

Toward metal-organic insulator-semiconductor solar cells, based on molecular monolayer self-assembly on *n*-Si

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Alkyl chain molecules on *n*-Si were used to test the concept of hybrid metal-organic insulator-semiconductor (MOIS) solar cells. Test structures were made by binding alkyl chain molecules via Si–O–C bonds to oxide-free *n*-Si surfaces, using self-assembly. With thiol groups at the terminals away from the Si, binding of Au nanoparticles, followed by electroless Au plating yields semitransparent top contacts. First cells give, under 25 mW/cm² white light illumination, open-circuit voltage $V_{oc}=0.48$ V and fill factor FF=0.58. Because with sulfur termination the molecules have a dipole that limits inversion of the Si, we also used methyl-terminated monolayers. Even though then we can work, at this point, only with a Hg top contact, without chemical bond to the molecules, we get, using only radiation (\sim AM 1.5) collected around the contact, the expected higher $V_{oc}=0.54$ V, and respectable 0.8 FF, justifying further MOIS cell development. © 2009 American Institute of Physics. [DOI: 10.1063/1.3076115]

Metal-insulator-semiconductor (MIS) junctions present a conceptually simple approach to photovoltaics (PVs). They attracted much interest in the past because of their potential for cheap solar cell production.^{1,2} In principle, in this structure the close proximity of the PV junction to the cell's illuminated side should allow better solar radiation collection, especially of short wavelengths, than in standard *p*-*n* junction solar cells. Best, single crystal Si-based, MIS cells achieved conversion efficiencies of up to 21%, approaching the best of their *p*-*n* junction analogs.³

The role of the interfacial layer in the MIS cell was studied theoretically, both analytically^{4–6} and numerically.^{7,8} These studies claim that the insulating layer can almost fully passivate the semiconductor surface. In that case the semiconductor's equilibrium band bending is dominated primarily by the difference between the (*n*-type) semiconductor electron affinity and the metal work-function, following the Schottky–Mott model. Then, with the appropriate semiconductor-metal combination (*n*-semiconductor/high work function metal; *p*-semiconductor/low work function metal) the semiconductor interface will be strongly depleted or even inverted. In the latter case a *p*-*n* homojunction forms underneath the insulating layer. The current-voltage characteristics of a cell with such depletion/inversion conditions will be:

- *in reverse and moderate forward bias*: the diode dark current is limited by thermionic emission of majority carriers over the potential barrier (depletion), or by minority carrier generation and recombination rates (inversion). In both cases forward current increases exponentially with applied bias with a slight difference in the pre-exponential factor between them, a situation we will refer to as “semiconductor-limited;”
- *at higher forward bias*: the current rises exponentially with bias until it equals the rate at which minority carriers are

supplied by tunneling from the metal. Beyond that, the diode becomes “tunneling-limited.”

The current under illumination is, ideally, a superposition of the photo- and dark currents. This is true if the insulator is thin enough that the uncompensated photocurrent can flow without the diode entering the tunneling-limited regime. Various analyses^{6,8,9} show that this notion is valid up to a 1.5–2 nm insulator thicknesses, depending on the energy barrier height within the semiconductor. With thicker insulators the fill factor (FF) drops rapidly, although the open-circuit voltage (V_{oc}) decreases only slightly.

Recently, it was shown that high quality nanometer-thick monolayers of insulating organic molecules can be formed controllably on semiconductors.^{10–12} With this development it should be possible to make metal-organic insulator-semiconductor (MOIS) solar cells. Then, the variety of organic molecules that can be formed on oxide-free, H-terminated Si should enable exploration and optimization of the role(s) of the insulator's physical and electronic properties for optimization in (inorganic) MIS PVs. A possible advantage of MOIS cells themselves could be milder preparation conditions with concomitant lower fabrication costs, than those of all-inorganic cells. Self-assembly of organic monolayers can be done at relatively low temperatures (<230 °C), and metallic top electrodes can be deposited nondestructively by various methods,¹³ including bottom-up techniques, such as growing and ripening of nanoparticles.¹⁴

To test the MOIS solar cell approach we set out to prepare an all solid-state covalently bound structure, by adsorbing a well-characterized thiol-terminated alkoxy monolayer onto *n*-Si via Si–O–C bonds.¹⁵ Samples were prepared by treating single side polished 1–10 Ω cm *n*-Si (100) with a solution of HOC₁₁H₂₂SH. The samples were then characterized by ellipsometry, water contact angle, Fourier transform infrared and x-ray photoelectron spectroscopy to verify monolayer quality and that the surface is free of measurable oxide, as explained elsewhere.¹¹ A continuous but porous, semitransparent Au film is then grown on the thiol terminated monolayer in a two-step process. First Au nanopar-

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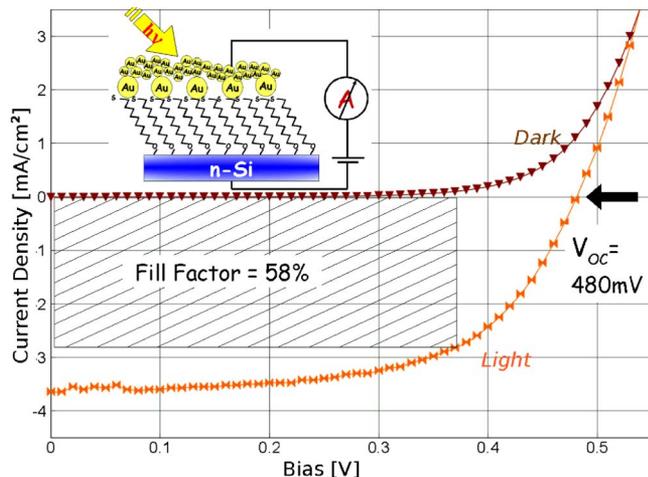


FIG. 1. (Color online) Current-voltage characteristics of a 2×2 mm n -Si-O-C₁₁-S-Au structure, fabricated by molecular self-assembly and electroless Au plating, under ~ 25 mW/cm² (~ 0.25 AM 1.5) illumination. The Au top contact is estimated to be 50%–60% transparent for visible and near-IR radiation (300–1100 nm). Here and in all measurements bias is applied to the top contact while the substrate's back contact is grounded.

ticles (NPs), 3–5 nm in diameter, are bound to the monolayer from a toluene suspension.¹⁶ The NPs serve to seed the top electrode for electroless deposition. This, all-covalently bound approach leads to a structure with well-defined insulator thickness (as compared to, e.g., Ref. 17 where PV behavior of methyl-passivated n -Si, contacted by spray-coating Au nanoparticles and subsequent sintering, is shown).

To make the NP monolayer into a useful solar cell top contact requires transforming the NP layer into an electrically continuous metal film with low sheet resistance, as transparent as possible to that part of the solar spectrum that can be absorbed by the absorber. Using slow electroless plating¹⁸ for 5 min, while monitoring film growth, gave a continuous film with 50%–60% overall transparency over the 300–1000 nm wavelength range.

Figure 1 shows current-voltage characteristics of a 2×2 mm n -Si-O-C₁₁-S-Au structure, fabricated as described above, under ~ 25 mW/cm² illumination. The open-circuit voltage, (V_{oc}), was 480 mV, higher than reported for plain n -Si-Au or even n -Si-SiO₂-Au cells¹⁹ and the FF was 58%. Results at 25 mW/cm² instead of a higher illumination intensity are shown, because increasing the intensity slightly increased the V_{oc} but decreased the FF dramatically (see supplemental material).²⁰ This behavior can indicate, as discussed above, that the uncompensated photocurrents approach the currents of the tunneling-limited regime.

The transition point between semiconductor- and tunneling-limited current regimes is easily found from temperature dependent I - V curves, using Hg as top electrode. To a first approximation tunneling does not depend on temperature. Therefore, the I - V plots in the tunneling-limited voltage regime should be temperature-independent, while in the semiconductor-limited regime currents increase with temperature, as expected for a thermally activated process. Remarkably, we found for alkyls on Si that currents at high forward bias decrease with increasing temperature, providing clear evidence for the voltage where the dominant transport mechanism changes.^{21,22}

Figure 2 presents temperature-dependent dark I - V measurements for an n -Si-O-C₁₁-S-Hg junction. Hg has a

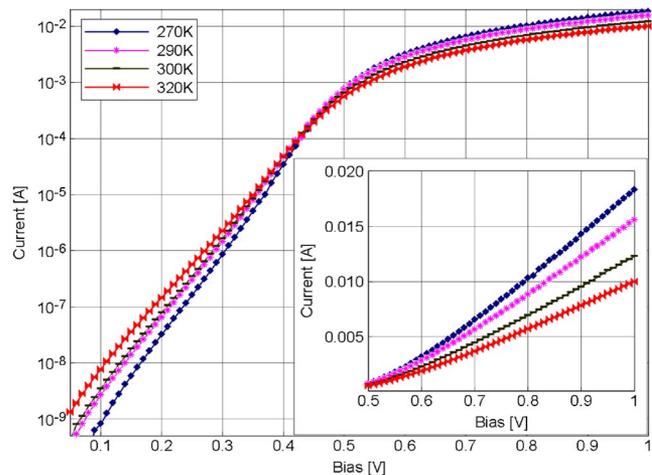


FIG. 2. (Color online) Temperature-dependent dark I - V measurements on an n -Si-O-C₁₁-S-Hg, Si-monolayer-Hg junction. The bias at which the temperature dependence switches from increasing to decreasing current with increasing temperature can be clearly discerned, around 470 mV.

work function of 4.5 eV, which is only slightly lower than the values 4.6–4.8 eV, measured for chemically deposited Au, using kelvin probe contact potential difference (CPD) measurements. The plots show the voltage where the temperature dependence changes from increasing to decreasing current with increasing temperature, with increasing forward bias, indicating that, indeed, around 470 mV the diode behavior becomes tunneling-limited, as expected from the PV measurements. The inversion voltage with the thiol-terminated alkoxy monolayer is in good agreement with our previous measurements of thiol-terminated alkyls, bound to n -Si through Si-C, instead of Si-O-C bonds, but is relatively low compared to the inversion voltage obtained with a methyl-terminated alkyl monolayer junction.²³ A likely reason is that the thiolated monolayer has a more positive dipole than the methyl-terminated one. Our CPD measurements of Si-C bound monolayers gave a 0.4 V difference in Fermi level between the thiol- and the methyl-terminated monolayer.²³

High density methyl-terminated self-assembled monolayers (SAMs) are chemically nonreactive and very hydrophobic. Deposition of a *semitransparent* solid state metallic electrode onto such a monolayer without penetrating it or creating pinholes is still a challenge. To be able, nevertheless, to test if changing the terminating group of the molecules will affect PV performance (by affecting the interface energetics) in the alkoxy systems, we used a methyl-terminated monolayer as an insulator in MOIS cells, but now with Hg as the top contact. PV measurements were done using a white light source, adjusted to yield roughly 100 mW/cm² with a 3300 K black body spectrum.

Naturally, with Hg as top electrode, the photocurrents, shown in Fig. 3, stem solely from light collected from the Hg electrode's periphery, making it not possible to normalize the current in terms of current density. However, because current is collected from the areas surrounding the electrode, it is likely to be more affected by surface recombination than in a usual solar cell or photodetector. Therefore, the V_{oc} and FF, measured on this structure, present lower limits for a full PV device.

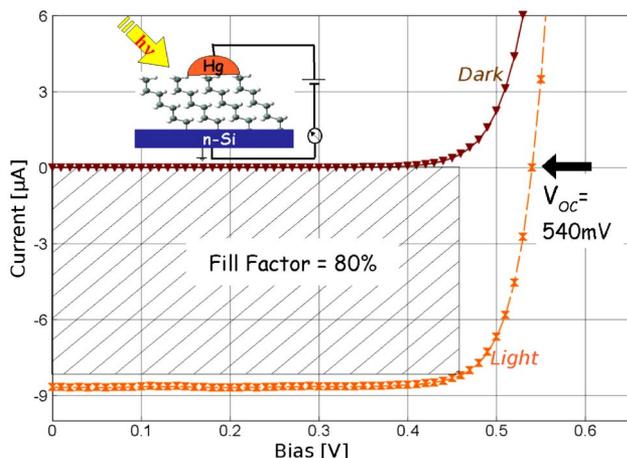


FIG. 3. (Color online) PV measurement on a junction, made by contacting an *n*-Si surface, to which a monolayer of $(\text{CH}_2)_{11}\text{CH}_3$ molecules is bound via Si–O–C bonds, with Hg (*n*-Si–O–C₁₁/Hg). Illumination was with a Zeiss KL-2500 fiber light source adjusted to produce ~ 100 mW/cm² with a 3300 K blackbody spectrum. The junction showed a low dark ideality factor $n=1.09$ and, under illumination, 80% FF and 540 mV open-circuit voltage. Geometric contact area: 0.2 mm².

The junction in Fig. 3 showed an excellent, low, dark ideality factor ($n=1.09$) and, under illumination, 0.8 FF. The V_{oc} was 540 mV, respectable for *n*-Si based MIS cells of that resistivity.²⁴

With the all-covalently bound approach, the MOIS cell's open-circuit voltage may be increased by using amine-rather than thiol-terminated alkoxies, to get a more negative dipole moment, while still allowing binding semitransparent metal films. Alternatively, physisorbing suitable transparent conductors on top of methyl-terminated monolayers so as not to damage the layer, should allow significantly improved performance of these cells. The work in these and other related directions is being pursued in our laboratory.

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