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Published in *Applied Physics Letters*, vol. 95, no. 23, 2009

AIP Applied Physics Letters

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Citation: Applied Physics Letters **95**, 233121 (2009); doi: 10.1063/1.3267144
View online: http://dx.doi.org/10.1063/1.3267144
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APPLIED PHYSICS LETTERS **95**, 233121 (2009)

Hot electron effect in nanoscopically thin photovoltaic junctions

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(Received 19 October 2009; accepted 3 November 2009; published online 11 December 2009)

The open circuit voltage in ultrathin amorphous silicon solar cells is found to increase with light energy (frequency), due to extraction of hot electrons. The ultrathin nature of these junctions also leads to large internal electric fields, yielding reduced recombination and increased current. A simple phenomenological argument provides a qualitative understanding of these effects and gives guidelines for designing future, high-efficiency, hot electron solar cells. © *2009 American Institute of Physics*. [doi:10.1063/1.3267144]

Hot electrons (and holes) are charge carriers photoexcited above a semiconductor conduction band edge, with a nonequilibrium distribution temperature higher than the lattice. Studied for more than 50 years, from Gunn diodes to integrated circuit diagnostics,[1–10] hot electrons are also anticipated to play an important role in high efficiency photovoltaics (PVs). One of the seminal concepts proposed for next-generation solar cells involves harvesting the excess energy of these hot electrons before it is dissipated as heat (phonons).[11] While early investigations in electrolyte-semiconductor junctions found some evidence for hot electron injection into the electrolyte,[12] no device has been shown to exhibit improved PV action associated with hot electrons. Here, we show evidence for such a hot electron effect in ultrathin *p*-*i*-*n* hydrogenated amorphous silicon (*a*-Si) solar cells, manifest as an increase of open circuit voltage V_{oc} with photon energy.

The key to observing this effect, one of several so-called third generation solar phenomena,[13] is to extract the hot electrons into harvesting contact electrodes very rapidly, on time scales well under 1 ps. In principle, this could be achieved with very thin absorbers, thinner than the diffusion/recombination lengths of the charge carriers, or with the use of narrow band energy filters at absorber-electrode contacts to facilitate isoentropic cooling.[11,14] In this letter, we employed the former technique, via a series of planar *a*-Si *p*-*i*-*n* junction solar cells prepared with ultrathin *n*- and *p*-doped regions (5 nm thick each), and with the thickness *d* of the intrinsic *i*-region varied between 5 and 300 nm. The total junction thickness was thus $D=d+10$ nm. Samples were prepared on indium tin oxide (ITO, 200 nm thick)-coated boroalumino-silicate glass substrates, and silicon deposition was done via plasma-enhanced chemical vapor deposition at 200 C using silane (SiH_4) and H_2 gases for the intrinsic/absorber (*i*-) layer, with diborane (B_2H_6) and phosphine (PH_3) gases additionally employed for *p*- and *n*-doping, respectively. Back contacts were made using 100 nm thick aluminum, thermally evaporated through a mask to define 3 mm diameter contacts, completing each solar cell. Silicon thicknesses for each of the *p*-, *i*-, and *n*-layer depositions were calibrated using atomic force microscopy and profilometry, and cross-checked by directly measuring *D* on a portion of each sample separate from that used for the PV measurements, using profilometry. While absolute cell areas are not critical to the data herein, a subset of measurements was performed on 1 cm^2 areas to confirm cell current density values. Current-voltage (*I*-*V*) data were taken under simulated terrestrial solar illumination (AM1.5) and under monochromatic light using red, green, and blue lasers. In the laser experiments, light intensities were adjusted to establish a wavelength-independent short-circuit current I_{sc}, and $V(I)$ and/or V_{oc} were recorded at the different optical wavelengths for each sample (each thickness *d*).

Figure 1(a) shows representative *I*-*V* data for our samples under AM1.5 illumination in the PV regime, here

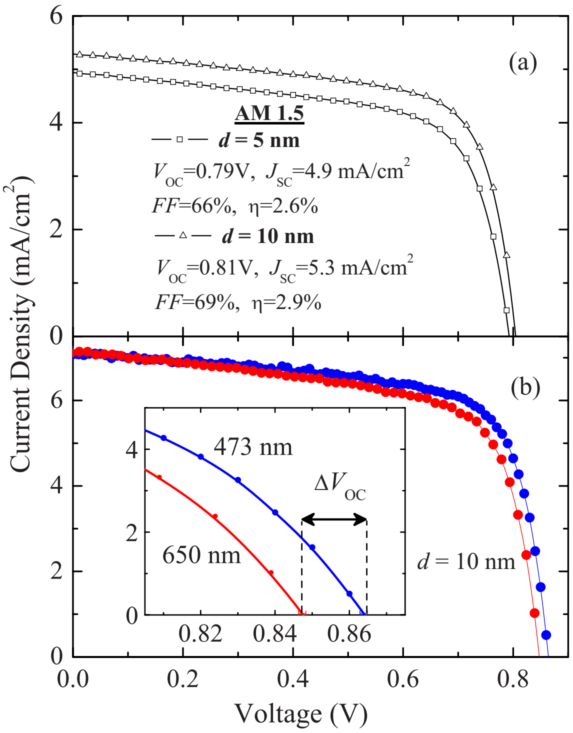

FIG. 1. (Color online) Current-voltage characteristics of ultrathin *a*-Si *p*-*i*-*n* junctions. (a) Junctions with *i*-layer thickness $d=5$ and 10 nm, under AM1.5 illumination. (b) Junction with $d=10$ nm, under blue ($\lambda=473$ nm) and red ($\lambda=650$ nm) laser illumination. The inset shows a zoomed-in section of the main plot near V_{oc}.

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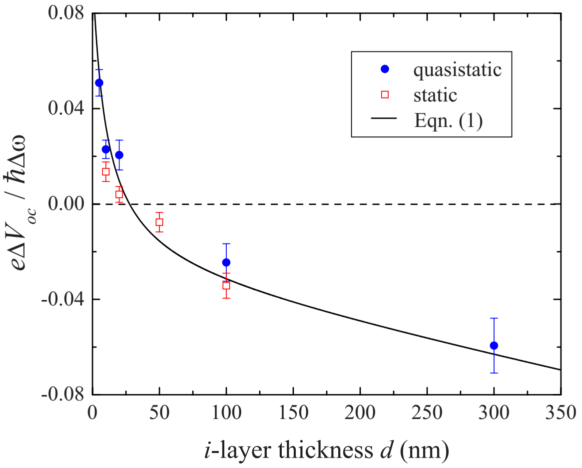

FIG. 2. (Color online) Open-circuit voltage change vs junction thickness. ΔV_{oc} from all PV experiments involving lasers, normalized by the difference in the corresponding photon energies per charge $\hbar\Delta\omega/e$, vs *i*-layer thickness *d* for fixed J_{sc}. Symbols represent the mean values, and the error bars are obtained from the standard deviations. The solid line is obtained by using Eq. (1). The largest effect measured was ΔV_{oc}=40 mV for d=5 nm.

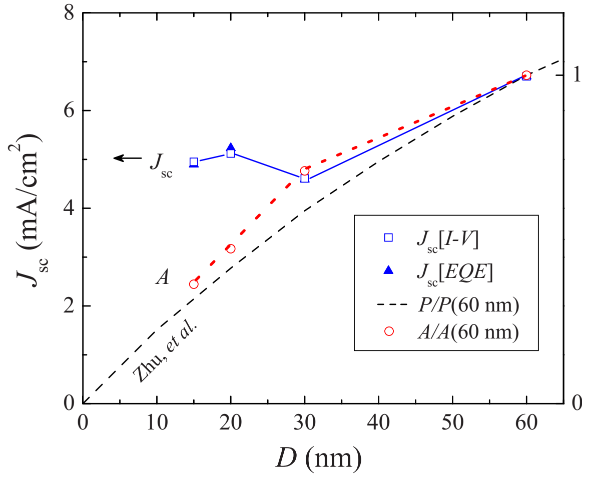

FIG. 3. (Color online) Variation of short circuit current density with total junction thickness. J_{sc} vs D under AM1.5 illumination, as measured from *I-V*s (squares), calculated by integrating EQE(λ) (triangles), integrated optical absorbance A, normalized to the D=60 nm value (circles), and normalized power density as modeled in Ref. 17 (dash).

for our two thinnest *i*-layer samples, d=5 and 10 nm (D=15 and 20 nm). These data demonstrate the high quality of the junctions, even with the ultrathin, 5 nm thick *n*- and *p*-layers. Note that this D=15 nm sample still achieved over 2.5% power conversion efficiency, a point to which we return later. Similar data were taken not under AM1.5 light, but under monochromatic laser light using lasers (RGBLase LLC). Figure 1(b) shows *I-V* data for the d=10 nm sample for blue (λ=473 nm) and red (λ=650 nm) illumination, with each laser intensity adjusted (via a diffusing lens) to assure the same I_{sc} (and thus short circuit current density J_{sc}). Here, it can be seen that there is an increase in V_{oc} for higher energy light over that of lower energy, with $\Delta V_{oc}=V_{oc}^{\text{blue}}-V_{oc}^{\text{red}}=16.7\pm1.1$ mV. Similar *I-V* data were taken for samples with d=5, 20, 50, 100, and 300 nm and ΔV_{oc} was extracted for each sample. To eliminate possible artifacts due to quasistatic transients (laser instabilities, ohmic heating, etc.), we performed, in parallel, quasistatic measurements for all samples and lasers, using a set-up that assures collection of data with rapid switching between open circuit voltage V_{oc} and closed circuit current I_{sc} configurations. The results are in excellent agreement with the static results based on the complete *I-V* data, showing that the quasistatic transients are negligible.

Combined results from all experiments involving lasers are shown in Fig. 2, where we plot ΔV_{oc} obtained as above as well as via $V_{oc}^{\text{blue}}-V_{oc}^{\text{green}}$ (all normalized by the difference in the corresponding photon energies per charge $\hbar\Delta\omega/e$, where $\hbar$ is Planck's constant and e is the electron charge) versus d for fixed J_{sc}=7.1 mA/cm^2, with symbols representing the mean values and error bars obtained from the standard deviations. With the employed normalization, the data congregate around a single line, which has the following phenomenological form:

$$\frac{e\Delta V_{oc}}{\hbar\Delta\omega}=\frac{D_c}{D}+\alpha+\beta D, \qquad (1)$$

where $\hbar\Delta\omega/e=2.62\ \text{eV}-2.20\ \text{eV}=0.42\ \text{eV}$ (for blue-green data), and $\hbar\Delta\omega/e=2.62\ \text{eV}-1.91\ \text{eV}=0.71\ \text{eV}$ (for blue-red data), and the adjustable constants are D_c=1.3 nm, α=−0.03, and $\beta=-1.2\times10^{-4}$ nm^{-1}.

Figure 2 represents the main result of this work: ΔV_{oc} is *positive* for ultrathin junctions, *decreases* monotonically with *i*-layer thickness d, and becomes *negative* for $d>30$ nm. This effect is quantitatively captured by Eq. (1), and can be explained by employing a simple argument. As stated earlier, hot electrons are generated by photons with $\hbar\omega>E_g$, where ω is the photon frequency and E_g the energy gap of the absorbing semiconductor. These hot electrons rapidly thermalize via direct phonon emission and indirect cooling through collisions with cold electrons in the doped regions, on a time scale of 0.1 ps.[7] Only a small fraction, of order D_c/D, of these hot electrons, generated within a very small distance D_c of the order of 1 nm away from the collector,[5,15] can be extracted with their original kinetic energy $(\hbar\omega-E_g)$. The ensemble-averaged energy of the electrons arriving at the collector is therefore $E_{\text{avg}}\sim(\hbar\omega-E_g)D_c/D$, and the resulting increase of V_{oc} is $\Delta V_{oc}\approx[(\hbar\Delta\omega)/e](D_c/D)$. This is the positive contribution which decreases monotonically with D ($\Delta V_{oc}\sim1/D$). The remaining hot electrons cool off by emitting phonons, which results in a temperature increase of the junction. This increase is proportional to the initial kinetic energy of the thermalizing electrons rapidly delivering energy to the thermal bath. The temperature is also expected to increase linearly with the number of thermalizing hot electrons, which in turn is proportional to $D-D_c\approx D$. Therefore, the temperature increment corresponding to this effect is $\Delta T\sim\hbar\Delta\omega D$. It is well known that increasing temperature *only* reduces V_{oc} in solar cells, with typically linear dependence near room temperature,[15] so that $\Delta V_{oc}\sim-\Delta T\sim-D$. Thus, hot electrons contribute to both the $1/D$ increase for small D and the linear decrease for large D, of V_{oc}. Combining both contributions, along with a D-independent term α, yields Eq. (1). With D_c=1.3 nm, of order of the 1 nm estimate above, we obtain the solid line in Fig. 2, which follows the measured data rather well. This phenomenological agreement strongly supports our interpretation of the data in Fig. 2 as an interplay between two competing effects: an increase of V_{oc} with light energy (i.e. $\Delta V_{oc}>0$) in ultrathin samples due to *extracted* hot electrons (a solid-state analog of the photoelectric effect),[16] and a decrease of V_{oc} ($\Delta V_{oc} < 0$) in thicker samples associated with *unextracted* hot electrons losing their energy to heat.

The observation of a measurable hot electron effect in our junctions is facilitated by the exceptionally short carrier escape time, due to the nanoscopic junction thickness. This small thickness also increases the junction electric field, increasing carrier velocities. This leads also to the anomalously large current observed: the J_{sc} of the ultrathin film samples ($d=5$ to 20 nm) under 1 sun is relatively large, 5 mA/cm^2 [Fig. 1(a)], already half that obtained for conventional ($d \sim 400$ nm) planar cells. Figure 3 reveals the reasons for this unusual behavior. First, the integrated optical absorbance A (shown normalized to the $D=60$ nm value) which governs the PV current for thin films, decreases with decreasing D, as expected, because thinner junctions absorb less light. Likewise, the dashed line representing a model by Zhu *et al.*,[17] of converted solar power as a function of film thickness in *p-i-n* *a*-Si solar cells, falls to zero as $D \rightarrow 0$. However, the transport J_{sc}, as well as that derived from the wavelength-integrated external quantum efficiency, deviate from this behavior for small D. This indicates that there is an improved extraction of carriers for ultrathin layers, sufficiently strong to overcome the reduced light absorption. We attribute this deviation to the very high junction electric field ($\sim 10^8$ V/m), which varies as $1/D$ and serves to reduce carrier recombination.[18] The overall power conversion efficiency of these ultrathin cells is thus enhanced by both excess voltage (hot electron effect) and excess current (high electric field effect), approaching $\eta \sim 3\%$ with absorbers less than 1/50th as thick as conventional cells. Practically speaking, however, this efficiency is limited by the essentially negligible light collection of such ultrathin junctions. On the other hand, with improved light trapping schemes, such as via nanowire configurations,[19] ultrathin hot electron solar cells could be engineered with significant increases in efficiency.

In conclusion, we have found that the open circuit voltage V_{oc} in ultrathin *a*-Si *p-i-n* solar cells increases with light energy. The observed increase is due to extraction of a residual population of hot electrons generated near the collector. The effect naturally changes sign for thick junctions, as hot electrons thermalize to the lattice and warm the junction. In addition to the observed hot electron-induced voltage changes, the ultrathin nature of the junctions leads to large internal electric fields, yielding reduced carrier recombination and increased current. A simple phenomenological argument provides a qualitative understanding of these effects, and gives guidelines for designing future, high-efficiency, hot electron solar cells.

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