Defect transition energies and the density of electronic states in hydrogenated amorphous silicon

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Abstract

Using photoluminescence excitation (PLE) spectroscopy, we report detailed measurements of the fundamental absorption threshold below the optical gap in hydrogenated amorphous silicon (a-Si:H). These measurements suggest that the density of neutral defects is much greater than the densities of charged defects in intrinsic a-Si:H. The positions and widths of the corresponding transition energies are determined and agree with two models proposed to describe the density of states in a-Si:H. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Though hydrogenated amorphous Si has been studied extensively, the distribution of the defect states in the energy gap is still the subject of considerable controversy. It is generally believed that there is one dominant point defect (commonly referred to as a dangling bond) which exists in three charge states, D^+, D^0, D^- resulting in two transition energies, $D^{0/-}$ and $D^{+/0}$.

We present detailed photoluminescence excitation (PLE) measurements of absorption near threshold (~ 1.2 eV) in nominally undoped, a-Si:H. The data allow us to determine the dominant radiative transitions and the corresponding positions and widths of the two defect energy levels. In conjunction with previous results, these new measurements demonstrate that the neutral charge state (D^0) plays a major role.

Although hydrogenated amorphous silicon (a-Si:H) is, in many ways, the prototypical amorphous semiconductor and the one used most extensively in electronic devices, the electronic density of midgap states due to residual defects remains the subject of considerable debate. The dominant midgap defect is a highly localized

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electronic state, commonly attributed to a silicon dangling bond, a site at which the silicon is three-fold-coordinated [1]. This defect (D) can exist in three charge states, D^+, D^0, and D^- where the designation is, respectively, +1, 0, and −1, in units of the electronic charge. The transition energy $D^{0/-}(D^0 + e \rightarrow D^-)$ is greater than $D^{+/0}(D^+ + e \rightarrow D^0)$ by an electronic correlation energy U. In typical a-Si:H (such as would be used in thin film transistors (TFTs), solar cells, or other electronic devices), the density of neutral defects is $< 10^{16}$ cm^{-3}. Although other defects, such as residual impurities, can exist in a-Si:H, the silicon dangling-bond defect is all that is necessary to explain the vast majority of the experimental data.

Presently, two competing models seek to characterize the density of states that describe the manifold of dangling-bond defects in a-Si:H. In an amorphous solid, such as a-Si:H, the transition energies are not well defined because of inhomogeneities introduced by variations in the local structural order. If the transition energy state distributions associated with each defect state are reasonably well defined such that their characteristic inhomogeneous widths σ are much less than U, then the picture described above with one specific defect is applicable. This model is commonly referred to as the standard defect (SD) model. Fig. 1(a) shows a schematic diagram of the density of states using commonly accepted values for the transition energies and widths for the SD model [2]. However, if the distribution width of transition energies, σ, is much larger than U, then one must consider a pool of defects into which the charge

will be distributed called the defect-pool (DP) model [3–6]. The defect-pool model was introduced to explain the electronic transitions in doped a-Si:H using the same manifold of dangling-bond defects as needed in nominally undoped (intrinsic) a-Si:H. In this model, the n-type (p-type) a-Si:H has transition energies $D^{-/0}(D^{+/0})$ that are less than $D^{+/0}(D^{-/0})$ in intrinsic a-Si:H. Fig. 1(b) shows a schematic diagram for the density of states in the defect-pool model, where we use values for the transition energies and widths as employed by Schumm [3]. These models serve as a basis for understanding the energy transitions responsible for absorption in a-Si:H.

2. Experimental

Samples of device-quality a-Si:H were grown on roughened glass substrates by the standard plasma-enhanced chemical vapor deposition (PECVD) method. Typical thicknesses were 8 μm. Because the absorption due to the defects is weak, PLE spectroscopy utilizing intense, tunable IR radiation from the Vanderbilt Free-Electron Laser (VUFEL) was employed to probe the absorption. The photoluminescence (PL) intensity of a broad luminescence feature centered at 1.3 eV is measured as a function of incident photon energy. These experiments provide the first measurements of energy-dependent absorption for this feature. In these experiments, the sample temperature was maintained at 80 K, and PL was detected over the range from 0.8 to 1.5 eV while exciting with light tuned over the range 1.0–1.2 eV. The excitation light was obtained by frequency-doubling of the 0.5–0.6 eV output from the VUFEL using a LiIO$_3$ crystal. This laser delivers a 30 Hz train of 2.5–5 μs macropulses, each of which is composed of a train of 10^4 1 ps micropulses separated by 350 ps. Peak powers of the doubled light were $\sim 10^5$ W during the micropulses. PL spectra have been corrected for the efficiency of the optical system.

3. Results

There are two primary PL processes in a-Si:H [7]. The first process, which is the dominant one in
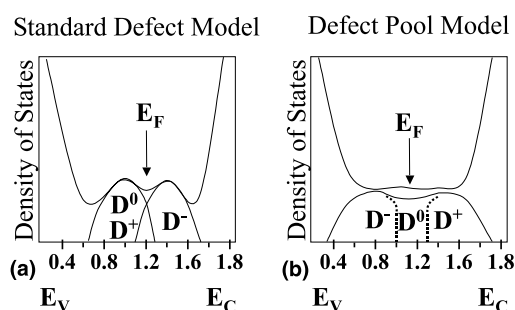

Fig. 1. Two competing models of the density of states in intrinsic hydrogenated amorphous silicon: (a) SD model and (b) DP model.

device-quality a-Si:H, generates a broad PL spectrum that peaks between 1.2 and 1.4 eV. This spectrum has a low energy tail that is roughly exponential and extends down to at least 0.7 eV. The process responsible for this PL is thought to be recombination of electrons trapped in conduction-band-tail states with holes trapped in valence band-tail states. In the following discussion, we will call this process band-tail PL. The second PL process in a-Si:H, which occurs in samples that have been exposed to band-gap light (optically degraded) or in samples with large densities of dangling-bond defects, is attributed to radiative recombination through these defects. This process shows a low-energy peak with its center at 0.8 eV in undoped and n-doped material and at 0.9 eV in p-doped material. Although it has long been controversial whether this radiative transition originates from the dangling bond or terminates at the dangling bond, as will be discussed below the present results support the former mechanism. In the following discussion we will call this process defect PL.

Fig. 2 presents the PL data for various excitation energies. Note that most of the PL intensity lies above the incoming photon excitation energy. This is the result of a two-step excitation of carriers through the manifold of dangling-bond defects [8–11]. These two-step excitation processes are the dominant absorption mechanism for PL at excitation energies below about 1.5 eV. The dependence of the PL intensity on the excitation in-

Fig. 3. PLE spectrum of amorphous silicon. Symbols indicate measurements. The solid line indicates the PLE spectrum predicted by the SD model with parameters $U = 0.2$ and $\sigma = 0.10$; the dashed line indicates the spectrum predicted by a DP model with $U = 0.20$ and $\sigma = 0.18$. See text for details.

tensity is known to be roughly linear even for the two-step excitation mechanism [8,9]. Although only measured over a limited range using the VUFEL, the data presented here were also found to vary approximately linearly with excitation intensity. In addition, our studies with a picosecond optical parametric generator also show linear response over a wide range of excitation intensities (about 4×10^{12}–2×10^{13} W/m^2).

The PLE spectra resulting from the PL data, a sample of which is shown in Fig. 2, are presented in Fig. 3 (solid circles). The PL measured at 1.3 eV was used to construct this spectrum. PLE spectra using PL data at other energies are essentially identical to the spectrum presented in Fig. 3. Also shown in this figure are previously published data [8] taken on the Stanford Mark III FEL laser (solid triangles). These latter data were constructed from a band of PL below about 0.8 eV. Because the a-Si:H sample used at the Stanford FEL had a larger defect density than typical, device-quality a-Si:H, the PL process represented by these data is dominated by recombination through localized defect states.

4. Discussion

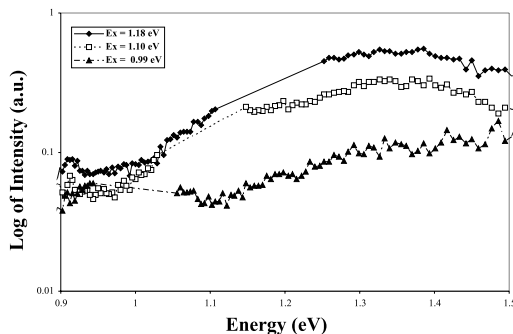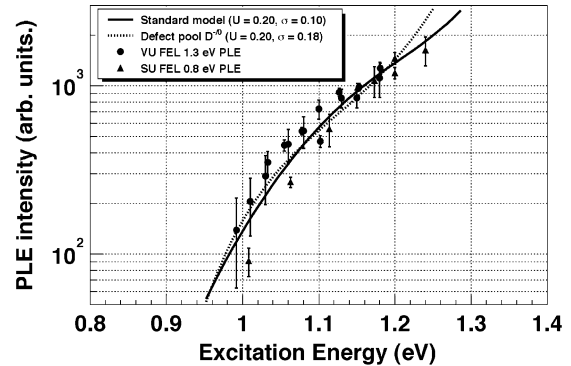There are other techniques that can measure absorption over the energy range covered in Fig. 3.

Fig. 2. Photoluminescence spectra of amorphous silicon for a range of excitation energies. The gaps in the individual spectra correspond to the energy of the exciting light.

Those most commonly employed are photo-thermal deflection spectroscopy (PDS) and the constant photocurrent method (CPM). In intrinsic a-Si:H, the PDS measurements typically probe surface absorption [12]. The shape of the CPM spectra is in general agreement with the PLE data in Fig. 3 despite concerns in assuming the connection between measured photocurrent and absorption. However, the magnitude of the CPM absorption measurements in comparison to the band-tail absorption is different [13]. In addition, the rise in absorption near 1.25 eV shown in Fig. 3 is consistent with transition energies obtained from deep level transient spectroscopy (DLTS) [14].

Fig. 3 shows the remarkable fact that the turn on for the two step excitation of the band-tail PL is very similar to the one step excitation of the defect PL, as measured in other experiments [8]. This fact has very important consequences for the interpretation of both the radiative (PL emission) and the absorptive (excitation) transitions. First, the cut-off in the band-tail PL must be due to the excitation energy falling below the larger of the two optical transitions. Second, from an examination of the electronic densities of states shown in Fig. 1, it is clear that the rise in the absorption shown in Fig. 3 can only result from a $D^{0/+}$ transition for the SD model. In the DP model, this transition must be $D^{+/0}$. Although one cannot absolutely rule out other, more complicated scenarios, the most logical transition to assign to the defect PL is clearly the $D^{-/0}$ or $D^{0/+}$ transition for the SD or DP models, respectively. However, the $D^{0/+}$ transition seems unlikely to be responsible for the defect PL because, when excited by light above the optical band gap, this PL process is dominant for n-type doping where the donors are compensated by D^{-} defects but is absent for p-type doping where the acceptors are compensated by D^{+} defects [7]. Before the results presented in this paper, both the $D^{-/0}$ transition [7] and the $D^{0/+}$ transition [15] were suggested as possibilities.

As the rise in the PLE near 1 eV in Fig. 3 is slower than the exponential decays of either the conduction- or valence-band-tails, this spectrum primarily represents the shape of the low-energy side of the D^{-} or D^{0} defect bands in either the SD or DP models, respectively. The curves in Fig. 3 are the

PLE spectra predicted from these two models using the commonly accepted densities of states. The curve for the SD model in Fig. 3 uses $U = 0.2$ eV and a Gaussian width of the defect band ($\sigma = 0.13$ eV) [16]. The parameters for the DP model are those of Powell and Deane [4]. Because both models fit the data within experimental error, one cannot use these results to distinguish between them.

5. Conclusion

Using powerful, broadly tunable infrared light from the Vanderbilt Free-Electron Laser, we have been able to study the below-gap photoluminescence excitation spectrum of device-quality a-Si:H. In addition to identifying various optical excitation and radiative recombination transitions, the present study also places some important restrictions on the electronic correlation energy for the dominant defect in a-Si:H. Because 'intrinsic' a-Si:H is slightly n-type, the Fermi level must lie above mid-gap. Coupled with the density of states shown in Fig. 1 for the SD model, this restriction places a lower limit on U of approximately 0.2 eV. The maximum value of U consistent with the PLE spectrum of Fig. 3 is 0.4 eV. These results are quite consistent with common models for the density of states.

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