

# Highly efficient charge transfer in nanocrystalline Si:H solar cells

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We demonstrate that in nanostructured films of nanocrystalline silicon imbedded in a hydrogenated amorphous silicon matrix, carriers generated in the amorphous region are transported out of this region and therefore do not recombine in the amorphous phase. Electron paramagnetic resonance (EPR) and photoluminescence (PL) measurements show that the EPR and PL from the amorphous phase are rapidly quenched as the volume fraction of Si nanocrystals exceeds about 30 vol. %. We propose the use of similar structures to dramatically increase the open circuit voltages in solar cell devices. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4795940>]

The quest for clean, inexpensive sources of energy has produced intense interest in low-cost methods for dramatically increasing the efficiencies of solar cells.<sup>1,2</sup> Standard solar cells have limitations<sup>3</sup> on their theoretical efficiencies in part due to the fact that carriers excited by light with energies above the semiconductor's band gap quickly lose some of their energy to heat (thermalize), which can be overcome by collecting the carriers before they thermalize.<sup>4–13</sup> However, since carriers thermalize over very short times and distances, one must employ a nanostructured morphology. This morphology is an inorganic analog to the bulk heterojunctions utilized in organic solar cells except that both carriers are collected in the same phase.

Here, we report results that suggest the possibility of using an amorphous semiconducting absorber in a nanostructured environment to collect carriers (both electrons and holes) in a crystalline matrix before they fully thermalize and recombine or get trapped. Even if the carriers relax into the localized band-tail states, we propose the use of these structures to increase the open circuit voltages ( $V_{OC}$ ) in solar cells by transferring carriers to a wider-gap crystalline phase before complete thermalization. Specifically, we demonstrate that carriers generated in the amorphous region are transported out of this region and therefore do not recombine in the amorphous phase. This result establishes the possibility of using a wide range of nanostructured amorphous matrices to dramatically increase the efficiencies of solar cells. Since amorphous materials can be grown over a much wider composition space than crystalline materials, this procedure greatly broadens the absorbing materials that can be used to increase the efficiencies of solar cells.

Ultimately one may imagine using amorphous absorbers to collect hot carriers. Since hot carrier solar cells ultimately rely on selective collectors that pick off the excited carriers

at the peak of their energetic distribution, the task is difficult with crystalline semiconductors where both momentum and energy must be conserved during the transfer but may be easier for amorphous absorbers where crystal momentum is not applicable. There have been a number of attempts, none completely successful, to collect the carriers before they thermalize by losing their excess energy to lattice vibrations (phonons),<sup>4–11</sup> and several of these attempts use crystalline Si quantum dots as the absorbing layers.<sup>6,8,10,11</sup> By carefully designing the nanostructures, cooling rates can be decreased.<sup>14</sup> Recently, the transfer of hot carriers from crystalline PbSe nano-crystals to a selective electron acceptor,  $TiO_2$ , and transfer of hot carriers from graphene have been demonstrated.<sup>15,16</sup> To date, little, if any, effort has been devoted to the potential of ultimately using amorphous materials as the absorber. In an amorphous semiconductor, carriers can be absorbed over a wide energy range of extended states that exist above the “mobility edge” that separates the localized electronic states from the extended states. The benefits of an amorphous absorber are the relaxation of the momentum selection rules,<sup>17</sup> and although somewhat controversial, slower relaxation rates than in crystalline counterparts.<sup>18</sup>

As a test bed, we employ a composite film consisting of 0% to >90% by volume nanocrystals of silicon imbedded in a hydrogenated amorphous silicon (a-Si:H) matrix (these composites are hereafter called nc-Si:H) made by plasma enhanced chemical vapor deposition. The nanocrystals are approximately elliptical (4 nm by 20 nm) with the long axis [110] aligned along the growth direction.<sup>19</sup> These nanocrystals are randomly distributed and uniform throughout the thickness of the film, which implies that the hydrogenated amorphous regions are of a similar size with a similar distribution.<sup>19</sup> (This uniform morphology is different from most of the samples reported previously.) For the volume fractions well above the classical percolation threshold (0.3 crystalline volume fraction for spheres in a continuum model), carriers that enter a Si nanocrystal diffuse to a contact entirely within the crystalline phase. The interfacial energetics of our test bed are not appropriate for a hot carrier solar cell because

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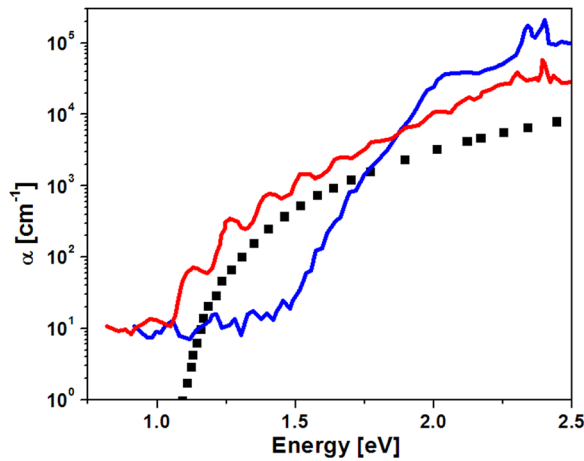


FIG. 1. Optical absorption spectra. Optical absorption spectra measured by photothermal deflection spectroscopy. Data for a-Si:H (black curve, blue curve online), data for nc-Si:H with a nanocrystalline volume fraction of approximately 0.5 (grey curve, green curve online), and bulk crystalline Si (squares, red squares online), all at 300 K. The absorption below 1.5 eV for a-Si:H is surface absorption. Above 2.3 eV, the spectra for a-Si:H and nc-Si:H are saturated and therefore not reliable.

the (indirect) band gap of the silicon nanocrystals (1.2 eV) is less than that of the amorphous form (1.6–1.9 eV, depending on the definition), and there is no selective collector state at the appropriate energy to match hot carriers in the a-Si:H. However, this test bed allows us to demonstrate that in a nanoscale amorphous matrix with dimensions on the scale of approximately 5 by 20 nm, carriers excited above the band gap can be transported out of the amorphous phase before they recombine (either radiatively or non-radiatively). If the collection medium was a wider gap semiconductor, such as smaller, quantum-confined Si nanodots or SiC nanodots with good electron and hole mobilities, then in solar cells even with amorphous absorbers, energy efficiencies can be increased by collecting carriers at higher energies. (Once in the crystalline phase, the carrier transport should be the same as in the samples described in this work, namely dominated by trapping and de-trapping from surface states on the nanocrystals.) This is particularly important because there is evidence that the mobilities in nanodots of Si can approach those of bulk crystalline Si (Ref. 20) especially if the dots are free of impurities, namely oxygen.<sup>21</sup>

The absorption spectra (semi-log scale) for nc-Si:H (with a crystalline volume fraction of 0.5 as measured by Raman spectroscopy and transmission electron microscopy),

a-Si:H, and crystalline Si at 300 K are shown in Fig. 1. Near 1.2 eV, the excitation is probably directly into the nanocrystalline phase or perhaps into surface states on the nanocrystals. On the other hand, above about 2 eV, the excitation is almost certainly in the amorphous regions since the contribution from crystalline Si, and therefore of the nanocrystalline component of nc-Si:H, is significantly weaker at all temperatures. Figure 1 shows that one can preferentially excite carriers in either the nanocrystalline or the amorphous region by changing the exciting wavelength from about 1.2 to 2.5 eV.

Figure 2(a) shows the low-temperature photoluminescence (PL) spectra excited at 2.4 eV (with the absorption occurring primarily in the amorphous regions) for three nc-Si:H samples with crystalline volume fractions varying from approximately 0.1 to 0.8. Also shown in this figure is the well-known PL spectrum for a-Si:H (zero crystalline volume fraction), which peaks near 1.4 eV. This spectrum is universally attributed to recombination between electrons trapped in localized conduction-band-tail states and holes trapped in localized valence-band-tail states.<sup>22</sup> At low temperatures, the quantum efficiency for these transitions is close to unity.<sup>22</sup> These localized electronic states exist at the edges of the bands as a result of the disorder in a-Si:H. At low temperatures, carriers trapped deeply enough in localized states either remain in these states or eventually recombine. Because the excited carriers quickly thermalize into these localized states where the mobilities are orders of magnitude lower than in the extended states of a-Si:H, there has been little interest in using a-Si:H to collect carriers at higher energies in devices.

However, the nc-Si:H samples in Fig. 2(a) also show a second PL band near 0.9 eV that is attributed to recombination between carriers trapped at defect states at the nanocrystalline grain boundaries.<sup>23</sup> This band is never present in high quality a-Si:H. It is apparent from Fig. 2(b) that there is a rapid quenching of the PL from the amorphous regions of nc-Si:H relative to the nanocrystalline regions as the nanocrystalline volume fraction exceeds approximately 0.4. As is well known from experiments on III-V quantum confined systems,<sup>24</sup> this PL quenching is an unambiguous signature that carriers created in the amorphous silicon regions migrate (up to about 10 nm) to reach the grain boundaries or interiors of the nanocrystalline regions where recombination occurs. In the present case, however, we know from the PL that the carriers transfer before they become immobilized in band-tail traps where they would contribute to PL from the

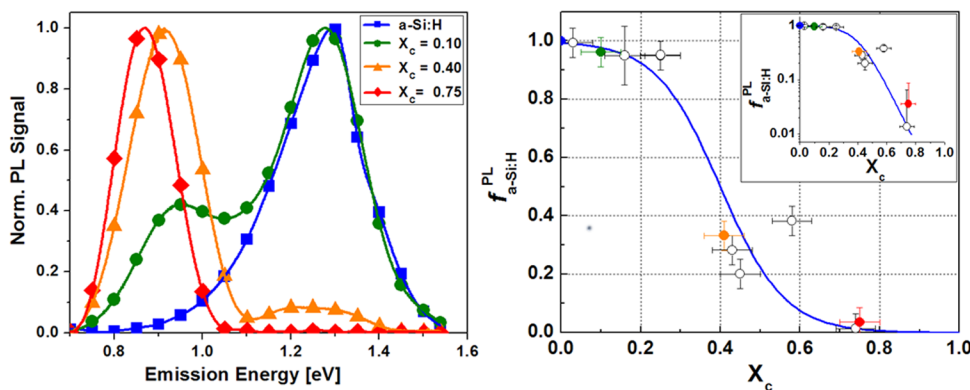


FIG. 2. Quenching of photoluminescence spectra as a function of crystalline volume fraction in nc-Si:H. (a) Normalized PL spectra for nc-Si:H films with nanocrystalline volume fractions of 0.0 (squares, blue squares online), 0.10 (circles, green circles online), 0.40 (triangles, orange triangles online), and 0.8 (diamonds, red diamonds online) excited at 2.4 eV. (b) Relative intensity of the amorphous PL to the total PL as a function of crystalline volume fraction. Inset shows the same data on a semi-log scale.

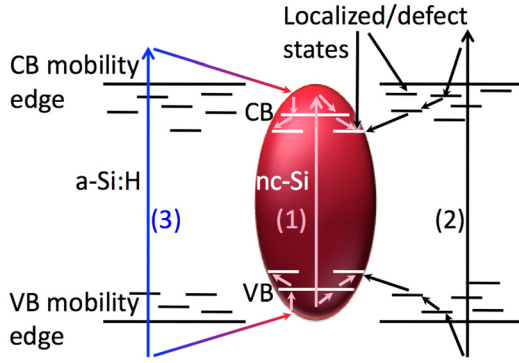


FIG. 3. Schematic diagram of potential relaxation mechanisms in nc-Si:H. Arrows labeled 2 and 3 (black and blue arrows online, respectively) are excitation/relaxation in the amorphous phase. Arrows 2 and 3 are excitation in the amorphous phase with transfer to the crystalline grain boundaries through the localized band-tail states (2) or without fully thermalizing (3). Arrows labeled 1 are excitation/relaxation at the crystalline grain boundaries or within the crystalline phase.

amorphous region. (The total PL intensity from the sum of the two peaks is essentially independent of crystalline volume fraction.) This behavior is depicted schematically in Fig. 3 where the arrows (1, 2, and 3) represent transitions leading to PL at the nanocrystalline interface regardless of the phase within which the absorption occurs. The arrows (2 and 3) represent transfer in the band-tail states (arrows 2) or before they fully thermalize (arrows 3) to the crystalline phase.

These PL results are confirmed by low temperature optically excited electron spin resonance (LESR) spectra (Fig. 4) on the same PL samples (except for  $X_c > 0.9$ , which is taken from a previous study<sup>25</sup>). While the  $X_c > 0.9$  spectrum is shown for 1.2 eV excitation, the lineshape is essentially independent of excitation energy between 1.1 and 2 eV. Also shown in Fig. 4 is a nc-Si:H sample with crystalline volume fraction approximately 0.5 excited at energies between 1.2 and 2.5 eV and the commonly observed LESR spectrum of a-Si:H. The LESR in a-Si:H is universally attributed to electrons trapped in localized conduction band tail states (narrow derivative feature) and holes trapped in localized valance

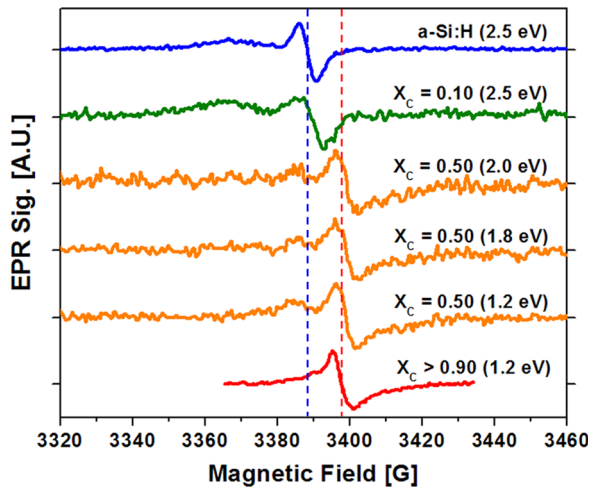


FIG. 4. LESR derivative spectra in nc-Si:H. LESR as a function of crystalline volume fraction and excitation energy. (Online colors match the coding in Fig. 2) The dashed lines near 3388 and 3398 G represent g-values of 2.006 and 1.998, respectively.

band tail states (lower-field, broad derivative feature for which the negative component overlaps the signal due to electrons). Independent of excitation energy, these two features are missing from the 0.5 volume fraction nc-Si:H sample where the LESR spectrum is clearly due to the nanocrystalline phase since the same lineshape occurs in nc-Si:H with crystalline volume fraction  $> 0.9$ . As in the case for the PL described above, this latter signal is commonly attributed to electrons (narrow line) and holes (broad line) trapped at the nanocrystalline grain boundaries.<sup>25,26</sup> The fact that the lineshape for the 0.5 volume fraction nc-Si:H sample is characteristic of the nanocrystalline phase, even at high energies where the absorption is in the amorphous phase, is in complete agreement with the PL quenching results.

There is additional evidence that carriers generated above the amorphous silicon mobility edges in nc-Si:H diffuse to the grain boundaries before recombining. The first piece is the absence of the degradation present in all a-Si:H (Staebler-Wronski effect) in the 0.5 volume fraction nc-Si:H, which is explained by the fact that the carriers do not recombine in the amorphous phase to create the Staebler-Wronski defects. The second piece of supporting evidence comes from theoretical estimates of the distance carriers can travel before recombination. At low temperatures in the localized band-tail states of amorphous silicon a rough estimate of this distance is given by<sup>27</sup>  $R = \frac{a_e}{2} \ln(\nu_0 \tau_0)$ , where  $R$  is the radius below which recombination is unimportant,  $a_e$  is the localization radius (approximately 1 nm),  $\nu_0$  is a typical phonon frequency ( $10^{12}$  Hz), and  $\tau_0$  is a dielectric relaxation time ( $10^{-8}$  s).<sup>27</sup> Using these values, one obtains  $R \approx 4$  nm.

Although transport in localized states is the common explanation for the transport of carriers to the nanocrystals (transitions 2 in Fig. 3), which is certainly correct for some, if not all, of the carriers, a possible alternative explanation that may play a role is the collection of “hot” carriers before they fully thermalize. An estimate of the distance,  $x_0$ , hot carriers can travel in a-Si:H before thermalization is given by<sup>28</sup>

$$\langle x_0^2 \rangle = \frac{\mu_0 (kT)^2}{\beta q} \left[ \left( \frac{2\Delta E_0}{3kT} \right)^{\frac{3}{2}} - 1 \right], \quad (1)$$

where  $k$  is the Boltzmann constant,  $T$  is the temperature,  $\mu_0$  is the mobility,  $\Delta E_0$  is the energy above the mobility edge, and  $\beta q$  is the rate at which carriers lose energy to polar phonons ( $\beta$  is the loss rate). Previous estimates of  $\beta q$  for a-Si:H range from  $5 \times 10^{11}$  to  $2 \times 10^{12}$  eV/s,<sup>29,30</sup> and there is evidence that these values depend on the excess energy of the carrier above the mobility edge.<sup>30</sup> Our terahertz measurements<sup>31</sup> on the 0.5 volume fraction nc-Si:H sample are consistent with  $\beta q \approx 3 \times 10^{11}$  eV/s. Expressing all energies in eV with  $\mu_0 \geq 10 \frac{\text{cm}^2}{\text{Vs}}$  in the extended states (using a lower bound on  $\mu_0$ , the actual value could be much larger) and  $kT \approx 25$  meV, one obtains  $x_0 \geq 10$  nm for electrons 1 eV above the mobility edge. The number will be slightly less (about a factor of 3) for holes since  $x_0 \propto \mu_0^{\frac{1}{2}}$ . These estimates of  $x_0$  for electrons and holes span a range that is also consistent with the approximate distance carriers need to diffuse in the a-Si:H phase to reach a grain boundary, and since the two processes (thermalization, and tunneling in band tail



states) are sequential, it is plausible that some of the carriers reach the grain boundaries before fully thermalizing.

The thermalization of carriers in a-Si:H is different from thermalization in crystalline Si because of a relaxation of the momentum selection rules in the amorphous phase, which allows all phonons to contribute. The thermalization in a-Si:H will be faster than in crystalline Si if the influence of a much larger number of phonons dominates,<sup>29</sup> but the thermalization will be slower if the influence of a large density of lower energy phonons dominates.<sup>17</sup> Experimentally, it appears that the latter explanation is correct.<sup>18,29,30</sup> Therefore, one would expect the carrier thermalization rates in all amorphous solids to be slower than in their crystalline counterparts, which may increase the usefulness of these materials as absorbers.

With the PECVD growth technique, there exists a minimum crystallite size that is stable against re-amorphization due to the interplay of bulk and surface free energies,<sup>32</sup> which in practice is about 4 nm. Therefore to make materials that contain crystallites small enough to increase the band gap due to quantum confinement, a more orchestrated growth method must be adopted.

In summary, the use of an amorphous material as the absorber has at least three potential advantages: (1) the rich combinatorial space from the compositional flexibility of amorphous films, (2) the possibility with appropriate nanocrystals of increasing the  $V_{OC}$  of an amorphous absorber, and (3) the relaxation of the momentum selection rules, which may ultimately provide more efficient capture of carriers before they fully thermalize.

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