

# Photoluminescence in Hydrogenated Amorphous Silicon

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Received May 25, 1993

The two dominant photoluminescence (PL) processes in hydrogenated amorphous silicon (a-Si:H) are reviewed. These two processes are indicated by (1) a PL peak near 1.3 eV that is attributed to radiative recombination between photo-excited electrons in localized conduction band-tail states and photo-excited holes in localized valence band-tail states and (2) a PL peak near 0.8 eV that is attributed to recombination of photo-excited carriers through the manifold of silicon dangling bond defects.

## I. Introduction

Amorphous semiconductors are often artificially separated into two different classes, those that are predominantly tetrahedrally-coordinated and those whose average nearest-neighbor coordination number is usually less than three. Amorphous silicon, and alloys based on this group IV amorphous semiconductor, fall into the first class while the chalcogenide glasses based on S, Se and Te usually fall into the second. Although this classification scheme is empirical and lacks any firm theoretical foundation, the optical properties of these two classes of amorphous semiconductors are different enough as to render the classification scheme of practical importance.

In this paper we discuss only the radiative recombination processes in the group IV, tetrahedrally-coordinated amorphous semiconductors, and we shall use hydrogenated amorphous silicon (a-Si:H) as the prototypical example. Excellent reviews of the PL in a-Si:H exist,<sup>[1-3]</sup> so in this paper we will very briefly review the important concepts and then concentrate on some more recent results. In this material, which can only be made amorphous in thin-film form, the hydrogen is added to remove defects such as three-fold-coordinated silicon atoms (Si "dangling bonds"). Hydrogenated amorphous silicon is the basis for many large-area, slow devices such as thin-film transistors for various switching applications in flat panel displays or optical readers, and as photovoltaic cells for applications in terrestrial power generation.

These electronic and photovoltaic applications depend critically on the fact that films of a-Si:H can be doped; however, in the present paper we shall concentrate on undoped, or "intrinsic", films of a-Si:H which are slightly n-type due to residual defects. In intrinsic a-Si:H the most important defects both optically and electronically are the silicon dangling bonds. These defects are present on a scale of at least  $10^{15}$  per  $\text{cm}^3$  in

the best, device-quality material, and the three charged states of these defects,  $D^+$ ,  $D^0$ ,  $D^-$ , all have energy levels that occur well within the optical energy gap. In a-Si:H the optical energy gap is somewhere between 1.7 and 1.9 eV as shown in the schematic electronic density-of-states diagram<sup>[4]</sup> in Fig. 1. The states above the dashed line (indicated by  $E_V$  in Fig. 1) in the valence band and the states below  $E_C$  in the conduction band are localized. The densities of these states are

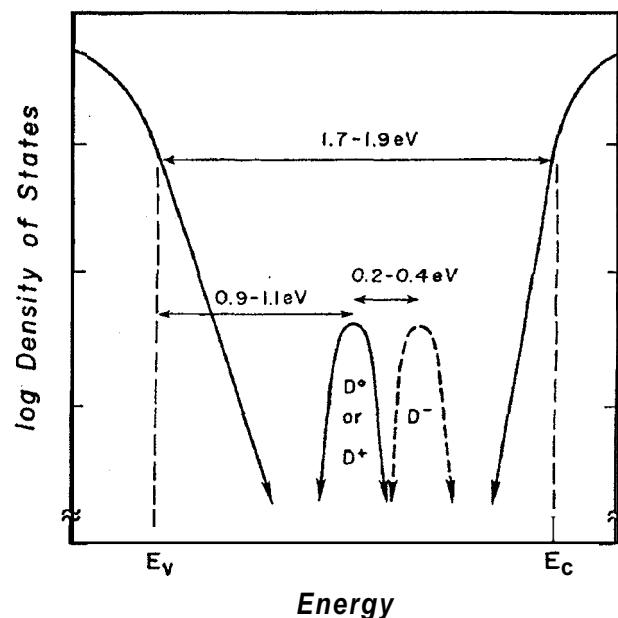


Figure 1: Schematic diagram of the density of electronic states in a-Si:H.  $E_V$  and  $E_C$  represent the valence and conduction band mobility edges, respectively. The defect states  $D^+$ ,  $D^0$  and  $D^-$  represent different charge states of the silicon dangling-bond defects as described in the text.

exponentially decreasing away from  $E_V$  and  $E_C$  with slopes ( $\sim 100$  meV) on the log scale of Fig. 1 that are approximately as shown. These states are commonly

referred to as "band-tail states". The optical transition energies for the defect states  $D^+$ ,  $D^0$ ,  $D^-$  with respect to the demarcation energies  $E_V$  and  $E_C$  are also shown in Fig. 1.

In intrinsic a-Si:H two characteristic photoluminescence (PL) bands commonly exist, a band that peaks near 0.8 eV that is thought to be due to radiative recombination through the manifold of D states and a second band that peaks near 1.3 eV that is thought to be due to radiative recombination between electrons in conduction-band-tail states and holes in valence-band-tail states. In intrinsic samples of a-Si:H at low temperatures ( $T \leq 300$  K), the dominant PL band is the one that peaks at 1.3 eV. In this paper we shall call this PL process the band-tail PL. In intrinsic samples of a-Si:H at 300 K and in material that contains larger densities of silicon dangling bonds, the PL that peaks near 0.8 eV dominates. We shall call this PL process the defect PL in this paper. In intrinsic a-Si:H the relative importance of the defect PL with respect to the band-tail PL is well known to scale with the neutral dangling bond ( $D^0$ ) density as measured by electron spin resonance (ESR) experiments. Whenever the density of  $D^0$  states increases, as for example when samples are made under non-ideal conditions or when hydrogen is driven off through high temperature annealing, the total PL efficiency for all PL processes decreases and the defect PL process becomes relatively more important even at low temperatures.

## II. Selected experimental results

Typical PL spectra<sup>[2]</sup> that illustrate the two cases where the band-tail PL process dominates and where the defect PL process becomes important are shown in Fig. 2. The PL for the sample with low defect density (solid line in Fig. 1) is stronger by about a factor of 5 than that of the sample with high defect density (dashed line in Fig. 1). The sample with high defect density was obtained by annealing one of the films made with low defect density at 500 C for 30 minutes. This procedure resulted in a decrease in the hydrogen concentration from about 10 at. % to about 3 at. % and a concomitant increase in the defect density from about  $10^{15}$   $\text{cm}^{-3}$  to about  $10^{17}$   $\text{cm}^{-3}$ .

Note that in the sample of high defect density the PL peaks around 1.1 eV instead of 1.3 eV. This decrease in peak energy can be explained by the decrease in the optical band gap as a result of removing most of the hydrogen from the sample. Note also that there appears in the PL spectrum for this sample a resolved shoulder near 0.8 eV that is the signature of the defect PL band. This PL band is actually stronger in the high-defect-density sample than the PL in this region in the low-defect-density sample. This behavior occurs because at 77 K the PL in the sample with low defect density is entirely due to the band-tail PL process.

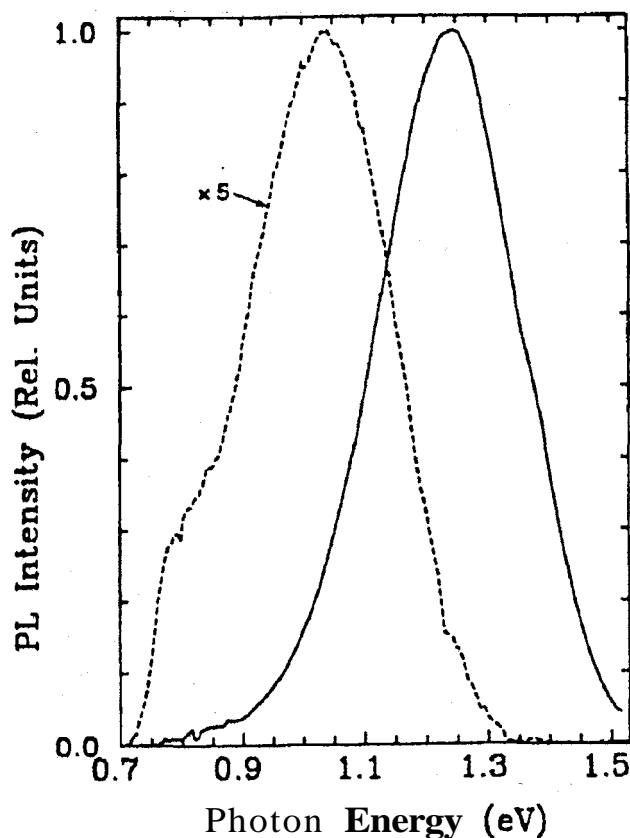


Figure 2: PL spectra of a-Si:H excited by an  $\text{Ar}^+$  laser (5145 Å) at 77 K: (---) sample with a high defect density; (—) device quality sample with low defect density.

Therefore, in this sample the PL at 0.8 eV is due to the low energy tail of the PL that peaks at 1.3 eV. Because of the substantial widths for both of these PL processes (several tenths of an eV), it is sometimes difficult to determine if one or two PL processes are contributing to the PL especially near 0.8 eV. Similar results are obtained when other methods are employed for increasing the defect density.

One must check to be certain that both the 0.8 eV and the 1.3 eV PL peaks have similar dependences on the exciting laser power if the lineshapes as shown in Fig. 2 are to be taken as unique. With drastically different power dependences, the effective PL lineshape will depend on the exciting laser power. In the case of a-Si:H, both PL processes have essentially the same power dependences ( $I_{PL} \propto I^\beta$  where  $I_{PL}$  is the PL intensity,  $I$  is the intensity of the exciting light, and  $\beta \approx 0.8$  to 0.9).

The temperature dependences of the two PL processes are also quite similar; however, the exponential decays with increasing temperature above about 100 K are enough different that the defect PL becomes dominant in essentially all samples at 300 K.<sup>[6]</sup> This fact is illustrated in Fig. 3 in which are plotted the relative

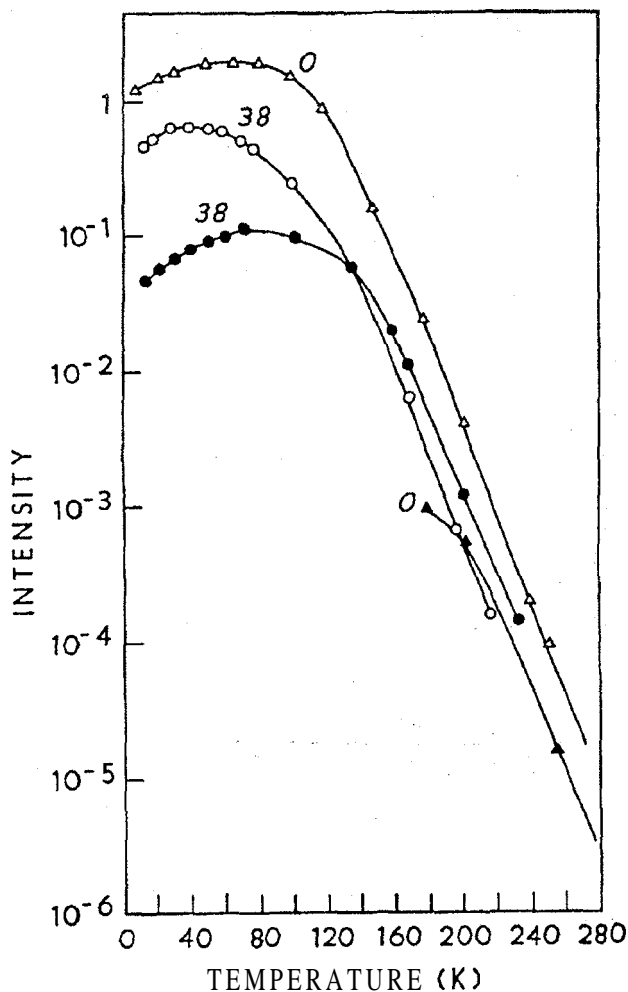


Figure 3: Integrated PL intensity for the band-tail (open circles and triangles) and defect (solid circles and triangles) recombination processes as a function of temperature for a-Si:H and for one alloy in the system a-Si<sub>1-x</sub>Ge<sub>x</sub>:H. The labels represent the Ge content in percent (100).

intensities of the band-tail and defect PL processes in pure a-Si:H and in a-Si<sub>1-x</sub>Ge<sub>x</sub>:H for x = 0.38. The different slopes for the two PL processes are particularly apparent for the silicon-germanium alloy. Note from Fig. 3 that in a-Si:H the defect PL is at least three orders of magnitude weaker than the band-tail PL at low temperatures.

Much additional information concerning the PL processes in a-Si:H can be learned by examining the PL efficiency as a function of the energy of the exciting light. These measurements are particularly instructive when the exciting light energies are below the optical band gap energy, which may be taken as about 1.9 eV in a-Si:H. Figure 4 shows the PL spectra (on a semi-log scale) in a sample with low defect density. The spectra labeled (a) through (e) in Fig. 4 are taken at different exciting light energies  $E_x$  from about 1.3 eV to about

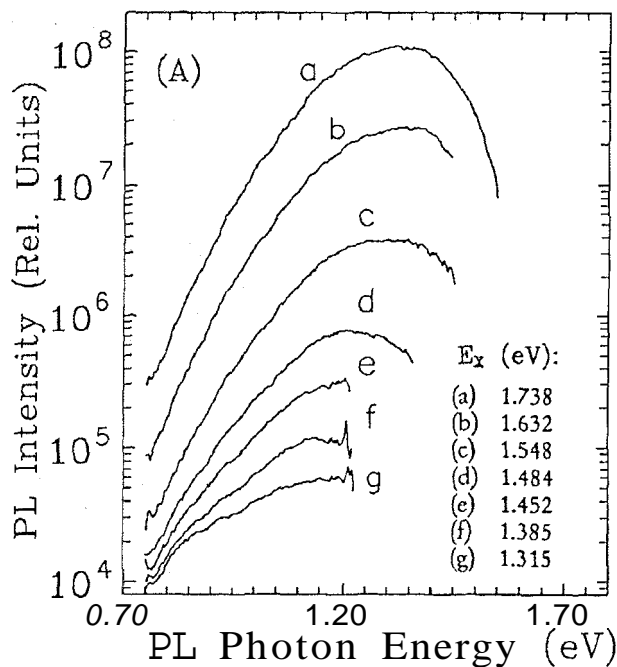


Figure 4: PL spectra at 77 K in a-Si:H as a function of excitation energy.

1.7 eV. Above 1.7 eV the PL spectrum is independent of  $E_x$  and agrees with other spectra taken with above-gap light<sup>[1-3]</sup> and, in particular, with the solid-line spectrum shown on a linear scale in Fig. 2. As the energy of the exciting light is lowered below about 1.7 eV, the peak of the PL spectrum moves to lower energies.<sup>[2,7]</sup> Of perhaps more importance<sup>[8]</sup> is the fact that the slope of the low-energy portion of the PL spectrum decreases continuously with decreasing  $E_x$  even though the PL is still dominated by the band-tail process at all values of  $E_x$ . Figure 5 shows the analogous PL spectra for the same sample of a-Si:H as shown in Fig. 4 after 4 hours of irradiation with 500 mW/cm<sup>2</sup> of 1.75 eV light at 300 K where the defect density has been increased from about  $10^{15}$  cm<sup>-3</sup> to  $5 \times 10^{16}$  cm<sup>-3</sup>. Even in this sample the defect PL is not apparent when  $E_x$  is above about 1.5 eV.

Using data similar to those shown in Figs. 4 and 5 one can plot the PL intensity at a given PL energy as a function of the energy of the exciting light. If these intensities are plotted at the exciting light energies, then the resulting curves are known as PL excitation (PLE) spectra. For a constant exciting light intensity, the PLE spectrum is proportional to the absorption coefficient provided that the quantum efficiency for the PL process is independent of  $E_x$ . For values of  $E_x$  greater than about 1.5 eV, the PLE spectra do indeed follow the absorption spectra in a-Si:H for both the intrinsic samples of low defect density and the samples whose defect densities are enhanced ( $\geq 10^{17}$  cm<sup>-3</sup>) because of varying the growth conditions or because of high-

temperature annealing or because of illumination with band-gap light.

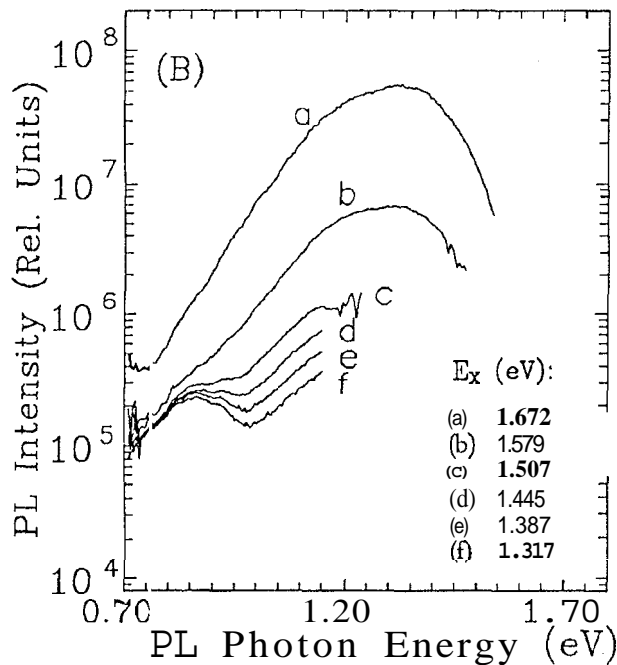


Figure 5: The PL spectra at 77 K in a-Si:H as a function of excitation energy after light soaking.

On the other hand, for  $E_x$  less than about 1.5 eV, the PLE spectra in a-Si:H with low defect density depart dramatically from the exponential Urbach absorption. At these low energies the radiative recombination efficiency actually increases rapidly.<sup>[8]</sup> This rapid increase has been attributed to the fact that the photo-excited carriers are created in localized states where diffusion to non-radiative defects is less probable.

A second important observation from the temperature dependence of the PLE spectra below about 1.5 eV is the fact that rapid changes occur in these spectra at temperatures between 100 and 200 K.<sup>[8]</sup> These rapid changes have been cited as evidence for the importance of phonon-assisted absorption in a-Si:H. This interpretation will be discussed in greater detail in the next section.

### III. Recombination and absorption mechanisms

As mentioned in the previous section, the two dominant radiative recombination mechanisms in a-Si:H are (1) recombination of photo-excited electrons in the localized conduction-band-tail states with photo-excited holes in the localized valence-band-tail states and (2) recombination of photo-excited electrons in the

conduction-band-tail states at silicon dangling-bond defects. As more silicon dangling bonds are created in a-Si:H the total PL efficiency decreases, and the defect PL becomes relatively more important. These two trends have prompted most authors to suggest that the silicon dangling-bond defects serve as both radiative and non-radiative centers in a-Si:H.

The band-tail PL peaks near 1.3 eV while the optical band gap in a-Si:H is somewhere between 1.6 and 1.9 eV depending on the definition one employs to describe the gap. The difference between the optical band gap and the PL peak energy is commonly thought to result from the interaction between two competing effects: (1) the probability for carriers to thermalize to lower energy states in the band tails, and (2) the probability for carriers in the two band tails to recombine radiatively. At energies where the density of states is higher, the carriers can diffuse to states of lower energy more easily, but at energies where the density of states is lower the carriers become trapped for times that are long enough so that radiative recombination with carriers in the opposite band tail predominates. According to this interpretation, the cross-over between these two processes occurs in a-Si:H at an energy separation of about 1.3 eV.

Because of the existence of exponentially decreasing densities of band tail states at the edges of the valence and conduction bands and because of the increasing localization of these states the further one gets from the mobility edges, one would not expect to find a unique recombination lifetime for either of the two PL processes. In fact, for both PL bands the decays are best described by power laws that correspond to very broad distributions in lifetimes. In this sense the PL in a-Si:H is very similar to that which occurs in other amorphous semiconductors.

So far we have concentrated on the recombination processes, but the first step in PL is, of course, the excitation process. Photo-excitation normally depends on the joint densities of states in the valence and conduction bands and the matrix elements connecting transitions between these states. Because the probability for a transition between two localized states is, in general, less than that between a localized state and an extended state, the latter transitions are the most important at all but the lowest excitation energies. At low temperatures these general considerations are all that apply, and in fact, the most common description of photon absorption in a-Si:H assumes that this picture is essentially complete at all temperatures.

There have been some descriptions of the absorption edge in a-Si:H that invoke the existence of phonon-assisted absorption, which is known as Urbach absorption and is sometimes called "thermal disorder";<sup>[9]</sup> however, the direct effect on the absorption is at best small. On the other hand, for below gap excitation of PL, where the distributions of the photo-excited carriers in

the band tails are critically important, the existence of polaron-assisted processes that contribute to the absorption has dramatic consequences.

As mentioned in the previous section, from the PLE spectra excited well below the optical gap at temperatures above 200 K, there appears to be a redistribution of the carriers in the band tails (partial thermalization) even at excitation energies as low as 1.3 eV. In addition, this partial thermalization occurs rapidly at temperatures that lie between 100 and 200 K. Since it can be shown that thermalization arguments alone do not account for these rapid changes,<sup>[8]</sup> it is natural to invoke a change in the absorption process itself. Thus, at temperatures above 200 K the optical absorption process itself also involves the absorption of several polarons so that the carriers are actually excited much nearer to their respective mobility edges than the energy of the polaron alone would indicate. In this way, the carriers can thermalize, at least partially, even when the excitation energies are very low.

#### IV. Summary

The photoluminescence in hydrogenated amorphous silicon involves two distinct processes. One of these processes is "intrinsic" in the sense that it involves recombination between photo-excited carriers in the localized conduction and valence band-tail states that are present in all amorphous solids. The second process is "extrinsic" in the sense that it involves recombination through the manifold of silicon dangling-bond defects whose densities vary with the method of preparation and with several other factors. The silicon dangling bonds also serve as non-radiative centers in a-Si:H.

#### Acknowledgements

The research described in this paper was partially supported by NREL under subcontract No. XAD-3-12114-2 and by ONR under subcontract No. N00014-91-C-0104.

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