ionization potential for InPcCl as 3.6 and 5.1 eV, respectively.

The work function is the energy to excite electron from fermi level to the vacuum level and it depends on doping, it has a value of 4.97 eV for Si [17]. The total built in voltage, $V_{bi}$, is due to the difference in work functions ($\psi_{Si} - \psi_{InPcCl} = 0.85$ eV), therefore $\psi_{Si} > \psi_{InPcCl}$. When two semiconductors with different electron affinities, band gaps and work functions are brought together to form a heterojunction diode, discontinuities form in the energy bands, thought to be due to the fermi level alignment. In an ideal case of free interface states and vacuum level alignment i.e., (without an interface dipole), the discontinuities in the conduction band ($\Delta E_c$) are equal to the difference in the electron affinities ($\chi$) of the two semiconductors, i.e.,

$$\Delta E_c = \chi_{Si} - \chi_{InPcCl}$$

(12)

This is known as the Anderson affinity rule [31]. The discontinuities in the valence band ($\Delta E_v$) are given by $\Delta E_v = \Delta E_c$, where $\Delta E_v$ is the difference in band gap between the two semiconductors. $\Delta E_v$ and $\Delta E_c$ have been calculated for p-Si/InPcCl heterojunction as 0.4 and 1.38 eV, respectively taking into consideration that the band gap of Si is 1.12 eV [17] and that of InPcCl is 2.9 eV [15]. In this work we found that:

$$\psi_{Si} > \psi_{InPcCl}, \chi_{Si} > \chi_{InPcCl}, E_{g, Si} < E_{g, InPcCl}$$

and $\chi_{Si} + E_{g, Si} < \chi_{InPcCl} + E_{g, InPcCl}$

Therefore, the band profile of Si/InPcCl heterojunction device can be constructed as shown in Fig. 11(a) [32].

For p–p isotype heterojunctions ($\psi_{InPcCl} < \psi_{Si}$), holes are depleted on the side containing the semiconductor with $\psi_{InPcCl}$ and are accumulated on the side containing the semiconductor with $\psi_{Si}$. This is referred to as a hole-accumulation/depletion heterojunction. The space-charge region in the Si layer consists of mobile electron charges, and the band is bent downwards from the bulk to the interface. In the InPcCl layer, the band is bent upwards, which causes an accumulation of holes near the interface. An energy diagram for this situation is given in Fig. 11(b). Generally, p-Si is considered to be a hole-transport material. However, in the InPcCl/p-Si heterojunction, not only hole carriers in the Si layer accumulated, but the Si layer may also exhibit strong band bending, which generates an inversion layer—an accumulation of electrons near the heterojunction interface. As a result, electrons can be transported in the Si layer, making InPcCl/Si p–p isotype.

3.4. Photovoltaic properties

Fig. 12 shows the effect of light illumination with intensity of 100 W/m² on the I–V characteristics of Au/p-InPcCl-D/p-Si/Al heterojunction solar cell. It can be observed that there is a significant increase in current upon illumination, indicating that the device has photovoltaic behavior. The absorption of light by InPcCl-D creates excitons and by Si creates electron-hole pairs. Excitons are dissociated into electron-hole pairs at the InPcCl-D/Si interface. Under the influence of the applied electric field electrons are transported immediately in Si and collected by Al electrode and holes are transported in InPcCl-D toward Au electrode. The power curve is shown in Fig. 13. The solar cell has open circuit voltage, $V_{oc}$, and short circuit current density, $J_{sc}$, of 0.352 V and 7.6 mA/cm², respectively. The fill factor, FF, is estimated from the relation given by [28]:

$$FF = \frac{V_M}{V_{oc}} \times \frac{I_M}{I_{sc}}$$

(13)

where $V_M$ and $I_M$ are the voltage and current at the maximum power point. The electrical conversion efficiency is determined from the relation given by [28]:

![Fig. 10. C–V relation of Au/InPcCl-D/p-Si/Al heterojunction diode.](image)

![Fig. 11. Energy band diagram for InPcCl/p-Si hybrid heterojunction device (a) with no light applied (b) modified energy band profile due to the presence of charged interface states.](image)

![Fig. 12. Photovoltaic properties](image)
transport mechanisms, in forward bias direction [34,37,38]. The conduction mechanisms, in the forward bias direction in both cases [34,37] is the thermionic emission followed by SCLC with single energy level of traps. In the reverse bias direction the suggested mechanism is generation- recombination of carriers that originate in the Si substrate [34,37]. The conduction mechanisms [38] in both heterojunctions are tunneling current mechanism and diffusion current mechanism operating simultaneously followed by space charge conduction, at potentials >0.4 V, which is controlled by interface states levels and trapping levels in amorphous silicon. The influence of the type of Si-substrate is clear on built-in potential barrier in particular the n-type Si increases the built-in potential (0.61 ± 0.05 V) and the p-type Si reduces it (0.46 ± 0.05 V). In H2Pc/n-Si device [33], the forward current involves tunneling and could be explained by a multi-step tunneling recombination model [33]. In this model, the electrons first stepwise tunnel from the conduction band of n-Si into empty interband states which are located in p-H2Pc and subsequently recombine through a stair case of closely spaced states in the depletion region. The C–V characteristics indicate an abrupt junction with built in potential of 0.42 V [33]. The metal substitution in Pc ring ([34–37] and present work) has no influence on conduction mechanisms operating in forward bias direction which are the thermionic emission followed by SCLC with single energy level traps; they have an influence on the potential range in which such conduction mechanisms are operating, the built-in potential and photovoltaic parameters.

4. Summary and conclusions

DC electrical parameters, conduction processes and photovoltaic properties of Au/p-InPcCl-D/p-Si/Al heterojunction diode were investigated by studying current–voltage and capacitance–voltage characteristics. The device showed a rectification behavior with a rectification ratio of 102 at ±1 V at room temperature. The thermionic emission conduction mechanism is observed at low forward applied voltage (<0.5 V), and the space-charge limited current controlled by single-trap energy level dominates at voltage in excess of 0.5 V. The device is non ideal in showing ideality factor of 3.28 at room temperature. The temperature dependence of the ideality factor and barrier height indicates the formation of non homogenous barrier height. The films showed trap concentration of $1.53 \times 10^{25}$ m$^{-3}$ at 0.11 eV above the valence band edge. The deduced barrier height deduced using the Norde’s function is in agreement with those predicted by thermionic emission mechanism. In reverse bias direction, the dark current originates in Si substrate and is controlled by generation and recombination of carriers. The junction is abrupt in its nature and the room temperature built-in potential is 0.85 V. The junction showed photovoltaic behavior and the room temperature electrical conversion efficiency under illumination intensity of 100 W/m$^2$ is estimated as 2.96%.

Table 2
Photovoltaic parameters of some heterojunction solar cells based on phthalocyanine, and their metal derivatives deposited on Si substrates [9,33–36,38,39]. The type of Si substrate has no influence on carrier’s

<table>
<thead>
<tr>
<th>Solar cell construction</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (Volts)</th>
<th>Fill factor (FF)</th>
<th>Efficiency ($\eta$ %)</th>
<th>Light intensity (mW/cm$^2$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/MgPc/p-Si/Al</td>
<td>3.76</td>
<td>0.35</td>
<td>0.35</td>
<td>1.05</td>
<td>50</td>
<td>[9]</td>
</tr>
<tr>
<td>Au/p-H2Pc/p-Si/In</td>
<td>17.5</td>
<td>0.34</td>
<td>0.38</td>
<td>1.5</td>
<td>150</td>
<td>[33]</td>
</tr>
<tr>
<td>Au/InPc/p-Si/Al</td>
<td>18.6</td>
<td>0.32</td>
<td>0.28</td>
<td>1.11</td>
<td>6</td>
<td>[34]</td>
</tr>
<tr>
<td>Au/CoPc/p-Si/In</td>
<td>18.67</td>
<td>0.46</td>
<td>0.34</td>
<td>3.76</td>
<td>80</td>
<td>[35]</td>
</tr>
<tr>
<td>Au/ZnPc/p-Si/Al</td>
<td>3.1</td>
<td>0.44</td>
<td>0.34</td>
<td>2.3</td>
<td>20</td>
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<tr>
<td>Au/InPcCl/p-Si/Al</td>
<td>7.6</td>
<td>0.35</td>
<td>0.31</td>
<td>2.96</td>
<td>10</td>
<td>Present work</td>
</tr>
<tr>
<td>Ag/CuPc/(a-Si)/p-Si/Ag</td>
<td>18.4</td>
<td>0.167</td>
<td>–</td>
<td>5.7</td>
<td>100</td>
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</tr>
<tr>
<td>Ag/CuPc/(a-Si)/p-Si/Au</td>
<td>11.4</td>
<td>0.178</td>
<td>–</td>
<td>2.5</td>
<td>100</td>
<td>[38]</td>
</tr>
<tr>
<td>ITO/MPP/ZnPc/Au</td>
<td>5.2</td>
<td>0.4</td>
<td>0.48</td>
<td>1.05</td>
<td>860</td>
<td>[39]</td>
</tr>
</tbody>
</table>

MPP is N,N'–dimethyl-3,4,9,10-perylenbiscarboximid.
References