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Tandem Heterojunction Photoelectric Cell Based on Organic-Inorganic Hybrid of AlPc-H_2Pc and n-Si

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The tandem heterojunction photoelectric cell has been fabricated on the basis of organic-inorganic hybrid of AlPc-H2Pc (aluminium phthalocyanine-metal free phthalocyanine) and n-Si using pressing technique along with vapor deposition. Initially, the AlPc-H2Pc heterojunction films of thickness 150 nm were deposited on the ITO coated glass and the n-Si substrates as well by vapor deposition. Both the substrates (ITO glass and n-Si) were pressed and fixed together by keeping the deposited heterojunction films face to face. The pressing was done at elevated temperature (60-80 °C), while fixing was carried out by using adhesive. A 100 nm thick silver (Ag) film was deposited on the back of n-Si substrate. The complete architecture of the device was as ITO/AlPc:H_2Pc/n-Si/Ag. The AFM and UV-visible spectroscopy were used to investigate the morphology and optical properties of the organic (AlPc-H_2Pc) films, respectively. The cell was characterized for current–voltage behavior in dark and also under illumination. The values of I_{SC}, V_{oc}, fill factor (*FF*) and efficiency under illumination of 290 W/m^2 were equal to 0.7 V, 2.17 mA/cm^2, 0.33 and 1.1 %, respectively.

Keywords: pressing technology; organic-inorganic; photoelectric cell; aluminium phthalocyanine

1. INTRODUCTION

Because of their low density, low temperature processing, flexibility and low cost, the organic photovoltaic cells are very attractive for the generation of electric power from the sunlight [1]. These cells have potential to fulfill the idealistic demands for the production of clean electric energy such as low price energy for consumer, pollution free device fabrication and efficient recycling of devices [2-5]. So, this potential can be explored by the development and implementation of organic-photovoltaic technology [6]. In the organic solar cell technology the methods of film deposition plays important role to produce low cost devices [7-9]. Some of the examples of these methods are doctor blading, screen printing, spin-coating and vacuum deposition (at 400-600^{o}C). Moreover, the technology of ink-jet printing for thin film deposition is under development [9-12].

Initially, it was thought that OSCs with 5% efficiency will be suitable for practical applications. In 1983 Chamberlain [13] in his calculation showed that the Schottky barrier solar cells can have efficiency of up to 10 %. In 2001 the efficiency of 2.5% was reported for the organic photovoltaic cell [14], recently which was exceeded than 10% [15, 16]. It has been predicted that the power conversion efficiency of greater that 20% can be achieved in organic solar cells (single junction) [16, 17]. The fabrication and investigation of single-layer, heterojunction (or bi-layer) and bulk heterojunction organic solar cells was carried out by various researchers [18-22]. The solar cells which are based on organic-inorganic heterojunction structures are considered promising. Because of their very low price as compared to Si wafers having p-n junction the n or p-type single crystal or polycrystalline Si may be used in organic-inorganic heterojunction cells [23]. The Ag/n-GaAs/p-CuPc/Ag based organic-inorganic cells showed 4% efficiency [24]. The performance of the OSCs can be enhanced by a tandem approach because of absorption spectra overlapping [25, 26]. To continue our activities for the development of energy devices [4, 5, 27], we present the fabrication and characterization of tandem heterojunction photoelectric cell based on organic-inorganic hybrid of AlPc-H_2Pc and n-Si**.**

2. EXPERIMENTAL

All the materials used for the fabrication of photoelectric cell were purchased from Sigma Aldrich. The phosphorus doped silicon wafer has thickness of 0.5 mm. The molecular structures of H_2Pc (metal free phthalocyanine) and AlPc (aluminum phthalocyanine) are shown in Fig.1a and Fig.1b, respectively. For the deposition of heterojunction thin films by thermal evaporation the powders of H2Pc and AlPc were mixed together in 1:1 (wt) and pressed in the form of pellet. The Edwards vacuum thermal evaporator (AUTO 306) was used to deposit H_2Pc-AlPc films of 150 nm thickness onto the n-Si and ITO glass substrates. On each substrate the area of deposited film was 500 mm^2. On the back of n-Si substrate a silver electrode of thickness 100 nm was deposited also by thermal evaporation. All the depositions were done at a rate of 0.1 nm/s under high vacuum (>10^{-6} Torr) and FTM5 crystal monitor was used to measure the film thickness. By keeping the AlPc-H_2Pc films face to face the n-Si and ITO glass coated samples were pressed with each other. The pressing was done at 60-80 $^{\circ}$C by applying pressure of 4.7 x 10^{-2} kg/cm^2 to 5.7 x 10^{-2} kg/cm^2 for 20-30 min. The pressed samples were also fixed by applying adhesive. The schematic illustrations of the samples before and after pressing are shown in Fig.2. The fabricated ITO/AlPc:H_2Pc/n-Si/Ag device has active surface area of 300 mm^2.

The work functions of H2Pc, AlPc, n-Si, ITO and Ag are the 4.04 eV, 3.8 eV, 4.1 eV, 4.7 eV and 4.3 eV, respectively [28-31]. In this tandem cell (ITO/AlPc:H_2Pc/n-Si/Ag) it may be deemed that the bulk heterojunction is formed by the H2Pc-AlPc film. The second cell is formed by n-Si in which H2Pc-AlPc film forms the top electrode. Moreover, the n-Si also acts as bottom electrode of H2Pc-AlPc bulk heterojunction photoelectric cell. For experimentation the filament bulb was used as light source. The HIOKI DT 4253 digital multimeter was used for the current and voltage measurements, while the FLUKE 87 digital multimeter was used for temperature measurement.

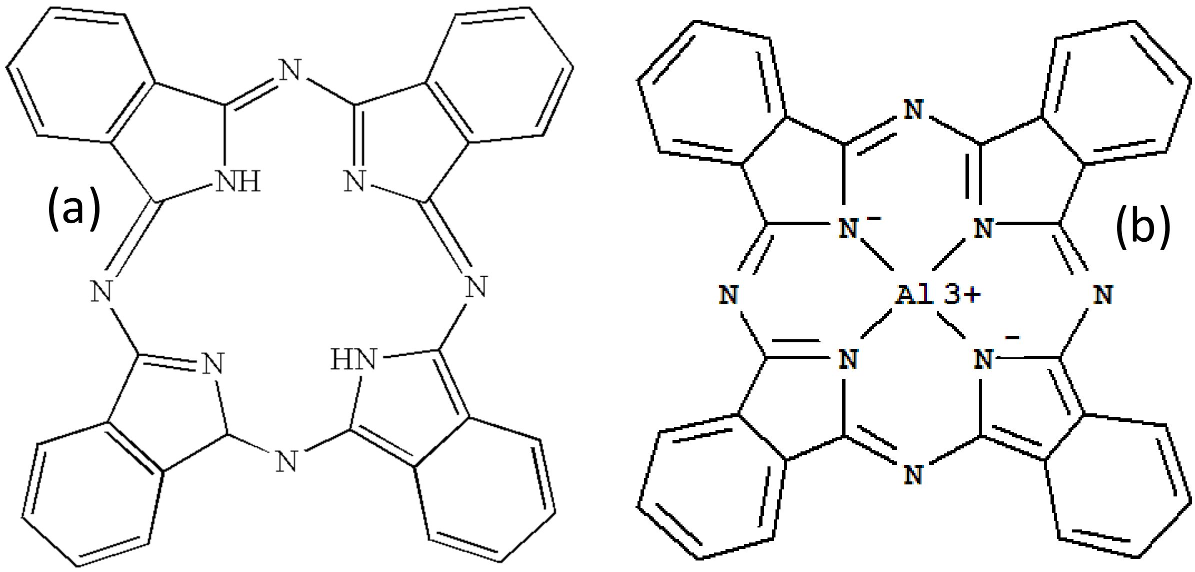

Figure 1. The molecular structures of metal-free phthalocyanine (a) aluminum phthalocyanine and (b).

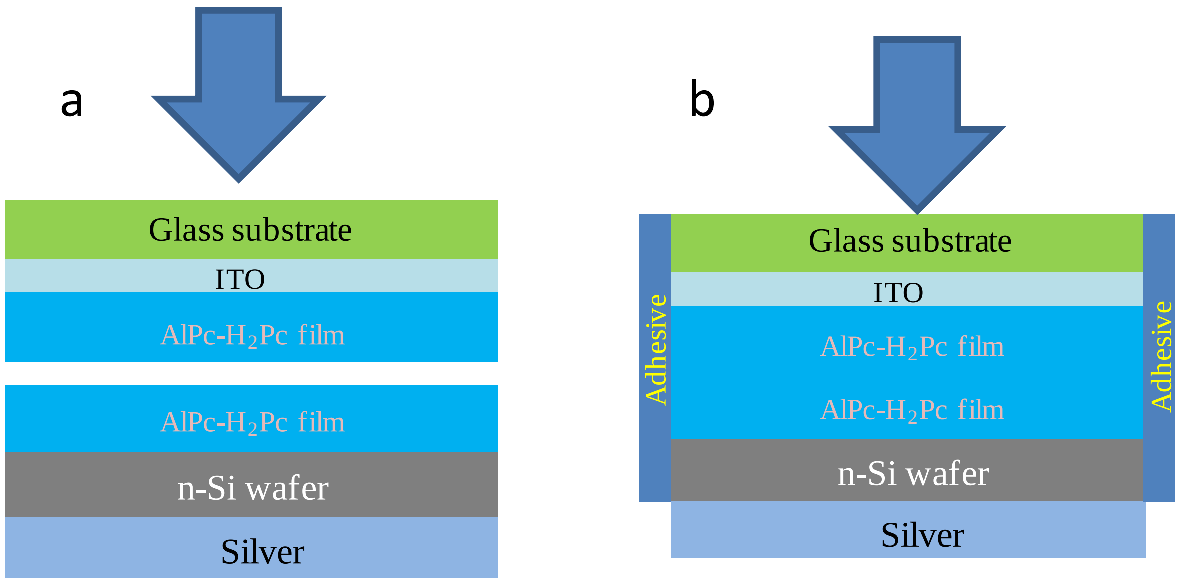

Figure 2. The schematic illustration of the tandem photoelectric cell (ITO/AlPc:H_2Pc/n-Si/Ag) before (a) and after (b) pressing

3. RESULTS AND DISCUSSION

The AlPc-H_2Pc blend's absorption spectrum is given in Figure 3a. It can be clearly observed from the Fig.3a that at 715 nm there is strong absorption, that may be credited to valance to conduction band transition. The AFM (atomic force microscopy) image of the AlPc-H_2Pc film is also shown in Fig.3b. As seen from Fig.3b that the film is pore-less and well developed which is vital for the better yield of incident light.

The room temperature I-V characteristics of the tandem heterojunction solar cell (ITO/AlPc:H_2Pc/n-Si/Ag) in dark condition are shown in Fig.4. On the application of forward bias potential to the ITO the rectification behavior was observed that can be seen in figure (Fig.4). The rectification ratio (*RR*) can be resolute as follows;

$$RR = {}^{I_F}/_{I_R} \qquad (1)$$

Here I_R and I_F represent the reverse bias and forward bias currents, respectively. The obtained value of rectification ratio is 2.0 on an applied voltage of 1.0 V. The I-V characteristics of the tandem heterojunction solar cell under illuminations of 296 W/m^2 and 256 W/m^2 are shown in Fig.5. The estimated efficiency of the solar cell is equal to 1.1%.

The stability is one of the imperative parameters of the photoelectric cells. Yoshida and others [32] reported on the base of their investigations that the phthalocyanine (organic semiconductor) based solar cell with conventional structure were less stable (up to 24 hour) as compared to inverted structure. The inverted structured (ITO/TiO2/organic layer/PEDOT:PSS/Au) photoelectric cells have good air stability in contrast to conventional cells (ITO/PEDOT:PSS/Organic layer/Al). The instability (degradation) of the normal structured cells is regarded to the Al oxidation at organic/Al interface, which intern reduces the metal layer's conductivity. Moreover, the cell's efficiency reduces because of the diffused Al in the organic semiconductor layer, which act as recombination sites [32]. Moreover, in the normal structured cells the acidity of PEDOT:PSS causes to crude the indium-tin-oxide (ITO) layer [6, 32]. Consequently, the inverted structured cell does not contain Al, while the PEDOT:PSS is not in a direct contact with ITO layer [32]. An inverted GaPc/PCBM photoelectric cell showed low (η= 0.059 %), stable efficiency. In the tandem cell (Fig.3), the AlPc:H2Pc (organic semiconductor) film is only in contact with n-Si wafer and ITO, which may bring a longer life for this photoelectric cell. The investigations about the stability of the cells will be carried out in future. Previously, investigation was done on the degradation of Ag/n-GaAs/p-CuPc/Ag (organic-inorganic) photoelectric cell, which was photoactive in UV-visible-IR region (200-1000 nm) [24]. In the year 2000, as a fresh cell its power conversion efficiency was 4%. In next five years an exponential degradation in the efficiency was observed i.e. from 4% to 0.6%. This stability in the efficiency of the cell was lasted for next ten years (till 2015) and was tested and used as a teaching aid as photoelectric sensor. The comparison of the efficiencies of tandem cells fabricated by various techniques and materials is shown in Table-1. It is evident from the data presented in Table-1 that the efficiency of fabricated ITO/AlPc:H2Pc/n-Si/Ag tandem solar cell is comparable with the efficiencies of already reported tandem cells.

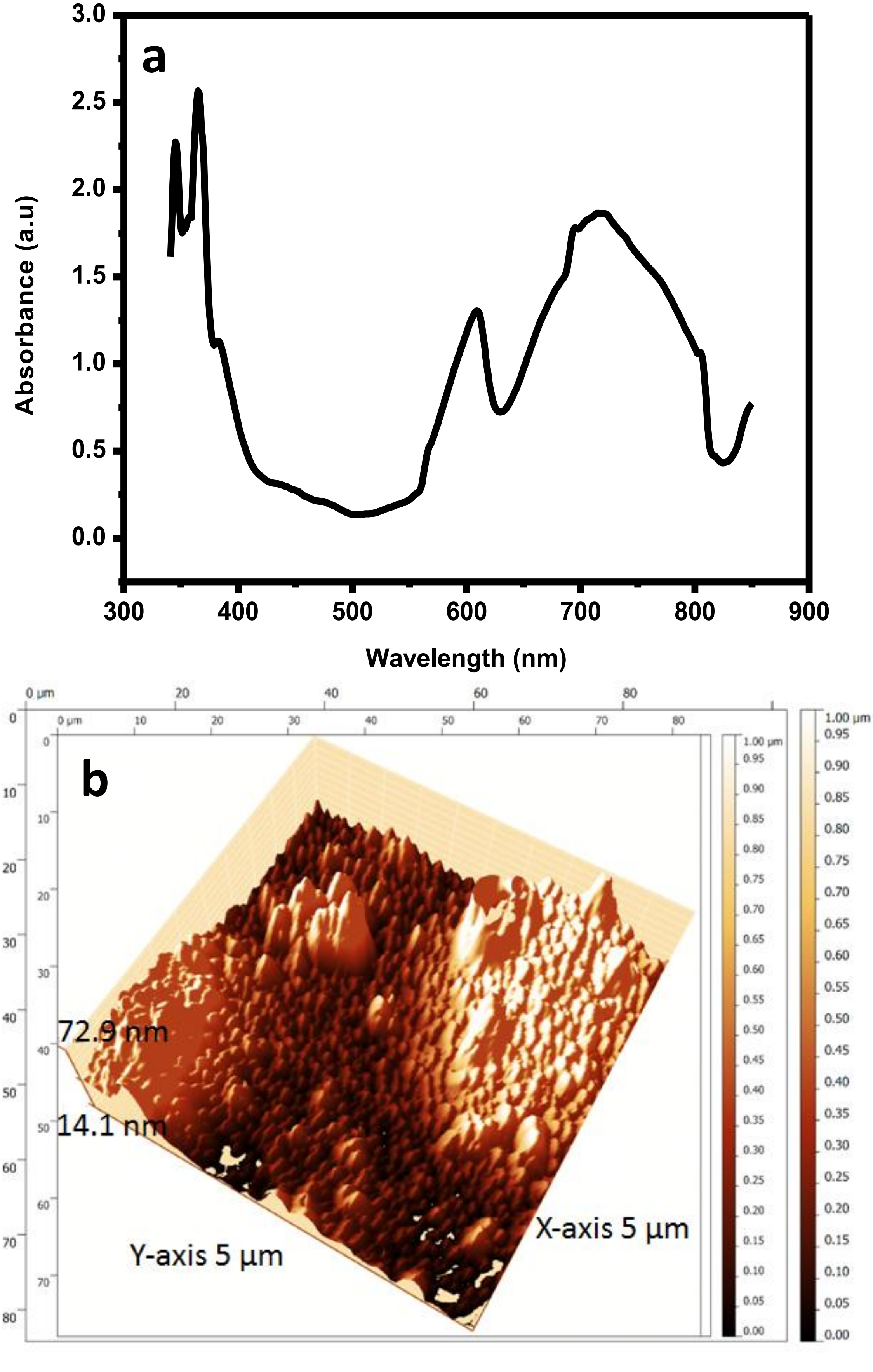

Figure 3. The absorption spectrum (a) and the AFM image (b) of the $AlPc\text{-}H_2Pc$ heterojunction film.

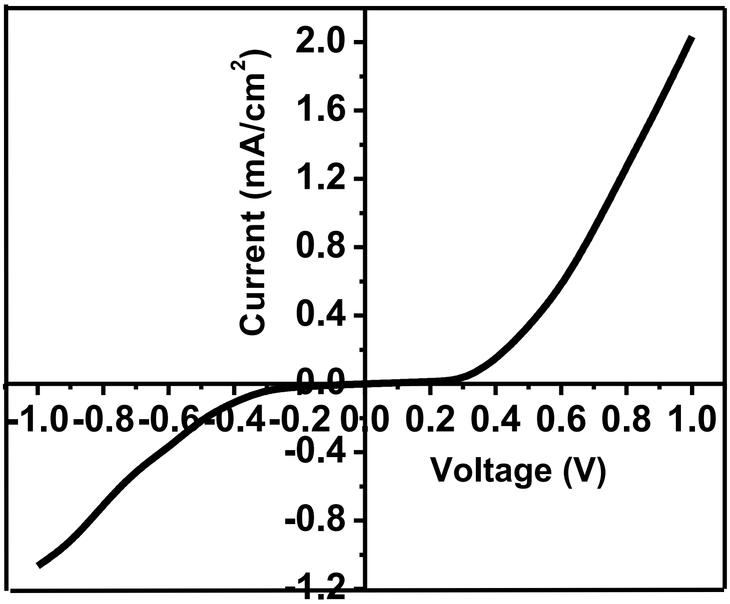

Figure 4. I-V characteristics of the tandem solar cell (ITO/AlPc:H_2Pc/n-Si/Ag) in dark condition.

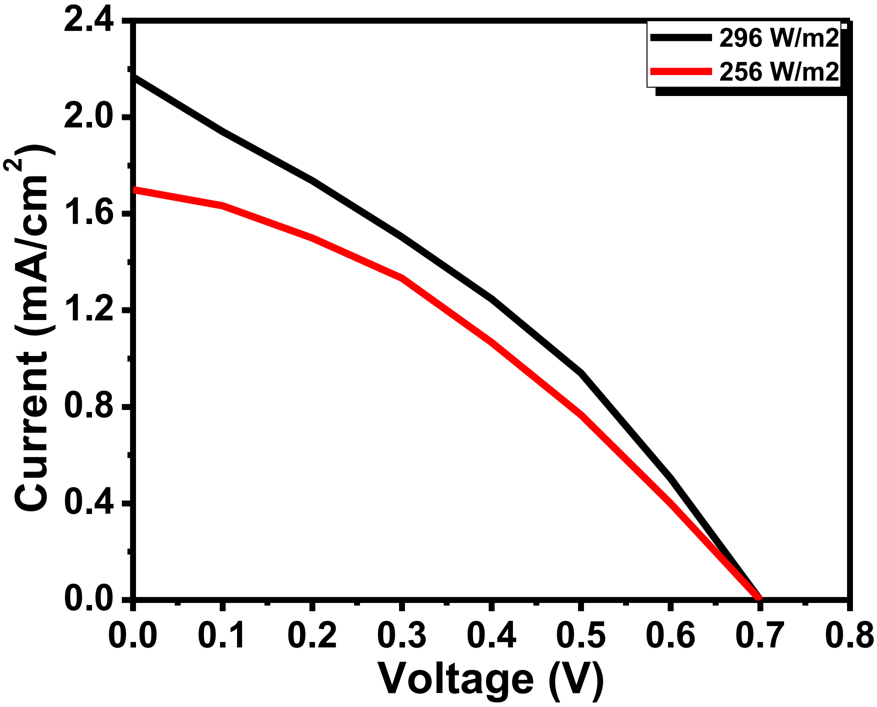

Figure 5. I-V characteristics of the tandem solar cell (ITO/AlPc:H2Pc/n-Si/Ag) under illuminations of 296 W/m^2 and 256 W/m^2.

The data presented in this paper shows that the pressing technology is used to fabricate the photoelectric cell (ITO/AlPc:H2Pc/n-Si/Ag) by pressing the films of same composition, which makes the process more consistent and the cell's properties more predictable. Moreover, contrary to stacked or tandem cells [33, 34] there is no connecting conductive layer between two cells, as applied in heterojunction structure [29]. So, combined structural features of heterojunction and tandem photoelectric cells are found in the ITO/AlPc:H_2Pc/n-Si/Ag cell. As for as stability is concerned, no significant changes were observed in the properties of the cell after 30 days of fabrication. This stability may be credited to the efficient encapsulation and isolation of the cell from environmental oxygen by the adhesive (Fig.2b). The effect of annealing time and temperature and environmental conditions on the performance of organic solar cells is well known [35]. The effect of annealing on the performance of the ITO/AlPc:H_2Pc/n-Si/Ag cell will be optimized as a future work.

Table 1. Comparison of the efficiencies of tandem cells fabricated by various techniques and materials

Sr.#	Active material	Fabrication technique	Efficiency (%)	Reference
1	PFDTBT:PCBM	Solution processed	0.6	[36]
2	P3HT:PCBM	Solution processed	1.2	[37]
3	CuPc/PTCB	Evaporated	1.0	[38]
4	AlPc:H2PC/n-Si	Pressing	1.1	Current study

The similar I-V characteristics of the tandem heterojunction solar cell (ITO/AlPc:H_2Pc/n-Si/Ag) shown in Fig.4 were observed in a number of investigations related to orange dye or CuPc Schottky or two layer organic semiconductor devices [39]. The rectification ratio (RR) and applied voltage relationship is shown in Fig.6: it can be seen that *RR* is equal to 2 and is independent of voltage. To analyze the dark I-V characteristics of the organic semiconductors devices in a narrow potential range (0 to 0.5 V) the Shockley equation in its modified form can be used [40-42]:

$$I = I_o \,[\, \exp\{q(V-IR_s)/nkT\} - 1 \,] + (V - IR_s) / R_{sh} \qquad (2)$$

where V and I are the terminal voltage and current, R_{sh} and R_s are the device shunt and series resistances, and n is the diode ideality or quality factor, T is absolute temperature, k is Boltzmann constant, while I_o is a reverse saturation current as expressed in ref. [40] :

$$I_o = A^* T^2 \exp(- q\Phi / kT) \qquad (3)$$

where $q\Phi$ is a height of contact barrier (Shottky barrier [29]) and A^* is the Richardson constant.

R_{sh} and R_s in Eq.2 were found by use of I-V characteristics (Fig.4) as highest resistance at reverse bias and lowest resistance at forward bias accordingly: R_{sh} =312 Ω and R_s =164 Ω.

To find the I_o (reverse saturation current) the experimental I-V data (shown in Fig.4) can be used. This method was expressed in [29] and implemented in [40, 41]. The I_o is calculated from the ln(I)-V curve's intersection with vertical axis (Fig.7) at V=0 and its value is equal to 0.04 mA (or density of current is equal to 0.008 mA/cm^2).

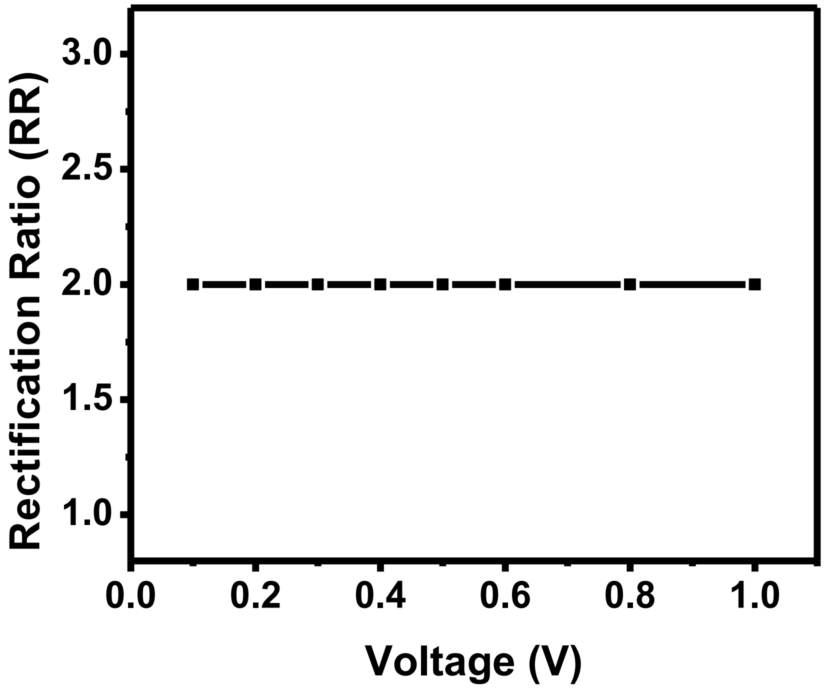

Figure 6. Relationship between rectification ratio (*RR*) and the applied voltage of the tandem solar cell (ITO/AlPc:H2Pc/n-Si/Ag)

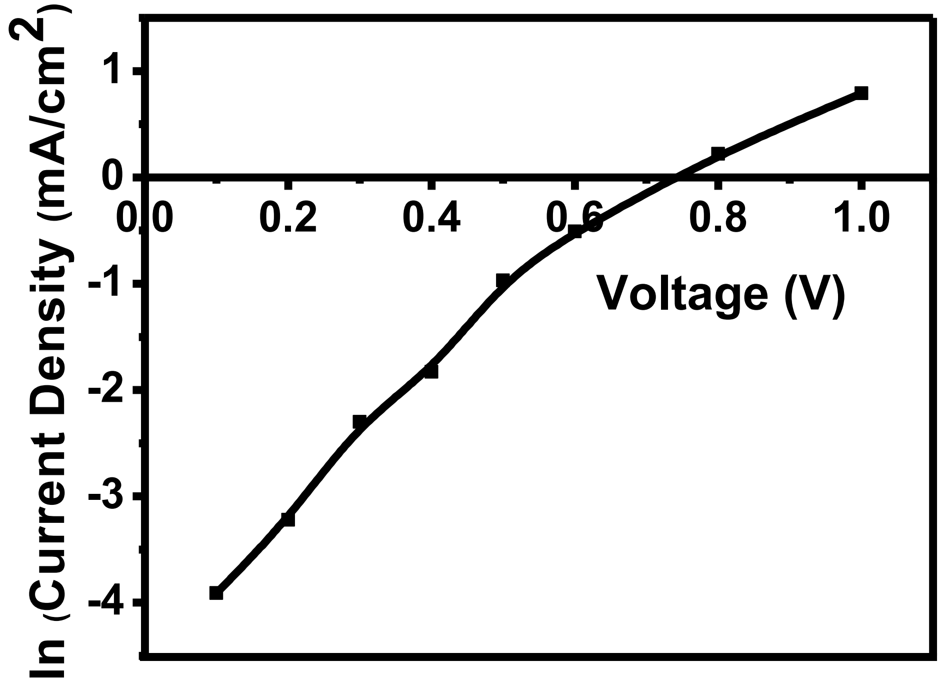

Figure 7. ln(I)-V relationship of the tandem solar cell (ITO/AlPc:H2Pc/n-Si/Ag)

Using Eq.2 the dependence of quality factor (*n*) on the applied voltage (V) can be found for the curve shown in Fig.4. The Fig.8 shows n-V relationship of the ITO/AlPc:H_2Pc/n-Si/Ag tandem heterojunction solar cell. It is evident from Fig.8 that first of all quality factor is voltage dependent and secondly as voltage increases the quality factor decreases from value of 11 to 1.6.

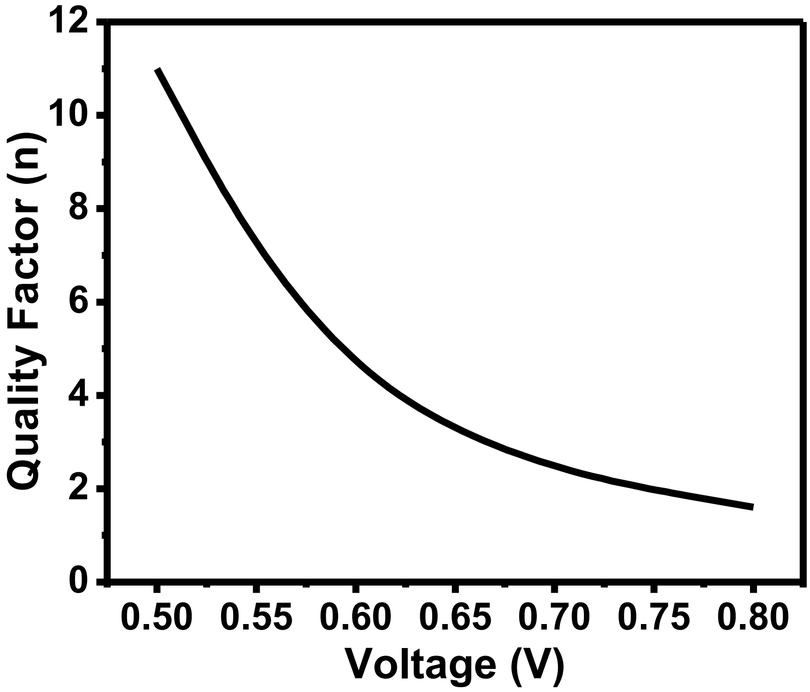

Figure 8. The n-V relationship of the ITO/AlPc:H_2Pc/n-Si/Ag tandem heterojunction solar cell

The I-V characteristics obtained under illumination of the solar cell shown in Fig. 5 can be simulated as it was done in [43] by use of the same Shockley equation where only light induced current should be added.

4. CONCLUSION

The pressing technology along with thermal evaporation technique was used to fabricate an organic-inorganic (ITO/AlPc:H_2Pc/n-Si/Ag) hybrid tandem heterojunction photoelectric cell. The fabricated cell was analyzed for I-V characteristics in dark and under illumination conditions. A number of parameters of the cell were obtained by simulation of I-V characteristics. By using this (pressing) technique may be used to develop photoelectric cells technology, especially, the more stable hybrid tandem cells. Furthermore, the simplicity of fabrication makes the cells more suitable device for teaching aid.

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