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***Journal of Scientific and Engineering Research*, 2020, 7(9):87-92**

Research Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Synthesis and Characterization of (PANi/n-PSi) Heterojunction Organicsolar Cells

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Abstract In this study, heterojunction organic solar cells were synthesis based on conductive polymer polyaniline (PANi-ES) doped by ionic acid. Polyaniline (PANi) was synthesis by chemical oxidative polymerization method using ammonium persulphate APS as oxidizing agent. Junctions have been fabricated by spin coating of polyaniline onto porous n-type silicon substrates. The final heterojunctions device structure was Al/n-PSi/PANi-ES/Au. The electrical properties of the resultant device were investigated by measuring the current–voltage (I-V), characteristics in the dark and under illumination. The I-V characteristics of PANi/n-PSi junction was measured at room temperature (303K) and after annealing at 373K. Dimethylformamide (DMF), was used as solvent for polymer doped (PANi-ES). The effects of these solvent on the photovoltaic cell parameters were investigated, and the open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), fill factor (FF), and energy conversion efficiency (η) were determined. It was found that heterojunctions fabricated using polyaniline PANi-ES dissolved in DMF, produced, Isc of 0.45 mA/cm^2, 0.62 mA/cm^2, respectively.The I-V curves under illumination were explained based on the back-contact barrier and surface recombination of electrons at the back contact. The linearity of Schottky plots indicated the formation of a heterojunctions between the conductive polymer and n-type Si wafer. The high values of shunt resistances R_{sh} were decreased under illumination, indicating that the efficiency of this type of heterojunctions solar cell was limited by shunt resistance and the narrow absorption range of solar spectrum by polymer polyaniline PANi.

Keywords Polyaniline-ES, Porous Silicon PSi, Solar Cells

1. Introduction

The semiconductor materials have been widely investigated because of their applications in optoelectronic devices such as organic solar cells, light-emitting diodes [1,2]. Electrical conductivities of conjugated polymers, such as polyaniline, and polyacetylene, can be different over the full range from insulator to semiconductor to conductor, through doping type (p-type or n-type). Actually, much research work has been carried out to be useful of conducting polymers used as active layer materials in electronic applications. Many of the practical properties of (p–n) junctions can be achieved by forming an appropriate semiconductor-polymer–metal contact [3–5]. Polyaniline PANi, one of the important types of conjugated polymers, has received much attention because of its interesting electrochemical characteristics and environmental stability. Unlike all other conducting polymers, the conductivity of Polyaniline depends on the degree of oxidation and crystallinity of polymer. It is known that a large increase in electrical conductivity can be obtained by using PANi-ES with solution of ionic acid [5,6]. Early publication describes how doped PANi-ES/n-Si as binary heterojunctions could be prepared [7–9]. Recently Wang et al, fabricated heterojunction solar cells using PANi doped by acid on crystalline n-type Si and deduced that the V_{oc} for cells fabricated with high electric conductivity PANi saturated at 0.5 V, while the saturated current density was 15 mA/cm^2 [10,11]. In this project, we used doped polyaniline PANi-ES as salty to prepare a heterojunction organic solar cell with porous n-Si. Polyaniline doped has a wide band gap, of which making it as a buffer layer in films of solar cells. In addition, the polymer can be used as a hole transporting active material in solar cells. J–V, and impedance characteristics were measured to evaluate and compare the electronic parameters of these heterojunction organic solar cells.

2. Experimental Procedures

Materials

Aniline (C_6H_5NH) from (Merck, schuchardt, Germany), was purified by vacuum distillation to reduced pressure before it is used. Ammonium peroxydsulfate (APS) was purchased from (Merck, Germany). Tetrahydrofuran (THF), isopropanol and HCl hydrochloride acidwere purchased from Sigma Aldrich. Methanol and (DMF) dimethylformamide, solvents were supplied from (Merck, Germany). Silicon wafers n-type <100> oriented (2 inches and the thickness 250-300µm).

Preparation of Doped Polyaniline PANi-ES/HCl

Polyaniline PANi was synthesized by chemical oxidative polymerization method use aniline in the presence of ionic acid (HCl), and ammonium peroxydsulfate (APX) as an oxidant agent. For the synthesis polymer, we took 50ml, 1M HCl, and 2ml of aniline were added into a 250ml beaker equipped with a Teflon coated magnetic stirrer at about -5C^o temperature. Then 6gm of ammonium peroxydsulfate ($(NH_4)_2S_2O_8$) aqueous solution in 50ml 1M HCl was drop wise added into the above solution. The polymerization temperature keep about 0C^o was maintained for 14 h to complete the reaction. Then the precipitate obtained was filtered. Then was washed successively by 1M HCl followed by double distilled water until the wash solution turned colorless. The product PANi was dried at 80C^o for overnight to get powder form polyaniline emeraldine salt (ES). The PANi produced was partially soluble in DMF, (0.05wt.%).

Fabrication of Heterojunction Structure [Al/PANi-ES/n-PSi/Au]

Silicon wafers, <100>-oriented n-type, (5-10 resistively, 250-300 µm thickness) The wafers of n-type silicon were cleaned by ultrasonic in isopropanol and then dried at 100 C^o. The wafers were etched in HF/Ethanol (10:40 Wt%) to remove the residual oxide and then immersed in deionized water and dried. Aluminum metal contact was deposited onto the back side using by vacuum evaporation machine (Edwards E306A). Thin layers of polyaniline (PANi-ES) were deposited on the n-type silicon wafer by spin-coating. The spin coating process was carried out at 3000 rpm using a (Model Chemat, KW-4A). The thickness of this layer was determined using filed effect scanning electron microscopy (FESEM) by cross-section method to be 48nm on average, as shown in Fig. 1b. FESEM image was recorded using a (Model: FEI Nova Nano SEM 450) operating at 20 kV. The wafers were dried at 60 C^o for 20 min. At front grid contact was fabricated by evaporation of target gold metal contact through a mask shadow using the vacuum-coating machine (RF magnetron sputtering A500 Edwards). A schematic of the Al/n-Si/PANi-ES/Au heterojunctions are shown in Figure 1(a).

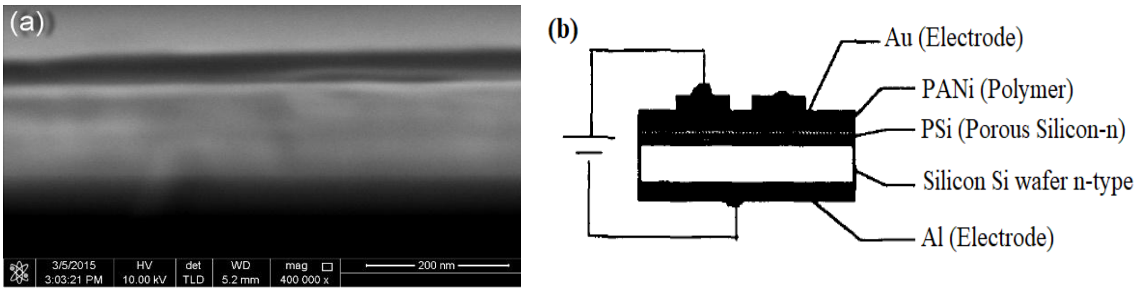

Figure 1: (a) FESEM image micrograph side view, showing the PANi-ES layer. (b) The Schematic Structure of heterojunction device of n-PSi with PANi-ES.

3. Characterization and Measurements

Thin films of conductive polymer PANi-ES prepared using a spin coating technique (CHEMAT Technology Spin Coater Model KW-4A) onto glass substrates. Morphological study of the films of PANi was carried out using by field effect scanning electron microscopy FESEM (Model: FEI Nova NanoSEM 450) operating at 20 kV. The PANi films were then placed on a hotplate with temperature of 373K for a 1hour for annealing. Aluminum (Al) contact in thickness about 90 nm was used vacuum evaporation system (Edwards Auto 306) onto the back side of the substrate Si. This was carried out under vacuum of 10^{-6} mbar with evaporation rate of 5 nm.sec^{-1}. Similar procedure was followed for the deposition of gold (Au) as contacts used (RF magnetron sputtering A500 Edwards) onto the polymer films, with thickness about 30 nm evaporated through a suitable mask shadow which provides device area of about $3x10^{-6}$ m^2. For electrical characteristics measurements of binary junction, a Keithley electrometer (Model 2400) was used to measure current density (J) as a function of applied voltage in range -0.1 V to 0.1 V. The photovoltaic properties of the heterojunction solar cells were measured under illumination using a solar simulator light source (white LED), the power output 100mW.cm^{-2}. All the measurements were fed to computer interfaced with equipment using LabVIEW software-based application (Forter Transient Measurement System).

4. Results and Discussion

I-V characteristics of PANi-ES/n-PSi junction at room temperature 303K and after annealing at 373 K are shown in Fig. 1(a, b). In this work we have check films in order to experimental reproduce. All samples of PANi/n-PSi show rectifying effect demeanor. According to the Shockley equation [12-14], the applied voltage (V) with taking into account the series and shunt resistances for the cell is given by:

$J = Jo \exp [q (V- JR_s) nKT- 1] + (V- JR_s)/R_{sh}$ (1) [13]

Whereas: $Jo= A^*T^2 e^{-Ø_B/KT}$ (2) [14]

where V is applied voltage, q is the charge, J_o is the saturation current, A* is called Richardson constant, and $Ø_B$ is the barriers height. R_s, R_{sh}, and ideal factor (n), as presented in Table 1. Jo and n were calculated from slope and y-intercept of the linear regression chart of Ln (I) against applied voltage V. Electronic characteristics parameters of structure Al/n-PSi/PANi-ES/Au heterojunctions organic solar cell under illumination (100 mW/cm^2) series resistance (R_s), shunt resistance (R_{sh}), and ideal factor (n).

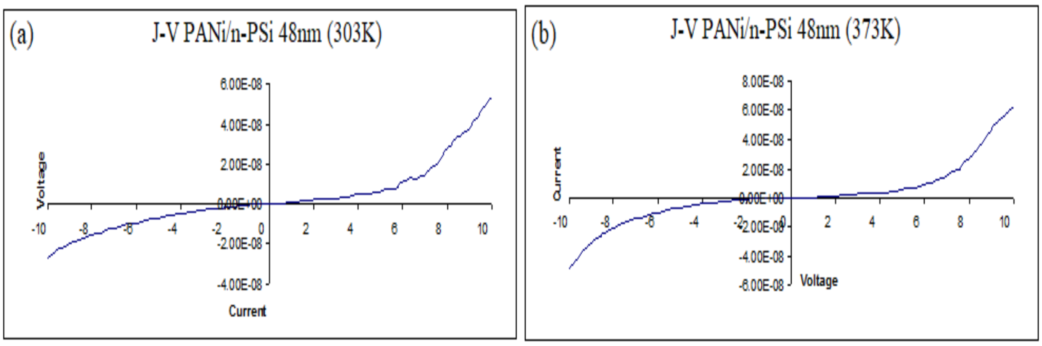

Figure 1: I-V Characteristics of PANi/n-Si at (a) room temperate (303K) (b) annealing at (373K)

Fig. (2) shows the relationship between Ln (I) and applied voltage (V) at room temperature (303K) and at annealing (373K). The extrapolation of the linear portion of the two curves give saturation current Io of about $4x10^{-6}$A and $4x10^{-4}$A respectively. Ideal factor (n) calculated from the slop of linear parts is 1.75 and 1.3 respectively. The barrier heights $Ø_B$ as estimated from equation. 2 are of 0.75eV and 0.62eV respectively. Table 1 shows the binary junction parameters of PANi-ES/n-PSi. All these results obviously indicate that annealing at 373K have the improving junction parameters.

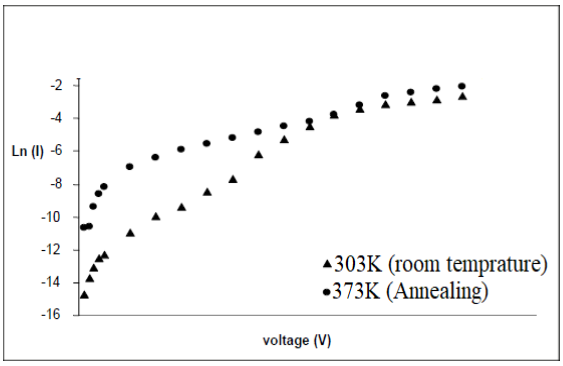

Figure 2: A relationship of Ln (I) with applied voltage for PANi/n-PSi at room temperature 303K and annealing at 373K.

Table 1: Values of (n-PSi/ PANi-ES) junction parameter

T (K)	**Barrier heights $Ø_B$ (eV)**	**Saturation current Io (A)**	**Ideal parameter (n)**	**Series resistance R_s (kΩ)**	**Shunt resistance R_{sh} (kΩ)**
303	0.75	$4x10^{-6}$	1.75	10	12
373	0.62	$4x10^{-4}$	1.3	35	16

J–V curves of these heterojunction organic solar cells in the dark can be describe by the initial value of R_{sh} was approximately calculated using a slope of the linear regression chart of the user specified shunt area and then refined by iteration to adjustment the model. Ideal factors (n) about near to 2 are attributed to recombination in the quasineutral area as a result of trap assisted tunnel and the field assisted recombination. High value of ideal factors can also be ascribed to nonlinear contact resistance. As well as, when the potential different across the cell exceeds the thermal voltage (KT/q), the Rs increase at high voltages may cause an increase in the ideal factor. The photogenerated electrons and holes are crucial for device efficiency. Therefore, the influence of light intensity on the J–V characteristic is important [15,16].

Heterojunction organic solar cells as a function of incident light intensity P_{in} as in Figures 3 show the linear Jsc against light intensity relationship indicates that charge carrier losses are controlled by recombination of impurities. This implies that some of part the charge carriers are trapped on the defect, subsequently recombining with charges of the opposite sign [16,17]. We suggested that PANi can act as a p-type or a buffer layer for n-type Si to complete the heterojunction organic solar cell. The rectifying of junction is expected to exist at the interface between the n-PSi substrate and the PANi-ES layer. This can be further justified by the fact that in this study used the PANi-ES is considered as hole transporting layer [18]. Current density–voltage characteristics for Al/n-PSi/PANi-ES/Au heterojunction solar cells as show in the Figures 3 (a, b) using PANi doped solved in DMF, both in the dark and under Illumination intensity. The characteristics of photovoltaic cell, i.e., open-circuit voltage (V_{oc}), short-circuit current density (Jsc), fill factor (FF), and energy conversion efficiency (η), were evaluated under illumination (100 mW/cm^2), and the results are presented in Table 2. The solar conversion power efficiency (η) is given by the equation:

$$\eta = (V_{oc}\, JscFF/\, P_{in}) \qquad (3)\ [14]$$

where Pin is the power incident light. The open-circuit voltage is Voc =0.215V, short circuit current density Jsc =6.2 mA.cm^{-2}, and fill factor FF=0.29. A good value of power conversion efficiency is 0.2% has been obtained after annealing temperature 373K, which is little value as compared with PANi/GaAs solar cell which was found to give efficiencies in the region of 4% [19]. The value of open circuit voltage calculated in this work compares well with the value 0.4V obtained for electronic devices PANi/n-PSi [20]. The small value of fill factor FF is associated with a high series resistance and a high shunt resistance. The high values for RS may originate from electrode contact resistance and high Rsh is related to morphology of thin films; a poor absorbance morphology limitative the hopping transport of electrons [21,22].

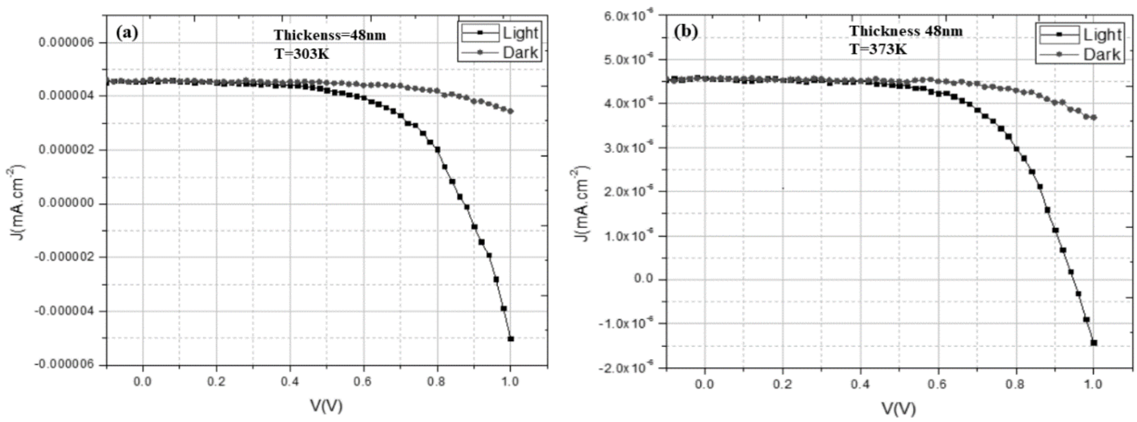

Figure 3: J-V function for [Al/n-PSi/PANi-ES/Au] heterojunction solar cell. under illumination intensity is (100 mW/cm^2), at(a) room temperate (303K) (b) annealing at (373K)

Table 2: Characteristics electronic parameters of heterojunctions [Al/n-PSi/PANi-ES/Au] under illumination (100 mW/cm^2), at room temperature (303k) and annealing (373k)

T (K)	V_{oc} (mV)	J_{sc} (mA.cm^{-2})	V_{max} (mV)	J_{max} (mA.cm^{-2})	FF	η (%)
(303K)	194	2.7	108	1.56	0.28	0.12
(373K)	215	6.2	116	2.7	0.29	0.2

5. Conclusion

Thin films of Polyaniline doped with ionic acid as hydrochloride acid were prepared by chemical oxidative polymerization method, then PANi-ES solvent in strong solvent as DMF onto porous n-type Si substrates by spin-coating technique. Heterojunctions prepared using PANi-ES doped have the highest values of J_{sc}, V_{oc}, and η. The result of J-V characteristic exhibited n-PSi/PANi-ES junction show rectifying behavior, the value of electronic parameter improvement by annealing at 373K, is increases up two orders to 4x10^{-4} A, became 1.3 and $Ø_B$ about 0.62 eV. The Solar cell power conversion efficiency under simulated solar light with intensity of 100mW/cm^2 found as good value about 0.2% is obtained for films with PANi thickness of 48 nm. The low efficiency obtained in this work was caused by the morphology of the polymer film with an inhomogeneities a combination of the interfacial insulator layer composition, and distribution of interfacial charges that occur at the n-PSi/PANi-ES interface.

Acknowledgment

We gratefully acknowledge the support of the Department of Physics and Materials Science, Polymer Research Center, University of Basrah, Iraq. I thank who gave access to the research facilities. Without their precious support it, would not be possible to complete this work. Also, many thanks to the technicians in the Physical properties laboratory at Polymer Research Center.

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