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Weining Wang
Syracuse University

Eric A. Schiff
Syracuse University

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Polyaniline on crystalline silicon heterojunction solar cells

Weining Wang^{a)} and E. A. Schiff

Department of Physics, Syracuse University, Syracuse, New York 13244-1130, USA

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Organic/inorganic heterojunction solar cells were fabricated on the (100) face of *n*-type silicon crystals using acid-doped polyaniline (PANI) with widely varying conductivities. For films with conductivities below 10^{-1} S/cm, the open-circuit voltage V_{OC} increases with increasing film conductivity as expected when V_{OC} is limited by the work function of the film. Extrapolation of these results to the higher conductivity films indicates that PANI could support V_{OC} of 0.7 V or larger. V_{OC} measurements for the cells with higher conductivity PANI saturated at 0.51 V. We speculate that uncontrolled surface states at the PANI/Si interface are reducing these values. © 2007 American Institute of Physics. [DOI: 10.1063/1.2789785]

Heterojunctions to crystalline silicon (*c*-Si) have long been of fundamental interest, and amorphous silicon (*a*-Si:H)/*c*-Si heterojunctions are now applied for some commercial “heterojunction with intrinsic thin layer” (HIT) solar cells.¹ These heterojunction cells have achieved efficiencies as high as 21.8%, which approach the best results (24.7%) for homojunction *c*-Si cells;² there is a sizable literature on the properties of this type of heterojunction.³ Conducting polymer/*c*-Si heterojunctions could also have attractive properties, and early work on polyacetylene/*c*-Si heterojunctions suggested open-circuit voltages (V_{OC}) under solar illumination as large as 0.64 V.⁴ While these results were comparable to those for homojunctions at that time, there has since been only sporadic work on polymer/*c*-Si solar cells and closely related devices.⁵⁻⁹

In this paper, we report our research on polyaniline/*n*-type silicon heterojunction solar cells. Doped polyaniline (PANI) conducts holes well (conductivities as high as 10^3 S/cm have been reported), and this near-metallic¹⁰ (or nanometallic¹¹) character along with its stability in air makes polyaniline interesting for this application. PANI/*c*-Si heterojunctions have been examined as gas sensors.⁵ In the present work, we primarily explored the open-circuit voltage V_{OC} of these heterojunctions under illumination. For PANI films with smaller conductivities ($<10^{-1}$ S/cm), the dependence of V_{OC} upon conductivity was consistent with limitation by the work functions of the two materials; work function effects on the performance of polymer light-emitting diodes incorporating polyaniline were reported previously.¹² Extrapolation of the measurements to the higher conductivity films suggests that PANI films could support V_{OC} values of 0.7 V or higher, which is about the current limit achieved with *a*-Si:H/*c*-Si heterojunctions. The largest V_{OC} we obtained was 0.51 V. Direct measurement of the built-in potential V_{BI} in these cells indicates that PANI/Si surface states are limiting V_{BI} and V_{OC} .

We used “emeraldine salt” dispersions of polyaniline in xylene from Sigma-Aldrich, Inc. (film conductivity $\sigma \approx 10^1$ S/cm) and from Ormecon GmbH ($\sigma \approx 10^2$ S/cm).¹³ To make solar cells, a dispersion was spin coated onto the freshly HF-etched, polished surface of *n*-type, (100) silicon wafers¹⁴ with an evaporated aluminum back contact; the area

of the PANI film was typically about 1 cm^2 . The films were dried in air following the manufacturer’s instructions [$80 \text{ }^\circ\text{C}$ for 24 h (Aldrich) and $100 \text{ }^\circ\text{C}$ for 1 min (Ormecon)], and a 1 mm diameter gold contact was evaporated onto the PANI film. Films spun from the Ormecon dispersion were $0.35 \text{ }\mu\text{m}$ thick.¹⁵ We prepared doped PANI films with widely varying conductivities (10^{-5} to 10^1 S/cm) from the Aldrich dispersion by increasing its xylene concentration. This dilution (from 2% PANI by weight to 0.3%) reduced the thickness of the spun films from 0.4 to $0.1 \text{ }\mu\text{m}$, which appears consistent with the effect of the reduced viscosity for diluted films. Scanning electron microscopy indicated that these films were continuous, although with somewhat differing morphologies for the differing dilutions.

The dependence of the current density upon voltage is shown in Fig. 1 for a PANI/*n*-Si diode (Ormecon dispersion) for the dark and for tungsten-halogen illuminations through the PANI (intensity of 0.1 W/cm^2). The saturated photocurrent density is 17 mA/cm^2 , which is reasonably consistent with the photon flux that reaches the *c*-Si after filtering by the PANI film. The open-circuit voltage V_{OC} is 0.51 V, which is about 0.1 V below the values observed for *c*-Si based cells with metal back electrodes.¹⁶ The low fill factor

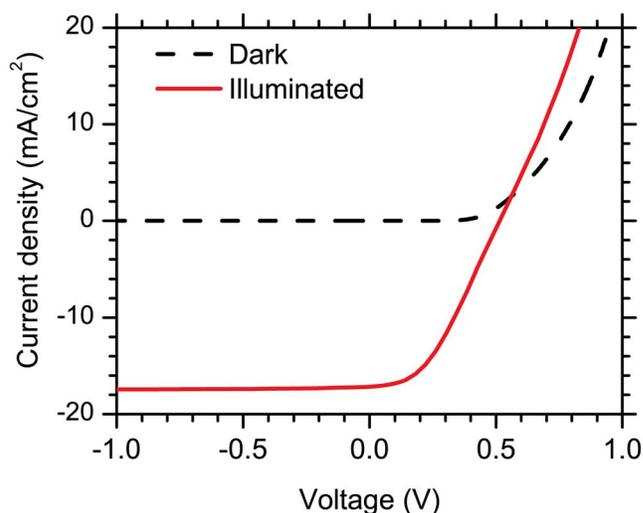


FIG. 1. Current density as a function of voltage across a PANI/*c*-Si diode (Ormecon dispersion, 1.2×10^2 S/cm). The white-light illuminator intensity was 0.1 W/cm^2 .

^{a)}Electronic mail: wwang@phy.syr.edu

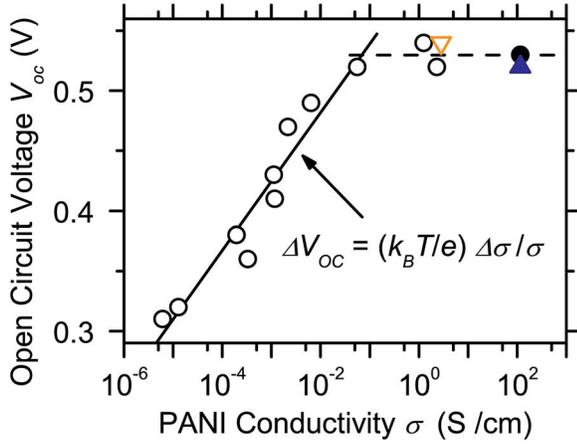


FIG. 2. Open-circuit voltages V_{OC} of PANI/ c -Si diodes for PANI films with widely varying conductivity. The closed symbols are for the Ormecon dispersion; the open symbols are for the Aldrich dispersions. Different symbol shapes indicate different sources for the silicon crystal (see Ref. 14). The illumination intensity was 0.58 W/cm^2 .

of 41% is due to the lateral resistance of the PANI film (and the absence of a top metallic grid). It is of interest that the light and dark curves cross at about 0.6 V; while such “crossover” is not typical for homojunction c -Si diodes, it has been reported previously for heterojunctions of [poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)] (PEDOT:PSS) on a -Si:H.^{6,9}

In Fig. 2, the open-circuit-voltages V_{OC} (at intensity 0.58 W/cm^2) for each of a series of PANI/ c -Si diodes are shown as a function of the conductivity σ of a PANI film casts onto glass using the same dispersion. V_{OC} was almost constant (at $V_{OC}^{\text{sat}}=0.52 \text{ V}$) as the conductivity of the PANI films varied from 10^{-1} to 10^2 S/cm . Below a threshold conductivity $\sigma_c=0.05 \text{ S/cm}$, the data are fitted satisfactorily by the form

$$V_{OC} = 0.53 + (k_B T/e) \ln(\sigma/\sigma_c), \quad (1)$$

where $k_B T/e=0.025 \text{ V}$ is the ratio of the Boltzmann thermal energy to the electron charge at room temperature. The large range of conductivities—about 10^5 —accessible by fairly modest dilution of emeraldine salt dispersions may be a useful complement to the similarly large effects found in blends of polyaniline with nonconductive (filler) polymers.^{17,18}

For $\sigma < \sigma_c$, the logarithmic dependence of V_{OC} is consistent with the idea that V_{OC} is limited by the built-in potential across the diode,¹⁹

$$eV_{OC} \approx eV_{BI} = E_F^{\text{Si}} - E_F^{\text{PANI}}, \quad (2)$$

where E_F^{Si} is the Fermi level of the (n -type) c -Si and E_F^{PANI} is the Fermi level of the p -type PANI film. Assuming that the conductivities of the PANI films are mainly determined by their Fermi levels (and work functions), we write

$$\sigma = \sigma_{00} \exp[-(E_F^{\text{PANI}} - E_V^{\text{PANI}})/k_B T], \quad (3)$$

where E_V^{PANI} is the transport energy for holes in the PANI films. We obtain for V_{OC} (in the built-in potential limit) that

$$eV_{OC} = (E_F^{\text{Si}} - E_V^{\text{PANI}}) - k_B T \ln(\sigma_{00}/\sigma). \quad (4)$$

Equation (4) accounts for measured slope $k_B T/e=0.025 \text{ V}$ of the dependence of V_{OC} on the natural logarithm of the film conductivity.

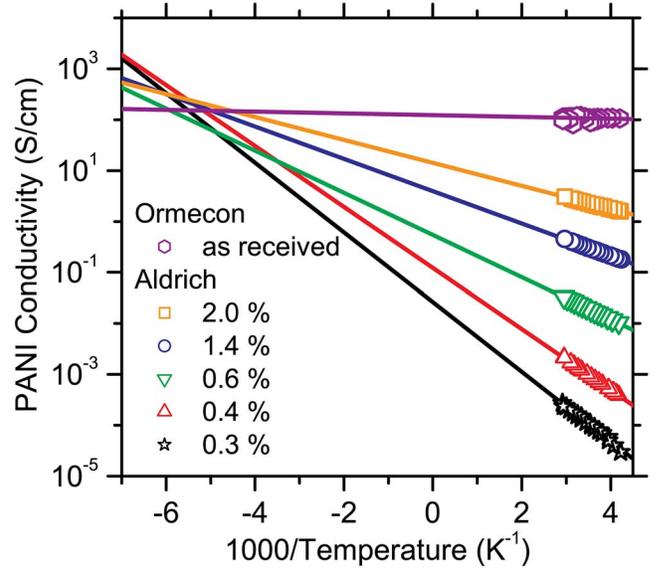


FIG. 3. Conductivity measurements as a function of reciprocal temperature of $1000/T$ for six PANI films cast onto glass from dispersions with differing dilutions. The percentages indicated in the legend are the weight percentages of PANI in xylene. While the measurements for each sample show simple activated behavior, the fitting lines converge at a negative Meyer-Neldel temperature $T_{M-N}=-180 \text{ K}$.

We checked that Eq. (3) does describe the temperature-dependent conductivities of our films. The results are presented in Fig. 3, which show that lower conductivity films have larger activation energies. The fitting curves roughly converge at a negative “Meyer-Neldel” temperature $T_{M-N} \approx -180 \text{ K}$ and a conductivity $\sigma_{M-N}=2 \times 10^2 \text{ S/cm}$. Inverse Meyer-Neldel behavior (i.e., negative values for T_{M-N}) is typically observed when the (temperature-dependent) Fermi level lies in a bandtail region.²⁰ Assuming that σ_{M-N} estimates the fundamental bandedge conductivity σ_{00} ,²¹ we can use Eq. (4) to infer the difference in energy levels between Fermi level in the c -Si and the hole transport level of the PANI; the result $E_F^{\text{Si}} - E_V^{\text{PANI}}=0.74 \text{ eV}$ is consistent with work function estimates in heavily doped PANI.²²

We now turn to the plateau value for V_{OC} of around 0.5 V that we found (Fig. 2) for PANI conductivities $\sigma > 10^{-1} \text{ S/cm}$. This value is of importance for potential applications. V_{OC} is reduced by our use of a metal back contact (instead of a back surface field) and by photon absorption by the top PANI layer; we estimate these reductions to add to about 0.05 V. The main effect reducing the saturated value for V_{OC} appears to be that the built-in potential V_{BI} did not reach the values of 0.74 V or larger that would be inferred from Fig. 2 for the highest conductivity films (from Ormecon GmbH). We determined the built-in potential for the heterojunctions incorporating high conductivity PANI using capacitance-voltage (C - V) measurements and a standard Schottky fitting ($1/C^2$ vs V). We obtained $V_{BI}=0.60 \text{ V}$, which is substantially lower than the extrapolated $V_{OC}=0.74 \text{ V}$ and indicates that for larger conductivity films, V_{BI} is lower than would be inferred from the conductivity.

We therefore speculate that the Fermi level at the interface of the PANI and the c -Si interface is not as low as would be anticipated for “bulk” PANI, thus leading to reduced values of V_{BI} across the c -Si. Such an effect could be due to a band of surface states that “pin” E_F at the interface for the heavily doped material. Angle-resolved ultra-

violet photoemission measurements do indicate interface-dependent electronic states for PANI on oxidized *c*-Si surfaces.²³ It is conceivable that these effects could be mitigated by grafting of PANI onto the *c*-Si surface²⁴ or other strategies.

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¹³Product 650013 from Sigma-Aldrich, Inc.; dispersion D1020 from Ormecon GmbH.

¹⁴Three types of (100) oriented *n*-type silicon crystals were used. (1) Atomergic Chemetals Corp., Czochralski, 2 Ω cm, 380 μ m thick; (2) Topsil Semiconductor Materials A/S, float zone, 0.5–1.5 Ω cm, 205–245 μ m thick; and (3) Montco Silicon Technologies, float zone, 2.6 Ω cm, 215 μ m thick. Sources 1–3 correspond to the circle, triangle, and inverted triangle symbols in Fig. 2, respectively.

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