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Junction model and transport mechanism in hybrid PEDOT:PSS/n-GaAs solar cells

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ABSTRACT

This study investigates the junction formation and interface properties of PEDOT:PSS/n-GaAs hybrid solar cells on planar GaAs substrates. Barrier height, photocurrent, dark saturation current and build-in potential at this hybrid interface are measured by varying n-GaAs doping concentrations. The work function and valence band edge of the polymer are extracted from ultraviolet photoelectron spectroscopy to construct the band diagram of the hybrid n-GaAs/PEDOT:PSS junction. The current-voltage characteristics were analyzed by using abrupt (p^+n) junction and Schottky junction models. Contrary to the earlier results from the PEDOT:PSS/n-Si solar cells, the experimental evidence clearly suggested that the interface between n-GaAs and PEDOT:PSS more likely exhibited a Schottky type instead of a p^+n junction. The current transport is governed by the thermionic emission of majority carriers over a barrier and not by diffusion. The dark saturation current density increases markedly owing to the increasing surface recombination rate in heavier n-doped GaAs substrates, leading to significant deterioration in solar cells performance.

1. Introduction

Given that solar energy has become a front-runner in the technological and environmental revolution, a growing interest in commercial solar power is becoming a common concern for business owners and individual consumers. Several different approaches can harness the sun's energy, and knowledge of the difference among these methods is significant for possible investors. Two of the most common forms of photovoltaics are silicon solar cells and organic solar cells. The cost, efficiency, and durability of each form are all considerable factors when considering solar use. Advanced photovoltaic technologies have already decreased the prices of solar cells by a factor of three since 1990 and promoted the production growth at the rapid rate of 35% in the past five years; however, photovoltaic solar electricity remains too expensive compared with conventional electricity [1,2]. Essential innovative efforts are needed to combine relatively low-cost production technologies (organic solar cells) with relatively high conversion efficiencies (inorganic solar cells) to decrease solar electricity costs to succeed in competition with conventional electricity. Solar cells based on crystalline silicon offer high efficiency, but these cells are expensive owing to the high temperature and doping processes required in their fabrication. The alternative approach using low-temperature process organic semiconductors is potentially cheaper, but the organic solar cells present low conversion efficiency. Similar to typical organic solar cells, hybrid devices use only low temperature ($<$ 150 °C) processing techniques and are extremely simple to fabricate. An organic semiconductor is spin-coated or evaporated on top of crystalline silicon, and subjected to metalization. Another advantage of the hybrid devices is the possibility of higher throughput – which is different from dopant diffusion, which is a slow step, organic inks can be deposited on silicon at extremely high speeds.

Similar to Si-based photovoltaic cells, light absorption and photogenerated charge separation in hybrid devices happen predominately in silicon, so losses attributed to poor light absorption and photogenerated carrier recombination are low. Theoretically, hybrid photovoltaic devices with extremely high efficiencies, which rival conventional crystalline silicon solar cells, can be achieved. Other than the direct benefits discussed above, the elimination of all high-temperature processes in conventional Si solar cell fabrication entail numerous indirect cost advantages. Therefore, hybrid solar cells that combine Si and conjugated polymers at low temperatures provide an alternative to simplify the fabrication processes and reduce costs [3–14]. The conjugated polymer called poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) is the most widely used organic material for hybrid solar cell devices. PEDOT:PSS is transparent and, conductive (1000 S/cm), and can produce a hybrid junction with Si [6–14]. Illuminative light is

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absorbed in the n-type Si, and a hole transport layer in PEDOT:PSS can extract holes generated in the Si substrate out of the device. Thus, the efficiency of the hybrid PEDOT:PSS/Si solar cell is comparable with a conventional Si p-n junction solar cell in principle. Techniques for improving hybrid PEDOT:PSS/Si solar cell performance, including surface structures [11,12], surface passivation [13], and the use of additives [9,10,14] have been widely studied and reported.

To date, several works involved hybrid heterojunction solar cells with III-V inorganic semiconductors, despite the high efficiency of III-V bulk solar cells. A GaAs hybrid photovoltaic device with an energy conversion efficiency of 1.04% was fabricated by spin-coating poly(3-hexylthiophene) (P3HT) onto n-type GaAs nanowire arrays synthesized by molecular beam epitaxy (MBE) [15]. Solar cells based on P3HT-coated GaAs nanopillars grown on a patterned GaAs substrate using selective-area metal organic chemical vapor deposition exhibited a power conversion efficiency of 0.6% [16]. This cell efficiency was further improved to 1.44% by the surface passivation of GaAs. A heterojunction solar cell based on PEDOT:PSS and vertically aligned n-type GaAs nanowires fabricated by direct nanoetching of GaAs exhibited a power conversion efficiency of 5.8% [17]. The efficiency of the cell was further increased to 9.2% by incorporating an electron-blocking P3HT layer [18]. A core-shell, organic-inorganic hybrid solar cell with the PEDOT shells of a controlled thickness coated onto periodic GaAs nanopillar arrays and the anionic dopants incorporated into the polymer showed a power conversion efficiency of 4.11% [19]. More recently, Sun et al. demonstrated a record power conversion efficiency of 13% by incorporating a heavily-doped p^+/lightly-doped n epi-layer by MBE into the GaAs surface/substrate to create a front-/back-surface field (FSF/BSF) structures [20].

Although recent experiments conducted on PEDOT:PSS/Si photovoltaic cells indicated that the PEDOT:PSS/Si interface should be described by a minority carrier-driven pn-heterojunction [21], the same working principle has yet been resolved in PEDOT:PSS/GaAs cells. In the present study, the interface and the device performance of planar PEDOT:PSS/GaAs cells are investigated in detail. Thus, we extracted the interface and solar cell performance parameters of hybrid devices based on GaAs substrates with different background doping densities. Current density–voltage (J-V), capacitance–voltage (C-V), and external quantum efficiency (EQE) were measured to extract the solar cell performance parameters. Experimental results are compared with parameters predicated by one-side abrupt (p^+n) junction and Schottky junction models. Moreover, ultraviolet photoelectron spectroscopy (UPS) was used to explore and establish a band structure for the hybrid PEDOT:PSS/n-GaAs interface.

1.1. Models of Schottky type junction and one-side abrupt (p^+n) type junction

Two junctions possibly formed when a highly conducting p-polymer is in contact with a moderately n-doped semiconductor substrate, namely, the Schottky junction and the abrupt p^+n-junction. The former junction is typically used to explain the interface area of a semiconductor to a metal, and the latter junction is used to illustrate regions between an n-doped semiconductor and a heavier p-doped semiconductor. Regardless of the selected junction model, the J-V characteristic of both types of junctions can be described in its simplest form by the ideal diode equation (equation (1)) under illumination [22].

$$J = J_o\left\{exp\left(\frac{qV}{kT}\right) - 1\right\} - J_{sc}. \tag{1}$$

Upon open circuit conductions (J = 0), we can derive equation (2) from equation (1), in which the open circuit voltage V_{oc} mainly depends on the dark current density J_o and the short circuit current J_{sc}.

$$V_{oc} \approx \frac{kT}{q} ln\left(\frac{J_{sc}}{J_o}\right). \tag{2}$$

In the case of a Schottky-type junction, the dark current density J_o can be expressed in terms of equation (3).

$$J_o = RT^2 exp\left(-\frac{q\Phi_{SB}}{kT}\right), \tag{3}$$

where R is the reduced effective Richardson coefficient and Φ_{SB} is the Schottky barrier height at the interface. In principle, the dominant transport mechanism is the thermionic emission of major carriers over the energy barrier Φ_{SB} at the interface between a metal and a conventional semiconductor such as Si or GaAs [23]. For a Schottky-type junction, equation (3) shows that J_o mainly depends on the Schottky barrier height Φ_{SB}. For an ideal junction between a metal and an n-type semiconductor, Φ_{SB} is expressed by the difference between the metal work function Φ_M and the electron affinity of the semiconductor χ_S, minus the so-called Schottky-barrier lowering $\delta\phi$ [22].

$$\Phi_{SB} = \Phi_M - \chi_S - \delta\phi. \tag{4}$$

Therefore, Φ_{SB} only weakly depends on the doping of the semiconductor because $\delta\phi \propto N_D^{\frac{1}{4}}$ [22]. Following equation (3), J_o should slightly increase with increasing doping in semiconductors, leading to a weakly decreased V_{oc} if J_{sc} remains constant. For typical semiconductor/metal junctions, Φ_{SB} is usually independent of the doping in the semiconductors because of the pinning of Fermi level at the presence of a high density of surface states in the bandgap of semiconductors [24].

On the other hands, for the abruptly changed doping profile between two semiconductors or the so-called one-side abrupt junction (p^+n-junction), the dark current density J_o is defined by equation (5). In contrast to the case in Schottky junction, the transport processes are dominated by the diffusion of minority carriers.

$$J_o = \frac{n_i^2 \mu_p kT}{L_p N_D}, \tag{5}$$

where n_i is the intrinsic concentration, μ_p is the minority carrier (holes in n-doped semiconductor) mobility, L_p is the minority carrier diffusion length, and N_D is the donor concentration. Notably, J_o now depends only on properties of the n-doped semiconductor and is inversely proportional to the donor concentration (N_D). Following equation (2), the V_{oc} in a p^+n junction should increase with increasing N_D.

In the following sections, the photovoltaic parameters of PEDOT:PSS/n-GaAs hybrid solar cells fabricated on GaAs substrates with different n-doping concentrations will be measured and analyzed. The junction type of the devices will be determined based on the aforementioned junction models.

2. Results and discussion

Hybrid PEDOT:PSS/n-GaAs solar cells based on three differently Si-doped (N_D) GaAs substrates with doping density of 6.9×10^{16} (sample A), 3.8×10^{17} (sample B), and 3.2×10^{18} cm^{-3} (sample C) have been fabricated, as shown in Fig. 1. Two-inch, silicon-doped GaAs wafers with a thickness of 350 μm were purchased from Conary Enterprise Co. Ltd. The wafers were cleaned sequentially in an ultrasonic bath with acetone, IPA, and deionized water for 5 min and in HCl solution (30%) for 1 min to remove surface oxide. After cleaning, the wafers were then immediately transported to an e-beam evaporation system for Ni/Ge/Au (300 Å/500 Å/2000 Å) back electrode deposition. Ohmic contact was formed by rapid thermal annealing at 420 °C for 35 s in an N_2 atmosphere. A highly conductive polymer solution was spin-coated onto the GaAs surface by mixing a PEDOT:PSS (PH1000 from Clevios) solution with 5 wt% dimethyl sulfoxide (DMSO) as a secondary dopant to increase conductivity, followed by thermal annealing at 120 °C for 10 min. The best performance of the planar hybrid solar cells was achieved at a two-step spin-coating rates of 500 rpm for 5 s and 3000 rpm for 25 s, respectively. The wafers were soft-baked at 120 °C