

Meaning of the photovoltaic band gap for amorphous semiconductors

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We introduce the concept of a photovoltaic band gap $E_{\text{pv}g}$ for amorphous solar cells. This is the minimum photon energy thermodynamically required for the generation, of *two* free carriers in an operating solar cell. For hydrogenated amorphous silicon the photovoltaic band gap is 1.57 eV at 1-sun illumination.

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The optical absorption edge in amorphous semiconductors is neither as steep nor as sharply defined as in crystalline semiconductors. This leads to an interesting problem when an amorphous solar cell is constructed. Can the low-energy infrared photons absorbed into the optical band tail¹ of an amorphous semiconductor contribute to the photovoltaic effect?

There are two aspects to this question: (a) in the first place, the thermodynamic free energy of a weak infrared photon may be insufficient to drive an electron around an external circuit at a finite open circuit voltage V_{oc} ; (b) the operation of any solar cell requires that the photon absorption event leads ultimately to the creation of both a mobile electron and a mobile hole. While band-to-band absorption easily fulfills this requirement, it is not clear whether an infrared transition from a localized state in the gap to an extended band state will contribute to the photovoltaic effect or not.

This suggests that we write the measured optical absorption coefficient $\alpha(\nu)$ of an amorphous semiconductor as being the sum of two components:

$$\alpha(\nu) = \alpha_2(\nu) + \alpha_1(\nu), \quad (1)$$

where ν is the optical frequency. The component $\alpha_2(\nu)$ represents all those absorption events which create *two* mobile carriers, both an electron and a hole. The component $\alpha_1(\nu)$ represents all other absorption events, especially those transitions from a localized trap state to an extended band state which generate only *one* free carrier.

It is to be expected that $\alpha_1(\nu)$ absorption would contribute to the photovoltaic effect only indirectly. For example, $\alpha_1(\nu)$ absorption might contribute as part of a two-step process whereby two optical transitions in sequence create a single electron-hole pair. Alternatively, one can imagine the opposite situation, that $\alpha_1(\nu)$ absorption might actually hinder solar cell operation by expediting some recombination process.

The effect of the $\alpha_2(\nu)$ absorption process, on the operation of a solar cell is better understood. A statistical mechanical analysis of solar cell operation shows that such an absorption event makes available a free energy of $h\nu - 0.35$ eV for unfocused sunlight at the earth's surface.² Therefore, to be consistent with thermodynamics the photon energy $h\nu$ must be greater than $eV_{\text{oc}} + 0.35$ eV in order to contribute to the photovoltaic effect in a single step absorption process. It follows that $\alpha_2(\nu)$ must drop to zero at low energies. (Here eV_{oc} is the free energy made available by the passage of an

electron through the external circuit.)

This point is illustrated by the following expression for the output voltage for an arbitrary absorption spectrum³ $\alpha_2(\nu)$:

$$eV_{\text{oc}} = kT \log \left[\frac{I_{\text{sc}}}{8\pi} \int \left(\frac{n\nu}{c} \right)^2 \alpha_2(\nu) \exp \left(\frac{-h\nu}{kT} \right) d\nu \right]. \quad (2)$$

In this expression T is the ambient temperature and I_{sc} is the short circuit current in electrons/cm²/s. The integral on the right-hand side of Eq. (2), representing the dark solar cell luminescence, should have as small a value as possible in order to obtain a high V_{oc} . Clearly, if the absorption spectrum $\alpha_2(\nu)$ rises more slowly than $\exp[-h\nu/kT]$ falls, the integral in Eq. (2) becomes extremely large, with the integrand peaking near $h\nu = 0$ instead of near the band edge. In order to avoid this infrared catastrophe, the absorption spectrum $\alpha_2(\nu)$ must truncate sharply on the low-energy side in a real solar cell. The energy at which the photovoltaic spectrum $\alpha_2(\nu)$ is truncated, we will call the photovoltaic band gap, $E_{\text{pv}g}$.

The essential assumption in all solar conversion materials is that there are two groups of quantum levels which act as reservoirs. Within each reservoir there is rapid thermal equilibration, but between the upper and lower reservoir the equilibration should be very slow so that the free-energy difference can be extracted as useful work. In semiconductors the upper group is the conduction band and those shallow electron traps in thermal equilibrium with it. Similarly, the lower group is the valence band and the shallow hole traps. The available free energy is the difference in the quasi-Fermi level ($E_{fn} - E_{fp}$) between the conduction-band group and the valence-band group.

This situation is represented in Fig. 1, where for *a*-Si:H the valence-band tail states are more numerous and extend deeper into the forbidden gap than the conduction-band tail. Therefore, most of the infrared band edge transitions are from the valence-band tail to states above E_c , the optical edge of the conduction band. Transitions from one deep localized state to another are not allowed in this model because of their spatial separation.

To contribute to the photovoltaic effect both the electron and the hole must be capable of becoming mobile before recombination. Shallow trapped holes will tend to be thermally excited into the mobile hole states prior to recombination, while deep trapped holes will recombine with free electrons before ever becoming mobile. In other words, shallow

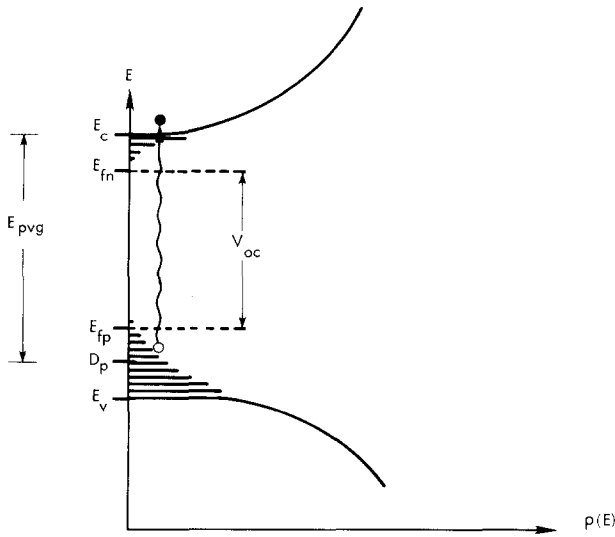


FIG. 1. Energy-level diagram appropriate to *a*-Si:H under illumination. The photovoltaic band gap is $E_c - D_p$, the difference between the electron mobility edge and the hole demarcation level. The wavy arrow illustrates an $\alpha_1(\nu)$ type photon absorption event producing a free electron and deep trapped hole.

holes are in equilibrium with the valence-band group of levels and will contribute to the photovoltaic effect, while the holes in deep traps can only contribute as part of a multistep process. The hole demarcation energy level⁴ D_p separates the two types of states. Therefore D_p defines the effective edge of the valence-band group of levels, and the photovoltaic energy gap is the separation ($E_c - D_p$). Absorption events from below D_p contribute to $\alpha_2(\nu)$ while absorption events from above D_p contribute only to $\alpha_1(\nu)$. A similar argument can be given for the electron demarcation level, but its contribution is expected to be negligible since the conduction-band edge is sharp compared to the valence-band edge.

In order to experimentally distinguish between $\alpha_1(\nu)$ and $\alpha_2(\nu)$ we used the experimental arrangement shown in the lower right-hand corner of Fig. 2. An *a*-Si:H solar cell consisting of an *n-i-p* structure was illuminated through a transparent conductive coating on the *n* layer. The light source consisted of a steady white light bias illumination and a weak monochromatic beam modulated at 7 Hz. The circuit was arranged so that the ac load resistor R_i was small enough for the lock-in amplifier to monitor the ac short circuit current induced by the modulated light beam. The dc output voltage of the solar cell was controlled by an adjustable load resistor R_L . The dc bias condition could be varied all the way from open circuit, $V = V_{oc}$, to short circuit, $V = 0$.

The output of the lock-in amplifier is plotted against modulation wavelength in Fig. 2. As the lowest curve in Fig. 2 shows, the infrared photons produce a *negative* photocurrent under dc open circuit conditions; i.e., they actually *reduce* the output power generated by the solar cell. Similar behavior was observed in all of the high V_{oc} solar cells which we tested. As the dc output voltage V is reduced from the open circuit condition, the zero crossing moves to longer wavelengths and the negative part of the infrared response goes to zero and then becomes positive. For the case shown in Fig. 2, the infrared response becomes zero when the solar

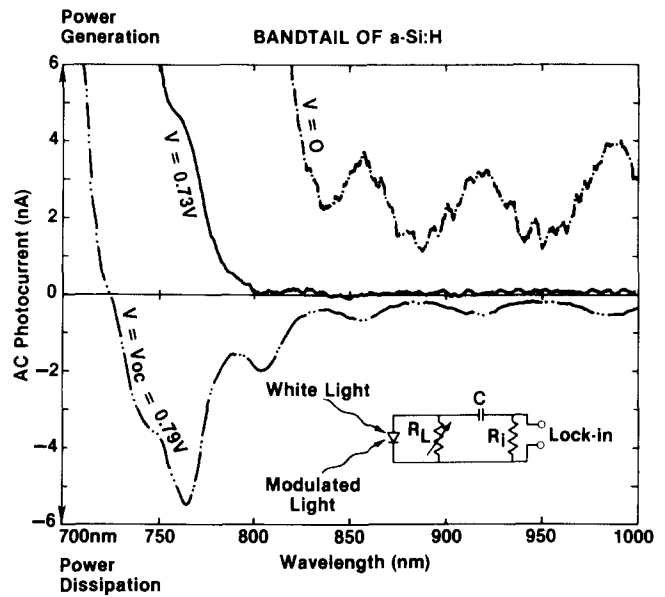


FIG. 2. ac modulated photoresponse of an *a*-Si:H solar cell under three different load conditions, open circuit (---), short circuit (—), and an intermediate case (— · —) at a dc output voltage = 0.73 V.

cell is loaded down to $V = 730$ mV, from an open circuit voltage $V_{oc} = 790$ mV. At all dc output voltages below 730 mV the infrared response in the 700–1400-nm range is positive, i.e., in the power generating direction.

The negative infrared response is due to the $\alpha_1(\nu)$ process which makes the material photoconductive, degrading the reverse leakage current without contributing to a net photovoltaic current.

The measurement in Fig. 2 was repeated at different intensities of the dc bias light. For each intensity the value of the dc output voltage was adjusted to null the infrared response. Two such spectra are plotted in Fig. 3. For comparison, the spectrum at zero output voltage is also plotted. The interference fringes of the raw data in Fig. 2 were suppressed by plotting the center point of each fringe in Fig. 3, and the spectrum was normalized to the incoming number of photons.

As can be seen, the photovoltaic band gap shifts to higher energies with increasing bias light intensity, due to a corresponding shift in D_p toward the valence band. The solid lines in Fig. 3 are a fit of $\alpha_2(\nu)$ to the expression

$$\alpha_2(\nu) = K \int_{E_c}^{\infty} \rho_v(E - h\nu) \rho_c(E) dE, \quad (3)$$

where K is a normalization constant which depends on the optical matrix element. Equation (3) is a convolution of the conduction and valence-band densities of states. The conduction-band state density above its optical edge E_c was modeled as a parabolic band $\rho_c \propto \sqrt{E - E_c}$. The valence-band tail state density was assumed to be exponential; $\rho_v = \exp[-E/E_0]$ for $E < D_p$. Above the demarcation level the state density is truncated by the Boltzmann probability for thermal ionization of the trapped hole:

$$\rho_v = \exp[-E/E_0] \exp[(D_p - E)/kT] \text{ for } E > D_p.$$

The exponential valence-band tail slope was taken⁵ as

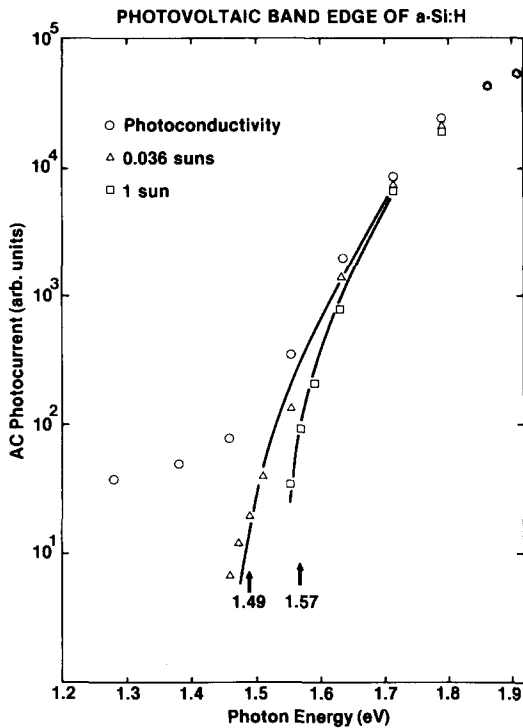


FIG. 3. Photovoltaic spectrum for a solar cell at two different intensities: (Δ) 0.036 suns and (\square) 1.0 suns. In each case the output voltage of the cell was adjusted so as to null the long wavelength response as discussed in the text. The solid curves are fits generated from Eq. (4) with E_{pvg} as indicated by the arrows; the circles (\circ) show a spectrum at zero output voltage for comparison.

$E_0 = 50$ meV. Adjusting only the energy D_p of the demarcation level, we found the best fit with a photovoltaic band gap of 1.49 and 1.57 eV for the two conditions of bias light illumination of 0.036 and 1 sun, respectively.

The location of D_p in the gap can be estimated from the definition of the demarcation level,⁴ namely that at D_p the capture rate for electrons equals the thermal detrapping rate for holes:

$$K_e n = K_h N_v \exp [(E_v - D_p)/kT], \quad (4)$$

where K_e and K_h are the capture probabilities for electrons and holes respectively, N_v is the density of states at E_v the

valence-band mobility edge, and n is the number density of free electrons. From measurements of electron mobility and photoconductivity⁵ we know that $n \approx 6 \times 10^{13}/\text{cm}^3$ in this material at 1-sun illumination. Also K_e/K_h has been estimated⁶ to be 200 and N_v is $\sim 10^{19}/\text{cm}^3$. With these estimates, $(D_p - E_v) = kT \ln(K_h N_v / K_e n) \approx 0.17$ eV. Adding this to E_{pvg} , the mobility gap is 1.74 eV which is in good agreement with estimates arrived at by other methods.⁷

At bias illuminations of less than 1 sun the free-electron density n in Eq. (4) is smaller, and therefore E_{pvg} is also smaller. Since the short circuit photocurrent in these solar cells scales linearly with light intensity F we assume the free-electron density n also scales linearly with F . Therefore, a reduction in bias illumination changes the photovoltaic band gap by $kT \ln(F/F_0)$, where (F/F_0) is the reduction in bias illumination between the two curves in Fig. 3 or 0.036. It follows that the shift should be 83 meV, in excellent agreement with the actual shift in Fig. 3 of $(1.57 - 1.49)$ eV = 80 meV.

In conclusion, we have shown that the photovoltaic response of amorphous solar cells truncates sharply to zero at long wavelengths even though the optical absorption and photoconductivity spectra remain finite. This sharp threshold is necessary to satisfy the requirements of thermodynamics and defines a photovoltaic band gap E_{pvg} , which is 1.57 eV in α -Si:H under 1-sun illumination.

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