Illumination and Dark Current-Voltage Characteristics of Polymer-Silicon Heterojunction Solar Cells

In this work, polymer-on-silicon solar cells were fabricated by coating different silicon substrates with conductive polyaniline layers. Different substrates with different resistivities were used to control the diffusion length of such configurations. Electrical measurements were performed in both illumination and dark conditions to study the characteristics of photo-generated carriers in the polymer layer contributing to the output of such solar cells. They show good agreement with the “hole mobility only” model for intensities ranging from 1% of AM1.5 up to AM1.5. In addition to low-cost fabrication and less-complex technology, such design interestingly compete the conventional and advanced configurations of solar cells.

Keywords: Solar cells, Silicon devices, Conductive polymers, Amorphous silicon

1. Introduction

After 20 years of work on the characterization of amorphous silicon and amorphous silicon solar cells, there has been no definitive, quantitative model for how the cells work, even under restricted conditions such as the as-deposited state [1]. The beginning of amorphous-silicon photovoltaics (PV) goes back to 1965, when Sterling et al. [2] reported deposition of silicon onto a substrate using a silane glow discharge. Hydrogenated amorphous silicon nitride layers have been intensively investigated during the last decade. The big interest in these layers is caused by their exceptional physical properties [3]. The improved set of measurements involves the use of a thickness series of cells and of a near-infrared laser to obtain uniformly absorbed illumination [4]. The solar conversion efficiency of as-deposited pin a-Si:H solar cells can be explained surprisingly well from hole mobility and optical absorption measurements on the intrinsic layer material [5].

Both solar cell materials (c-Si wafers, polycrystalline and amorphous thin films) as well as solar cells itself are investigated by photoconductivity methods in view of their recombination parameters characterisation. The efficiency of a solar cell is influenced by recombination parameters, e.g., the bulk minority carriers lifetime, the emitter saturation current and the effective surface recombination velocity [6].

Since its first successful application to amorphous semiconductors in the early 1980’s [7], exponential-bandtail multiple-trapping (usually abbreviated as simply “multiple-trapping” or “MT”) has become the standard approach to analyzing most transport experiments in hydrogenated amorphous silicon (a-Si:H) and related materials such as amorphous silicon-germanium alloys. The model assumes an exponential bandtail of localized states lying at the bottom of the conduction band, or at the top of the valence band. The application to transport also assumes the existence of a “transport edge,” with the property that the only carriers that contribute to electrical transport are those occupying electronic states lying above this edge (for electrons) or below it (for holes); it has generally been assumed that this edge is the “mobility-edge” dividing localized and extended electronic states [8]. Perhaps 20 or more parameters are required if all possibly relevant electronic transport and recombination processes are treated, and veteran scientists might well despair of gaining insight from the daunting exercise of matching so many parameters to such simple measurements [9,10].

It is highly required to obtain a set of cell measurements using intense, near-infrared, monochromatic laser illumination that is uniformly absorbed in the cell [11]. Under white-light illumination, a good deal of the power generated by a single-junction cell is due to strongly absorbed illumination; models for such cells are quite sensitive to the absorption spectrum of the intrinsic and p-layers, but are less sensitive to transport and recombination properties of the intrinsic layer than are
measurements with uniformly absorbed illumination [12].

For thicker cells, the internal electric field no longer extends across the cell, and some holes photogenerated in the “back” of the cell (i.e., closer to the n/i interface) are lost to recombination. This “collapse” of the field [13] is just a consequence of the buildup of slowly-moving, positively charged holes near the p/i interface. We gain some confidence in this view because we find that reducing the incident flux by a couple of orders of magnitude noticeably improves the fill-factor. The qualitative explanation for this effect is that, for lower incident flux, there are fewer drifting holes, and less positive space-charge to collapse the voltage. The simulations agree fairly well with the measurements for fluxes in the range $10^{15}$-$10^{17}$ photon/cm² [14].

The open-circuit voltage ($V_{oc}$) is nearly independent of thickness and this essential result also emerges from the bandtail-only simulations, although there are some subtle differences in the behaviors. The hole drift mobilities and valence bandtails are the main elements determining the solar conversion efficiency of a-Si:H based solar cells in their a-deposited state. It is also plain that the conversion efficiency in the light-soaked state is markedly reduced from the as-deposited state [15].

There have been several reports of drift-mobility measurements in microcrystalline silicon in the last decade or so since it became clear that this material could be prepared with properties that are interesting for solar cells [4-8,16]. There is, of course, an enormous range of possible structures in microcrystalline silicon materials. For each sample there is a spectrum of sizes for the component nano- and micro-crystallites. Even more poorly understood, for each sample there is also a jumble of non-crystalline material that lies between the crystallites [17].

It is worth noting that disorder affects holes and electrons very differently. The conduction bandtail in amorphous silicon has a width around 22meV [18]. Electron properties in samples similar to those used in this work have been studied using post-transit time-of-flight [19]; bandtail multiple-trapping did not apply for these transients.

2. Experiment

Simple solar cells were fabricated by coating a layer of conductive polyaniline onto a silicon substrate. Two kinds of silicon substrates were used in this experiment: (i) n-type, orientation (100), R=2Ω.cm and (ii) n-type, orientation (111), R=3000Ω.cm. Large area, 50nm thick aluminum contact was evaporated onto the back (unpolished) side of the wafer. Immediately before the polymer film was applied, the silicon wafers were etched in a 2.5% HF solution. The solvent is dichloroacetic acid (DCA); the dopant is 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA). The polyaniline solution was made following the procedure of Adams et al. [20]. The area of spin-cast doped polyaniline film was around 0.5cm². The films were annealed in air at 80°C for 6 hours after casting. A circular nickel contact (50nm thick) was then evaporated onto the polyaniline film. The polyaniline films were typically 5µm thick and the resistivity of the doped films was about 0.1Ω.cm.

The current-voltage characteristics were measured at room temperature with a Keithley 616 meter. The intensity-dependent measurements were done using illumination from a 632.8nm laser. The transient photocurrents were measured in the pin diodes following illumination by 532nm laser pulses (SHG Nd:YAG) through the n-layer. The photocurrent was independent of the applied voltage, and a transit-time was discernible in the transient. Additionally, the photocurrent at short times was linear in the applied voltage, which is consistent with transport that is linear with electric field.

Measurements were recorded over a wide range of illumination intensities. The more definitive set of measurements shows good agreement with the “hole mobility only” model for intensities ranging from 1% of AM1.5 up to AM1.5.

3. Results and Discussion

Figure (1) shows two current-voltage (I-V) curves for two different diodes from the same batch, using the 2Ω.cm substrate. The current-voltage (I-V) characteristics are highly asymmetrical as expected for a p-n heterostructure device; the reproducibility is fairly good. Figure (2) illustrates the I-V curves observed in one diode at several times up to about 2 weeks after its fabrication; the diode was stored in a desiccators when not under study. Interestingly, the diode’s forward bias current first increases, and then recovers to nearly the initial state. As the origin of these effects; both room-temperature curing of the polymer and also room-temperature changes at the polymer-Si interface may be envisioned. Aging effects have been noted for polyaniline/c-Si diodes in previous work [21,22].

Figure (3) illustrates the effect of changing the c-Si substrate doping level. It was presumed that the higher resistance of the 3000Ω.cm substrate affected the diode principally via the
series resistance of the substrate; obviously, this effect is modest.

\[ I = I_s \exp \left( \frac{q}{nKT} \left( V - IR_s \right) \right) \]  \hspace{1cm} (1)

where \( q \) is the electronic charge, \( n \) is the ideality factor, and \( R_s \) is the series resistance, then a straight line by a graph of \( I(dV/dI) \) vs. \( I \) is obtained from:

\[ \frac{dV}{dI} = \frac{nKT}{q} + IR_s \]  \hspace{1cm} (2)

The fit to this form for the 2\( \Omega \).cm substrate for lower currents (<10mA) yielded \( n=1.8, R=49\Omega \); the fit for the 3000\( \Omega \).cm yielded \( n=1.8, R=77\Omega \).

Two diodes were prepared with varying polyaniline thickness on the 2\( \Omega \).cm substrate and the results are illustrated in Fig. (4). The illuminator was a 250W ENH tungsten-halogen bulb and the diode was illuminated through the polyaniline. The dark currents are fairly similar; there is slightly less dark current for the thicker diode. Under illumination, both diodes show a saturated reverse-bias current. It is surprising that the diode with the thicker polyaniline film has a larger saturation current.

Although a serious analysis of these diode properties was not conducted, it should be presumed that photo-carriers generated throughout most of the polyaniline should not contribute to the saturation current, and indeed the thicker film might have optically filtered some of the photons. It may be that the polyaniline film has different properties for the two thicknesses, at least near the c-Si interface.

Two diodes were made from two different silicon substrates. The polyaniline thickness of both diodes was 5\( \mu \)m. The current-voltage (I-V) characteristics of the two diodes under illumination are shown is Fig. (5) and they are quite different. Under forward bias, the principal effect appears to be that the high resistivity substrate led to a significant series resistance.
Interestingly, under reverse bias the high resistivity substrate shows a substantially larger reverse bias current. This presumably corresponds to an increased diffusion length in the higher resistivity substrate.

Fig. (5) Light I-V characteristics of two polyaniline/c-Si heterostructure diodes made on c-Si substrates with 2 different (n-type) resistivities (#1, 2Ω.cm and #2, 3kΩ.cm). The doped polyaniline layers were about 5µm thick

4. Conclusion
Current-voltage characteristics of polymer-silicon p-n heterojunction solar cells showed that such low cost and simple design devices show good agreement with the “hole mobility only” model for low intensities up to AM1.5 condition. The ideality factor of the prepared samples was ranging over accepted values at low illumination condition. Results explained that the substrate resistivity highly affects the electrical characteristics of such heterojunctions. Under reverse bias, the high resistivity substrate shows a substantially larger reverse bias current.

Acknowledgement
Author would like to thank Dr. Raid A.W. Ismail and Mr. Oday A. Hamadi for their valuable notes and comments as well as school of applied science at the University of Technology (Baghdad, Iraq) for experimental assistance.

References