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Bandtail Limits to Solar Conversion Efficiencies in Amorphous Silicon Solar Cells

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ABSTRACT

We describe a model for a-Si:H based *pin* solar cells derived primarily from valence bandtail properties. We show how hole drift-mobility measurements and measurements of the temperature-dependence of the open-circuit voltage V_{OC} can be used to estimate the parameters, and we present $V_{OC}(T)$ measurements. We compared the power density under solar illumination calculated with this model with published results for as-deposited a-Si:H solar cells. The agreement is within 4% for a range of thicknesses, suggesting that the power from as-deposited cells is close to the bandtail limit.

INTRODUCTION

For most of the interval since its discovery thirty years ago, a fairly large proportion of basic research on hydrogenated amorphous silicon (a-Si:H) has been concerned with its "D-centers," or silicon dangling-bond defects. These defects are certainly electronically active, and they exhibit fascinating metastabilities (the Staebler-Wronski and related effects) that have eluded fundamental understanding for decades.

For solar cells, the fascination with defects obscures the possibility that a-Si:H solar cells may be fairly close to their "zero-defects" conversion efficiency. "Zero-defects" simply means the limit for solar cell parameters that would be achieved if the density of D-centers or other defects were zero. In Figure 1 we have illustrated some measurements on *pin* solar cells from United Solar Systems Corp. both in their as-deposited and light-soaked states [1]. We have also illustrated an idealized model calculation that uses parameters consistent with typical hole and electronic drift-mobility measurements, but that neglects defects altogether. Subsequently, we describe this model in more detail. The model calculation very accurately predicts the conversion efficiency of as-prepared cells. The agreement of the calculation and the measurements suggests that the power density of the as-prepared state can be largely understood without recourse to defects.

Indeed, because the electron drift-mobilities in a-Si:H are *much* larger than hole drift-mobilities, they are also largely irrelevant to the power-density, and this is why we used

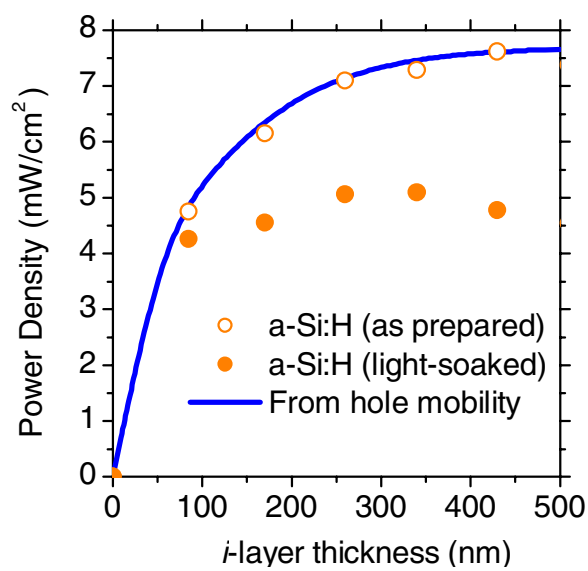

Figure 1: Symbols indicated the power (under solar simulator illumination) for a-Si:H solar cells with varying absorber-layer thickness. The line is a model calculation described in the text.

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the legend "from hole mobility" to label the model calculation in Figure 1. Since the very low drift-mobility of holes in a-Si:H is a consequence of the broad valence bandtail in a-Si:H, the "zero-defects" model is the "bandtail limit" to conversion efficiencies.

In this paper, we first discuss the relationship hole drift-mobility measurements to the valence bandtail parameters conventionally used for modeling of hole tr ansport in non-crystalline semiconductors. As we shall see, the valence bandtail parameters are not completely specified by the hole measurements. We then discuss the use of open-circuit voltage measurements to add additional about bandtails.

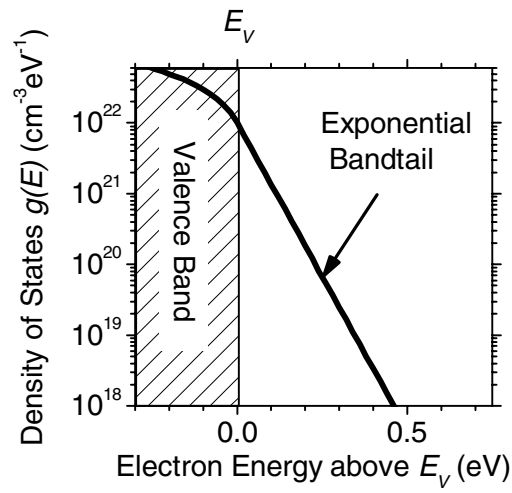

Figure 2: An exponential bandtail lies above the valence band in a-Si:H and other non-crystalline semiconductors; the bandtail leads to very low hole mobilities in a-Si:H.

MODELING AND HOLE DRIFT MOBILITY MEASUREMENTS

Valence Bandtail Parameters for Solar Cell Modeling

Figure 2 illustrates the density of electronic states *g(E)* near the edge of the valence band. Note the exponential bandtail that extends beyond the edge E_V of the valence band. This figure is the basis for most electrical transport models for holes in amorphous semiconductors; four independent parameters are involved. Holes occupying valence band states are mobile, possessing a "microscopic" or "band" mobility μ_h^0. Bandtail states (beyond E_V) act as traps that capture and immobilize holes moving in the valence band proper ($E < E_V$); the width of the bandtail ΔE_V is of course very important. Only two other parameters [2] are required to characterize hole transport:

1. The effective bandedge density-of-states N_V.
2. The capture coefficient b_t that describes the rate of capture of a free hole to a particular bandtail trap; b_t is usually assumed to be the same for all bandtail states.

Parameterization of Hole Drift Mobility Measurements

The "drift-mobility" of holes determined by measuring their time-of-flight across some specified distance is much lower than μ_h^0 because of the trapping processes. In addition to μ_h^0, the drift-mobility is determined by the width of the exponential bandtail ΔE_V, and also by an "attempt-to-escape" frequency ν. ν describes the rate R at which a trapped carrier is thermally released; more specifically, $R = \nu \exp(-\delta E/kT)$, where δE is the binding energy of the carrier to the trap. ν is equated by "detailed-balance" to the product $N_V b_t$.

In Table I, we summarize these three parameters as they have been reported for

Table I: Valence Bandtail Parameters from Hole Drift-Mobility Measurements

Sample	ΔE_V (eV)	ν (s^{-1})	μ_h^0 (cm^2/Vs)	Ref.
PSU (1999)	45	1.0×10^{12}	0.7	3
ECD (1990)	48	7.7×10^{10}	0.27	4

two a-Si:H materials. We shall take the ECD (1990) measurement as characteristic of earlier samples (cf. [4]). We shall take the PSU (1999) measurements as characteristic of "contemporary" materials [3]. The particular parameterizations are less significant than the fact that the PSU mobility (1999), and more generally the hole drift-mobilities in contemporary a-Si:H, have increased several times over values for earlier samples. There has not yet been a study of the best procedures for estimating the parameters from drift-mobility measurements, nor are there systematic studies of how the valence band parameters vary with deposition conditions.

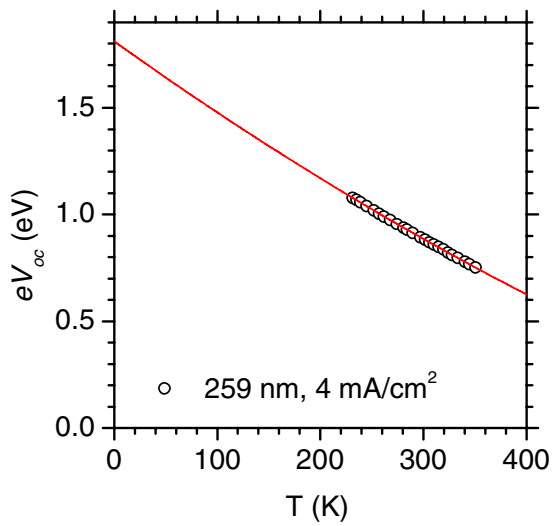

Figure 3: The symbols indicate the temperature-dependence of the open-circuit voltage (laser illumination at 685 nm, 4 mA/cm^2; sample thickness 259 nm). The solid line is the best quadratic fit.

OPEN-CIRCUIT VOLTAGES AND THE BANDEDGE DENSITY-OF-STATES

Within the exponential bandtail model, it is interesting that the hole drift-mobility requires only 3 parameters for its description, whereas general hole transport processes require 4. The fundamental reason for this difference is that hole drift-mobilities are measured in a "linear response" regime, in which photocurrents depend linearly upon the intensity of illumination. The additional valence bandtail parameter is necessary to describe nonlinear effects, which certainly include operating solar cells. In addition, even the simplest bandtail-limited model also requires the bandgap E_G, the effective conduction band density-of-state N_C., and the recombination coefficient b_R describing electron capture by a hole in the valence bandtail. The parameter b_R has been estimated from high-intensity photoconductivity measurements; two independent measurements gave essentially the same value $b_R = 10^{-9}$ cm^3/s [5,6]. We neglect the conduction bandtail; electron drift-mobility measurements indicate the conduction bandtail does not affect electron transport near room temperature.

We now report on our effort to estimate the remaining three parameters, N_V, N_C, and E_G, by using temperature-dependent V_{OC} measurements. This approach is based on the assumption that V_{OC} can be modeled using only bandtail parameters, so that defects are negligible, and p and n layer interfaces are ideal. Given these assumptions, V_{OC} may be analytically calculated for uniform photogeneration G [7]:

$$eV_{OC} = E_G + \frac{kT}{2}\left\{\ln\left(\frac{G}{b_R N_C^2}\right) + 2\ln\left(\frac{G}{b_T N_V^2}\right)\right\} - \frac{(kT)^2}{2\Delta E_V}\ln\left[\frac{b_R}{b_T}\left(\frac{G}{b_T N_V^2}\right)\right] \qquad (1)$$

This expression is valid for $kT < \Delta E_V$. Note that the linear term in T is determined primarily by N_C and N_V; the exponential bandtail causes a curvature in the V_{OC} vs. T relation.

Temperature-Dependent V_{OC} Measurements

We have measured $V_{OC}(T)$ for a series of three *pin* solar cells prepared at United Solar Systems Corp. with varying intrinsic layer thickness. The measurements were done with a diode laser (λ = 685 nm) adjusted to maintain constant photocurrent density of 4 mA/cm^2 under reverse bias. Results for one cell are shown in Figure 3 along with a simple quadratic fitting.

The quadratic fitting parameters cannot be directly identified with the parameters in equation (1) because the bandgap itself is temperature-dependent. We adjusted the fitting parameters for the temperature-dependence of the bandgap published by Cody [8]. We measured the bandgap optically (using the peak of the electroabsorption spectrum) for one sample at 200 K and 300 K, and found that Cody's form was consistent with our measurements.

Table II: Bandtail parameters estimated from $V_{OC}(T)$

Sample	$N_C = N_V$ (cm^{-3})	ΔE_V (meV)	E_G^e (293K)
259 nm	4.2×10^{20}	49 (5)	1.74 (0.01)
445 nm	4.5×10^{20}	56 (6)	1.76 (0.01)

With this adjustment, we calculated the parameters in Table II from the quadratic fit. We set $b_T = N_V/\nu$ using the value of ν from the PSU (1999) sample in Table I. We assumed $N_C = N_V$; this assumption is arbitrary, but unavoidable at present. We have indicated some statistical errors in parenthesis. The thickest sample (599 nm) was not well described by the quadratic form, and we have not included fitting parameters. We do not know why the quadratic form failed in this case; one speculation is that the *p/i* interface is degraded for the thicker sample.

The most interesting outcome of this fitting experiment is the value for N_C and N_V, which is about 4×10^{20} cm^{-3}. These values seem fairly compatible with estimates of the bandedge density-of-states $g(E_V) = 10^{22}$ $cm^{-3}eV^{-1}$ from electron photoemission experiments [9] (see endnote [2] for a formula connecting $g(E_V)$ and N_V).

One indicator of the systematic errors of this fitting procedure is the bandtail width that was estimated from the curvature of the $V_{OC}(T)$ relation. If the theoretical approach is correct, we expect these estimates to agree with those from photocarrier time-of-flight; in reality, they are somewhat larger. There are at least two possible sources for this modest systematic error in the analysis. First, the parameter ν is taken from hole drift-mobility measurements on different material than the solar cell measurement; we hope to rectify this deficiency in future work. Second, we have neglected both intrinsic-layer defects and interfaces in the theoretical expression for V_{OC}.

We do have evidence that defects are affecting V_{OC} under the conditions of our temperature-dependence measurements. In Figure 4 we show the correlation of V_{OC} with the midgap absorption coefficient α for the intrinsic layer. The different symbols represent successive states of light soaking. α was measured using the infrared photocurrent of the cell under reverse bias, and is an indication of the density of defects in the intrinsic layer of the cell.

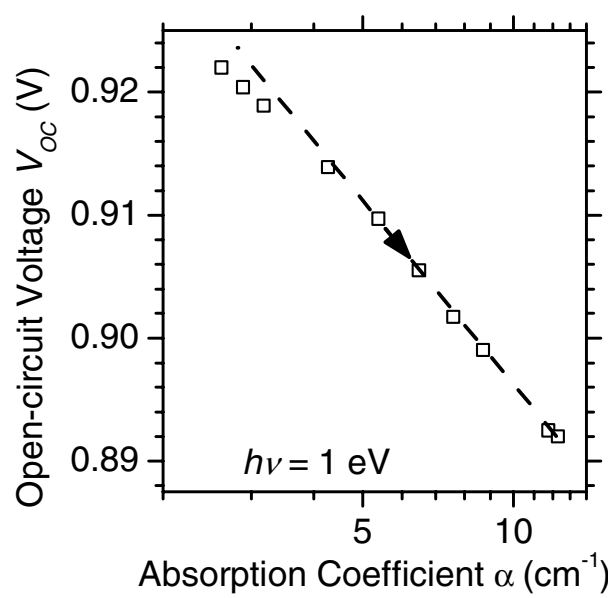

Figure 4: The decline in the open-circuit voltage ($\lambda = 685$ nm, 4 mA/cm^2) as light-soaking proceeds is plotted parametrically against the infrared absorption coefficient (1 eV photon energy). The intrinsic layer thickness was 445 nm.

The leftmost data in Figure 4 indicate the state of the sample following the $V_{OC}(T)$ measurement. In the low defect-density limit, we expect the line traced by the curve to be essentially horizontal (i.e. independent of the

defect density). It is evident that the measurements have not reached this limit.

SOLAR CELL MODELING

The solid line in Figure 1 is a computer calculation for the power-density in a-Si:H solar cells with varying thicknesses based on the bandtail parameters introduced in this paper. The calculations were done using the AMPS 1D program (Pennsylvania State University®). In this section we summarize the main issues in this modeling.

We used the minimal set of intrinsic-layer parameters in Table III. These are based on the hole time-of-flight measurements (bandtail width, band mobility, and attempt-frequency; PSU [1999] sample) in Table I; since the AMPS 1D program limits bandtail widths to multiples of 10 meV, we needed to modify the fitting parameters, accepting a somewhat inferior fit. We took the bandgap and the effective band densities-of-states $N_V = N_C$ from the 259 nm sample in Table II, but did not use the bandtail width from this table; the time-of-flight measurements are plainly more appropriate. The bandtail-trapping coefficient b_T was calculated using detailed balance ($b_T = \nu/N_V$). The recombination parameter b_R was taken from high-intensity photoconductivity studies [5,6]. The modeling program actually uses cross-sections $\sigma = b/v_{th}$, where v_{th} is (arbitrarily) set to 10^7 cm/s. The exponential valence-bandtail prefactor $g(E_V)$ was calculated from N_V and ΔE_V using the formula in endnote [2], which assumes that the bandedge E_V lies within the exponential bandtail.

Table III: Summary of Bandtail Parameters

Parameter	*AMPS 1D Symbol*	*Value*
Electrical Bandgap E_G	EG	1.74 eV
Conduction band density of states N_C	NC	4×10^{20} cm^{-3}
Electron band mobility μ_e	MUN	2 cm^2/Vs
Valence band density of states N_V	NV	4×10^{20} cm^{-3}
Hole band mobility μ_h^0	MUP	0.3 cm^2/Vs
Valence bandtail width ΔE_V	ED0	0.040 eV
Bandtail prefactor g_V^0	GD0	6×10^{21} $cm^{-3}eV^{-1}$
Bandtail trapping cross-section 10^{-7} b_T	TSIG/PD	1.3×10^{-16} cm^2
Bandtail recombination cross-section $10^{-7}b_R$	TSIG/ND	10^{-16} cm^2

The p and n layer parameters will not be discussed here; we chose parameters that yielded "ideal" n and p layers that did not significantly affect the calculated results.

We assumed that the front surface and back surface reflectivity of the interfaces to the cell were zero; the optical absorption properties of the cell are "typical values" for a-Si:H prepared by RF plasma deposition, and were not specifically matched to the particular series of cells in Figure 1.

DISCUSSION

The agreement between the calculated power density in Figure 1 and the experimental measurements on an as-deposited series of cells is striking. The quantitative agreement needs to be understood in the context of the generic optical properties (reflectivity and absorption) that were assumed by the model; it is probable that there are discrepancies of several percent in the absorbed photon flux for the model and the actual cells.

The power densities in Figure 1, for both the measured points and the calculated curve, tend to saturate for thicknesses greater than about 150 nm. Although we cannot discuss this in greater depth here, for the model this thickness is determined by the hole drift-mobility [7]. In essence, there is a space-charge region of slowly drifting hole photocarriers near the *p/i* interface, and nearly all of the electrical power generated by the cell is associated with photocarriers absorbed

in this space-charge region. The agreement between the calculations and the as-deposited cells suggests that the as-deposited cells are close to the fundamental bandtail limit to conversion efficiencies, and thus that further improvements in the as-deposited cells will require improvements in valence bandtail properties.

The (intentional) limitation in these considerations is that they do not apply directly to the light-soaked state, which has a power density lower by about 30% than the as-deposited state. Still, it is odd that the light-soaked cells are as close to the bandtail limit as they are; while a 30% diminishment in cell efficiency is very harmful to device application, it is not a vast change in how the cell operates. One doesn't know that improving bandtail properties will lead to improvements in light-soaked properties as well, but the nearness of the light-soaked and bandtail-limited states for cells suggests that this will be an interesting direction for further device physics research.

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