

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



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ARTICLE INFO

Article history:

Received 3 November 2014

Received in revised form 30 May 2015

Accepted 9 June 2015

Available online 17 June 2015

Keywords:

Phthalocyanine derivative

InPcCl-D/Si heterojunction device

Conduction mechanisms

Capacitance–voltage characteristics

ABSTRACT

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 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, η , are estimated as 0.31 and 2.96%, respectively.

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1. Introduction

Phthalocyanines (Pcs) and metalophthalocyanines (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 π -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 the Au/AlPcCl/n-Si cells. Placencia et al. [11] created organic photovoltaic cells (OPV) with good near-IR photo activity from highly textured titanylphthalocyanine

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(TiOPc)/C₆₀ heterojunctions. Post-deposition solvent annealing of TiOPc thin films resulted in transition of the existing phase to IpPhase II which broadens the absorbance spectrum of the Pc film from 600 to 900 nm and produces absorptivity ($\alpha = 10^5 \text{ cm}^{-1}$), along with substantial texturing of the Pc layer. Current–voltage (*J*–*V*) responses for white light illumination of ITO/TiOPc/C₆₀/BCP/Al/OPVs show a near doubling of the short circuit photocurrent (JSC), with only a small decrease in open-circuit photo potential (*V*_{oc}), and a concomitant increase in power conversion efficiency. 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 (ClAlPc)/fullerene (C₆₀) planar heterojunction. Optimization is achieved with the use of a molybdenum oxide (MoO_x) and an underlying 3, 4, 9, 10-perylene tetracarboxylic acid (PTCDA) interlayer at the hole extracting electrode, the latter is acting as a structural template for the subsequent growth of the ClAlPc 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 (*J*_{sc}) showing an ~25% improvement relative to a device without a templating layer. The effect of the MoO_x 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 MoO_x. Lessard et al. [13] fabricated preliminary planar heterojunction (PHJ) organic photovoltaic (OPV) devices using F-AlPc as an electron donating material paired with C₆₀ and a ternary device including a Cl-AlPc interlayer. Additionally, an all AlPc device where F-AlPc functioned as the electron donor and Cl-AlPc 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 Cl-AlPc and F-AlPc 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 $> 10^5 \text{ cm}^{-1}$. 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.

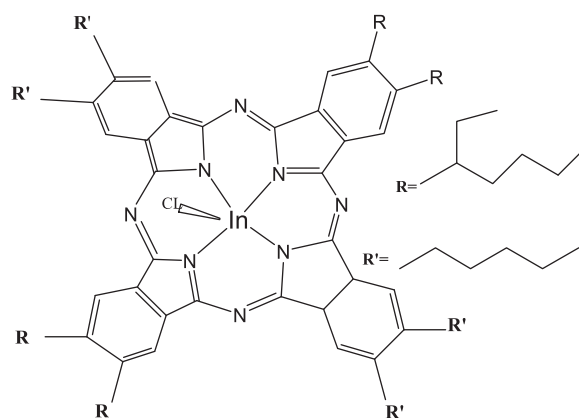


Fig. 1. Molecular structure of InPcCl-D.

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 NH₃ + 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 substrate 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

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