

Blocking thin-film nonuniformities: Photovoltaic self-healing

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An approach is developed to block the effects of lateral nonuniformities in thin-film semiconductor structures. The nonuniformity modulates the surface photovoltage distribution. When exposed to light and immersed in a proper electrolyte, this distribution will generate laterally nonuniform electrochemical reactions. Such treatments result in a nonuniform interfacial layer that balances the original nonuniformity. This approach has been implemented for CdTe/CdS photovoltaic devices, in which it improved the device efficiency from 1%–3% to 11%–12%. © 2004 American Institute of Physics. [DOI: 10.1063/1.1644049]

Large-area semiconductor thin films play a key role in such rapidly growing fields as terrestrial photovoltaics (PV), light-emitting panels, and liquid-crystal display drivers. With active area requirements of up to 1 m², crystalline devices cannot be made, and are either polycrystalline or amorphous; examples are CdTe, copper indium gallium diselenide, and amorphous silicon (*a*-Si:H). Associated with their non-crystallinity are lateral device nonuniformities over micron-length scales. The underlying structure fluctuations include variations in grain size, chemical composition, etc. The structural fluctuation effects are aggravated by barrier-controlled transport that is exponentially sensitive to the barrier parameters related to the device junctions and grain boundaries. Considerable lateral nonuniformities have been observed in all major thin-film PV by different mappings, and in the form of variations between nominally identical devices (see Refs. 1, 2, and references therein). They have also been indicated in multicrystalline silicon solar cells.³

Understanding of lateral fluctuations lies in the device diode nature and in the electrode resistivity that is substantial for optically transparent electrodes. Hence, an equivalent circuit of random microdiodes connected in parallel through a resistive electrode represents a thin-film PV cell.^{1,2} In the ideal-diode approximation, each microdiode current–voltage (*j*–*V*) characteristic is

$$j = j_0 \{ \exp[e(V - V_{oc})/kT] - 1 \}, \quad (1)$$

where *kT* and *e* have their standard meaning. The open-circuit voltage *V*_{oc} fluctuations have exponentially strong effects, and seem to be the major source of nonuniformity.

Weak (low *V*_{oc}) microdiodes are most detrimental to the device, since they find themselves under forward bias generated by their more robust neighbors. As a result, they (a) rob currents, thereby decreasing the device-generated power; and (b) localize stresses and thus promote nonuniform degradation.^{1,2,4} Based on this understanding, blocking weak diodes seems to be a straightforward way of improving device performance and stability. A nontrivial part of the problem dealt with in this letter is to devise a treatment that selectively

blocks the weak diodes while keeping the rest of the device intact (curiously, a red wine can be such a treatment⁵).

Our approach is illustrated in Fig. 1, where the surface photovoltage varies across a semiconductor film exposed to light and immersed in an electrolyte. The surface potential variations bring about currents in the electrolyte that (in accordance with Le Chatelier's principle) tend to reduce those variations. In a properly chosen electrolyte, this may result in selective etching and/or depositing local surface “clogs” at the weak diode spots where the electric potential is a minimum. If these surface modifications are electrically insulating or otherwise active (electric double-layer, etc.), then the weak diodes will be blocked (passivated) and will not affect the device performance after subsequent metal deposition. We call such a process self-healing to reflect the fact that it selectively acts on the weakest spots of the device.

This process can also be described in terms of an interfacial layer (IFL) deposited on a semiconductor thin film to level out its lateral nonuniformity. Indeed, it was recently shown⁴ that a properly selected IFL can cause such an effect in commercially available thin-film CdTe devices, although the mechanisms behind the IFL action remained a puzzle.

Theoretical Analysis. Two factors were taken into account in designing a proper electrolyte treatment. The first one is to use the fluctuations of *V*_{oc} to drive electrochemical reactions that selectively target weak spots.

The second factor is the electrolyte resistivity *ρ*. On physical grounds, the smaller the value of *ρ*, the larger is the characteristic length *L_e*, across which electrically different spots in the film surface interact through the electrolyte [cf.

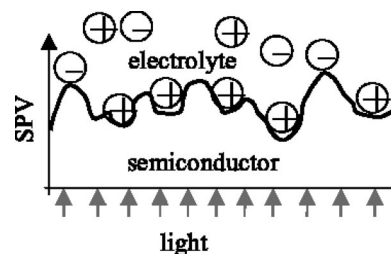


FIG. 1. Sketch of the experimental setup of selective electrochemical treatment. The fluctuating surface photovoltage (SPV) corresponds to the CdTe surface of CdS/CdTe polycrystalline device.

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Eq. (3)]. To ensure that the treatment effectively levels out the nonuniformities, L_e needs to be greater than the characteristic nonuniformity length in a completed device under working conditions.

To further specify the latter criterion, one should discriminate between the microstructure nonuniformity length l and the length of the electric nonuniformity L induced by variations in local microdiode parameters. Typically, l varies in the range of microns to hundreds of microns.^{1–3} L is determined by the presence of an electrode, through which a micrononuniformity extends its influence across significant distances (say, $L \sim 1$ cm), as explained next. Since $L \gg l$, the criterion becomes $L_e > L$.

The length L can be expressed as¹

$$L = \sqrt{|u|/Rj_0}. \quad (2)$$

The physical meaning of L is that the electric potential fluctuation u is balanced by the potential drop $j_0 L^2 R$ across the resistive electrode of linear dimension L . Here, R is the sheet resistance and the current is $j_0 L^2$. The maximum L_{\max} corresponds to a dead shunt ($u = V_{oc}$). The minimum L_0 is defined by Eq. (2) with $u = kT/e$. Given the typical PV parameters ($j_0 \sim 20$ mA/cm², $R \sim 10$ Ω/□, and room-temperature $kT/e \sim 0.025$ V), $L_0 \sim 3$ mm under 1 sun illumination.

The electrolyte screening length L_e can be derived along the same lines. We take into account that the electric potential drop balancing the nonuniformity u occurs across the effective three-dimensional resistor of the characteristic size L_e , whose resistance is $\sim \rho/L_e$. This yields

$$L_e = |u|/\rho j_0. \quad (3)$$

For a numerical estimate, we consider an electrolyte whose resistivity $\rho \sim 10$ Ω cm, on the order of that of 1 M aqueous NaCl solution. Substituting $kT/e \sim 0.025$ V and $j_0 \sim 20$ mA/cm² as well yields $L_e \sim 1$ mm. The required inequality $L < L_e$ can also be presented in the form

$$\rho < RLj_{0s}/j_{0e}, \quad (4)$$

where j_{0s} and j_{0e} are the currents j_0 corresponding to the light intensities under the device working condition and the electrolytic treatment, respectively. With typical $R \sim 10$ Ω/□ and $L \sim 1$ cm, this results in $\rho \leq 10$ Ω cm. The inequality in Eq. (4) remains valid for higher ρ in combination with lower j_{0e} . Based on Faraday's law, such lower j_{0e} will deposit an equally massive layer over a longer time period $\propto 1/j_{0e}$.

Experimental results. The typical experimental device consists of a 0.15 μm layer of CdS followed by a 3.5–4 μm CdTe layer deposited on commercially available SnO₂-coated glass substrates. The conductive oxide layer of a sheet resistance $R = 15$ Ω/□ served as the front electrode. The semiconductor layers were created by the vapor transport deposition, after which the samples were submitted to the standard anneal in the presence of CdCl₂, which generally leads to improved electrical characteristics.⁶ After the anneal, the typical grain sizes for CdTe were about 1–2 μm. Copper was introduced at the metal–semiconductor junction through the anneal step. This is believed to also lead to the formation of a strongly doped *p*-layer at the CdTe surface,

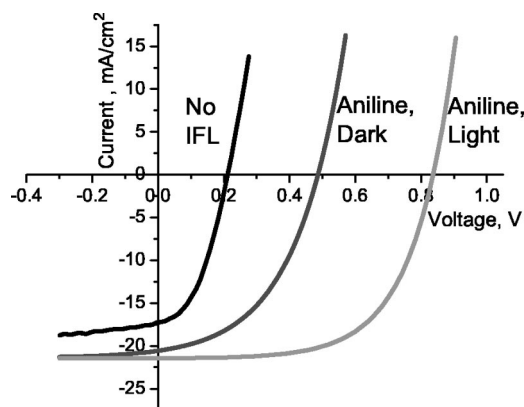


FIG. 2. Effect of electrolyte surface treatments and 1 h, 1 sun exposure to light on the CdS/CdTe I – V curves.

helping in the formation of a good back contact.^{7,8} After the electrolyte treatment (if any), a metal layer was sputtered to form the back contact to CdTe.

For the electrolyte treatments, we used a mixture of 0.2 M aniline, 0.01 M *p*-toluenesulfonic acid, and NaCl in deionized water. (Aniline was chosen for its ability to electropolymerize in acidic media at low potential,⁹ comparable to surface photovoltage fluctuations.) The solution resistivity was in the range from 1 to 200 Ω cm depending on the NaCl content. Light of intensity 0.01 to 1 sun came through the glass side of an incompleting device (before the back contact deposition). The electrolyte was applied at room temperature onto the CdTe side of the structure shown in Fig. 1. The tungsten-halogen lamp light used in our experiments was completely absorbed in CdTe and thus did not interact with the electrolyte. Correspondingly, any difference between the results of “light” and “dark” treatments were attributed to the light-induced effect in the device and not in the electrolyte. A change in the color of CdTe surface to a lighter gray was noticed after effective light treatments but not after dark treatments.

Results shown in Fig. 2 indicate, indeed, a strong positive effect of the electrolyte treatments applied under the light, as opposed to the dark electrolyte treatments. In many cases, the light treatment improved the solar cell efficiency from, say, 2% to more than 11% (some positive effects in the dark-treated cells were not consistent).

We verified that decreasing the light intensity from 1 to 0.1 sun and simultaneously increasing the exposure time by a factor of 10 led to similar improvements in the device parameters. However, over such a long period of time, the acid present in the solution might cause an etching effect, thereby modifying CdTe surface.

To further verify the possibility of etching, we used aniline-free mixtures. Again, a considerable improvement of the light- (but not the dark-) treated samples was observed, even though the degree of improvement was not as significant as that for the aniline-containing solution. When a solution consisting of only NaCl was used, no improvement was observed as compared with a nontreated sample. More experimenting is needed to understand the chemical nature of the aniline effect. Two plausible mechanisms are “clogging” weak diodes and voids (that would otherwise evolve into shunts as metallized), and forming a layer that protects the etched surface from oxidation before the metal is deposited.

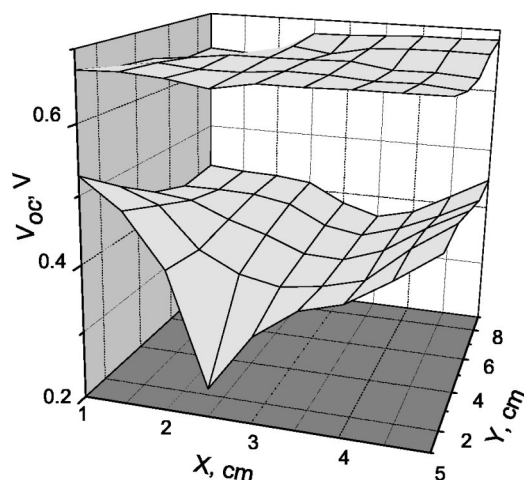


FIG. 3. Open-circuit electric potential variations of CdS/CdTe device with intentionally high resistive back contact (5 nm chrome) under low light of 0.01 sun for the electrolyte treated and untreated cases.

We have also observed that after a given exposure time, the treatment lost its efficiency as the solution resistivity increased. However, simultaneously decreasing the light intensity to the level that keeps the product rj_{0e} intact, and increasing the exposure time $\propto 1/j_{0e}$, restored the treatment effect. This observation is fully consistent with our theoretical understanding and the criterion in Eq. (4). We were able to quantitatively verify the latter criterion by using the parameters of our devices and the measured solution resistivity.

Finally, we have verified a considerable change in the degree of nonuniformity between the light- and dark-treated samples by mapping the V_{oc} distribution in $10 \times 5 \text{ cm}^2$ samples with deposited thin (5 nm) chrome layer, whose sheet resistance ($\sim 1 \text{ k}\Omega$) is high enough to keep the local areas at a distance of $L \sim 1 \text{ mm}$ electrically insulated (under 1 sun illumination). As shown in Fig. 3, the treated samples are indeed more uniform and have higher V_{oc} . Remarkably, the

surface photovoltage in the light- and dark-treated devices was the same before the metal deposition. This is consistent with our understanding of weak microdiodes as a primary nonuniformity source that extend their influence through the electrode.

In conclusion, we have put forward the concept of photovoltaic self-healing that selectively blocks the effects of lateral nonuniformities in thin-film semiconductor structures. We have quantitatively described the required parameters of the underlying electrolyte treatment and devised a specific chemical composition of such a treatment for CdTe/CdS photovoltaic devices. A dramatic improvement in the device efficiency is demonstrated. Our approach may have implications in other semiconductor thin-film technologies.

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¹V. G. Karpov, A. D. Compaan, and D. Shvydka, *Appl. Phys. Lett.* **80**, 4256 (2002).

²D. Shvydka, A. D. Compaan, and V. G. Karpov, *Appl. Phys. Lett.* **82**, 2157 (2003).

³B. L. Sopori and R. Murphy, *Proceedings of the 12th European Photovoltaic Solar Energy Conference*, edited by R. Hill, W. Patz, and P. Helm (Stephens, Bedford, UK, 1994), p. 1797; K. Drope and H. J. Moller, *ibid.*, p. 1359.

⁴D. Rose, R. Powell, U. Jayamaha, and M. Maltby, *Proceedings of the 29th IEEE Photovoltaic Specialists Conference, New Orleans, LA, 18–22 May 2002* (IEEE, New York, 2002), p. 555.

⁵V. G. Karpov, D. Shvydka, Y. Roussillon, and A. D. Compaan, *Proceedings of the 3rd World Conference on Photovoltaic Energy Conversion, Osaka, Japan, 11–18 May 2003* (to be published).

⁶P. V. Meyers, C. H. Liu, and T. J. Frey, U. S. Patent No. 4,710,589 (1987).

⁷R. H. Bube, *Photovoltaic Materials* (Imperial College Press, London, 1998).

⁸R. Birkmire *26th IEEE Photovoltaic Specialists Conference Proceedings, Anaheim, CA, 29 September–3 October 1997* (IEEE, New York, 1997), p. 295.

⁹S. Pruneanu, E. Veress, I. Marian, and L. Oniciu, *J. Mater. Sci.* **34**, 2733 (1999).