PHYSICAL REVIEW B VOLUME 35, NUMBER 17 15 JUNE 1987-I

Photoluminescence in a-$Si_{1-x}Ge_x$:H alloys

R. Ranganathan, M. Gal,* J. M. Viner, and P. C. Taylor
Department of Physics, University of Utah, Salt Lake City, Utah 84112

(Received 13 January 1987)

The photoluminescence (PL) of alloys in the system a-$Si_{1-x}Ge_x$:H shows the presence of two bands, one which peaks at higher energies (1.2—1.4 eV in a-Si:H) and one which peaks at lower energies (0.8—0.9 eV). For all values of x studied ($0 \leq x \leq 0.52$), the position of the low-energy peak is independent of Ge concentration. The samples we have studied exhibit a low-energy tail to the PL efficiency which is of constant magnitude independent of x. There is a departure from this behavior only when the low-energy PL peak is present.

I. INTRODUCTION

Radiative recombination processes in hydrogenated amorphous silicon (a-Si:H) have been studied in great detail, and reasonably comprehensive model descriptions of these processes have emerged.[1-3] Street[1] has suggested that the electron-hole pairs created by optical excitation do not diffuse very far apart before they become trapped and that, at least at low-excitation intensities, each pair created eventually recombines independently of all other pairs. Dunstan,[2] on the other hand, has suggested that optical excitation creates "distant pairs" with random separations, and that the recombination events cannot be identified with the specific electron-hole pairs which were created. Although the first explanation is the most commonly accepted, the exact model is still a matter of some debate.

A common feature of essentially all models for the photoluminescence (PL) processes in a-Si:H and related alloys is the assumption that the recombination occurs between electrons in localized "band-tail states" at the bottom of the conduction band and holes in similar states at the edge of the valence band. This so-called "band-tail to band-tail" recombination process proceeds at low temperatures by the tunneling of electrons and holes in the localized band-tail states.[1,4] There is also thought to be a Stokes shift of a few tenths of an eV between the excited state and the emitted photons.[4]

Recently it has been suggested that the PL process may involve a specific set of defect states near the conduction or valence-band edge and that the recombination process involves transitions between an excited state of this defect and the ground state.[5] This alternative explanation was suggested in order to explain the appearance of a "universal" low-energy tail in the PL spectra of a-$Si_{1-x}Ge_x$:H alloys.

Several general experimental observations concerning the PL processes in a-Si:H and related alloys are by now well established.[4] The main observation in a-Si:H is the occurrence of a broad PL band centered at about 1.3 eV (usually between 1.2 and 1.4 eV) which is strongest at temperatures below about 77 K. As the temperature increases above about 80 K, this peak shifts to lower energies and the PL efficiency rapidly decreases. We henceforth refer to this process as the high-energy PL. There is also another PL band which has often been reported in undoped a-Si:H. This band, which has been associated with dangling-bond defects, peaks at lower energies (usually between 0.8 and 0.9 eV) and usually dominates the PL at room temperature. There is some evidence that there may be more than one band contributing to the PL at these lower energies.[4] We refer to the PL which peaks near 0.8 eV as the low-energy PL.

In the present paper we describe the results of a detailed study of the PL processes in the a-$Si_{1-x}Ge_x$:H alloy system with x between 0 and 0.52. These studies have employed samples from several different sources and samples made by different techniques. In Sec. II we briefly describe the experimental procedures employed as well as some relevant details concerning the preparation of the samples. Section III describes the results, and Sec. IV discusses the significance of these results for the models proposed to explain the radiative recombination processes in a-Si:H and related alloys.

II. EXPERIMENTAL ASPECTS

Samples were prepared by the glow discharge of silane, germane, and sometimes hydrogen, using procedures described previously.[5] The glow-discharge system was a standard one operating at a pressure of approximately 1 Torr with substrate temperatures of about 200 to 220 °C and growth rates of several Å/sec. Most samples were prepared on 7059 glass substrates. The silicon-germanium ratios were determined by the inductively coupled plasma technique. Although the hydrogen content was not directly determined, infrared absorption and other diagnostic techniques indicate that between 5 and 15 at. % of hydrogen is incorporated in all samples.

The thicknesses of the films varied generally from ~0.1 to ~0.5 μm. Transmission spectra were routinely taken on all films to ensure that fringing effects due to sample thickness were not contributing to the PL line shapes. In addition, for several values of x, PL spectra were determined using several sample thicknesses. In most cases presented the exciting light at 2.41 eV was completely absorbed within the amorphous film.

The PL was generally excited using an Ar^+ laser (5145

Å) with a power of ~100 mW and detected in a phase-sensitive fashion using a cooled Ge photodiode (North Coast, model No. 617L). Spectra were recorded and averaged with a LeCroy Model No. 3500SA system. All PL spectra were corrected for spectrometer and detector response. Measurements were taken between 4 and 300 K using a variable-temperature cryostat (Janis varitemp).

III. RESULTS

For all compositions studied the PL line shapes are essentially independent of temperature for temperatures below about 80 K. Above 80 K the line shapes generally change with temperature. The low-energy PL peak near 0.8 eV becomes more important with increasing temperature in most samples. The position of this low-energy peak is independent of both temperature and germanium concentration. The high-energy PL peak shifts to lower energies with increasing temperature and increasing germanium concentration. For germanium concentrations in the range $0 \leq x \leq 0.38$, the low-energy PL process does not contribute to the observed PL spectra at low temperatures (<150 K), and the spectra in these cases can be considered as due to a single process.

The temperature dependence of the integrated PL intensity is shown in Fig. 1 for several values of x. The excitation power density used for these measurements was 4 W cm^{-2}. At this excitation intensity the integrated PL exhibits a broad maximum somewhere between 40 and 70 K. This broad maximum becomes less pronounced and shifts to lower temperatures with increasing x. At lower excitation intensities the PL intensities are nearly independent of temperature up to about 70 K. At higher temperatures (above about 70 K) the PL intensities decrease with increasing temperature. The rates of decrease are essentially independent of excitation intensity. All of these features have been observed previously in a-Si:H and attributed to Auger recombination.[6]

The occurrence of two PL processes in these alloys is illustrated for the case of $x=0.38$ in Fig. 2 where the PL spectra are shown at several different temperatures. For this sample the PL spectrum at 10 K is dominated by the high-energy peak (near 1.2 eV for this value of x). As the temperature is increased the low-energy peak becomes more prominent and at 165 K this peak dominates the PL spectrum (top spectrum in Fig. 2). Notice that at 135 K the two contributions to the PL spectrum are not resolved and one might easily misinterpret this isolated spectrum as due to a single PL process. The occurrence of two distinct processes is, however, very apparent in the 10- and 77-K spectra of Fig. 2. The point that one cannot always tell from the shape of the PL spectrum whether there is more than one PL process contributing to the observed PL spectrum will become important when we discuss the low-energy behavior of the PL spectra in these alloys in the next section.

The low-energy PL peak, which has a maximum near 0.8 eV in all alloys in the hydrogenated silicon-germanium system, becomes relatively more important as the germanium content is increased. This fact is illustrated in Fig. 3 where the PL spectra for temperatures around 200 K are shown for $x=0$, 0.38, and 0.52. In a-Si:H the high-energy PL is the dominant band while for $x=0.52$ the low-energy PL is the dominant band. Both bands are of roughly equal importance for $x=0.38$ at these temperatures.

The fact that the peak of the low-energy PL spectrum is independent of x is illustrated in Fig. 4. This figure also displays the dependence of the band gap as a function

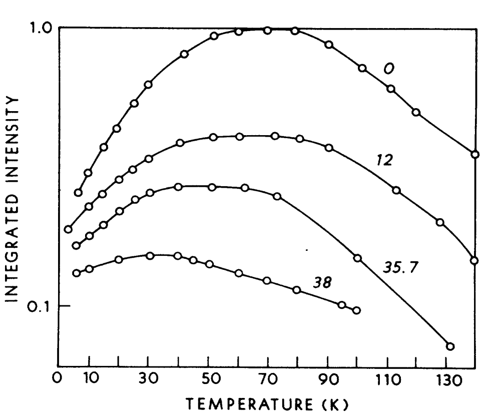

FIG. 1. Integrated PL intensity as a function of temperature for a series of alloys in the system a-Si$_{1-x}$Ge$_x$:H. The labels refer to the values of x. All data were taken at excitation power densities of 4 W cm^{-2}.

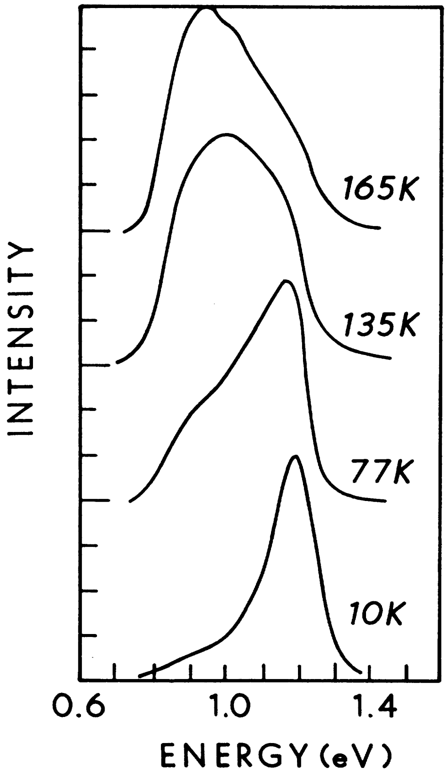

FIG. 2. Temperature dependence of PL spectra in a-Si$_{1-x}$Ge$_x$:H for $x=0.38$.

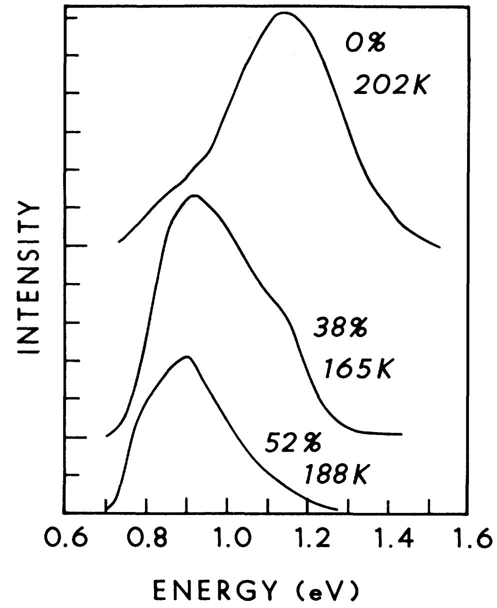

FIG. 3. PL spectra for selected alloys in the system a-$Si_{1-x}Ge_x$:H ($x=0$, 0.38, and 0.52). Spectra shown are those indicative of intermediate temperatures of around 200 K. Note the increasing importance of the PL peak at 0.8 eV with increasing x.

of x on the same relative energy scale. It is clear from this figure that in these alloys the PL process which is associated with the peak at 0.8 eV does not depend on the magnitude of the energy gap. In the next section we will discuss the constraints which this behavior imposes on possible microscopic models for the PL process.

When viewed on a log scale, previous measurements[5] have shown that there is a remarkable universality to both the slope and the magnitude of the PL spectra at low energies in a set of a-$Si_{1-x}Ge_x$:H alloys so long as only the high-energy PL process is important. The traces shown in the top portion of Fig. 5 illustrate this fact for a series of alloys made in the same deposition system.[5] In the bottom portion of Fig. 5 we illustrate the point that this universal behavior is masked when the low-energy PL process becomes important (even at low temperatures) as it is for the samples with $x=0.435$ and 0.52 in this figure. The universal tail occurs only when the high-energy PL is the only important PL process. Figure 6 further illustrates this point. In this figure we compare two curves from the previous figure [$x=0$ and 0.346 which are reproduced as curves (a) and (c), respectively] with PL spectra obtained from samples made by magnetron sputtering from two separate targets.[7,8] The PL spectrum for the sample of a-Si:H made by magnetron sputtering was found to be essentially identical both in shape and magnitude with the sample prepared by the glow discharge of silane. Hence, both samples are indicated by the curve labeled (a) in Fig. 6. The curve labeled (b) in Fig. 6 was grown by magnetron sputtering with a composition given by $x=0.30$. This curve shows an apparent departure from the universal behavior just discussed. That is, the intensity of the PL in sample b exceeds that observed for a-Si:H (sample a) in the energy range $h\nu < 1.1$ eV.

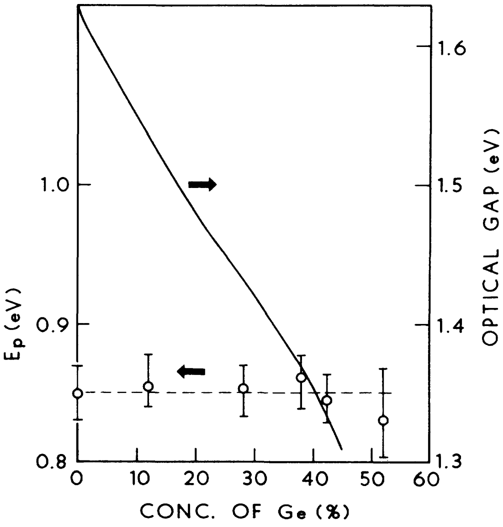

FIG. 4. Position of the low-energy PL peak at 0.85 eV as a function of germanium content in alloys of the system a-$Si_{1-x}Ge_x$:H. Also shown for comparison on the same relative scale is the variation of the optical band gap in the same alloys.

The reason for the apparent departure of sample b from the universal tail can be understood by examining the temperature dependence of the PL spectra as shown in the central and bottom portions of Fig. 6. Notice that the PL which peaks at 0.8 eV (low-energy PL) dominates the high-temperature spectrum for sample b while this PL process remains relatively insignificant in the high-temperature spectrum of sample c. Thus, the apparent departure from the universal behavior is due to the presence of a second PL process in this particular sample.

In these samples there are at least two characteristic features which forecast that a second (low-energy) PL process is important in determining the low-temperature PL line shape in any given set of a-$Si_{1-x}Ge_x$:H alloys

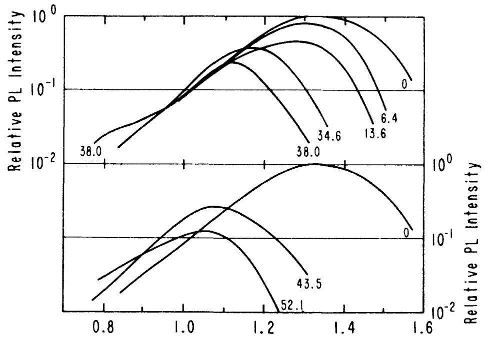

FIG. 5. PL spectra at 77 K for alloys in the system a-$Si_{1-x}Ge_x$:H. The numbers denote the Ge content in percent (100x). The peak of the PL spectrum for a-Si:H ($x=0$) has been normalized to unity, but all other intensities are absolute with respect to the curve for $x=0$. (After Ref. 5.)

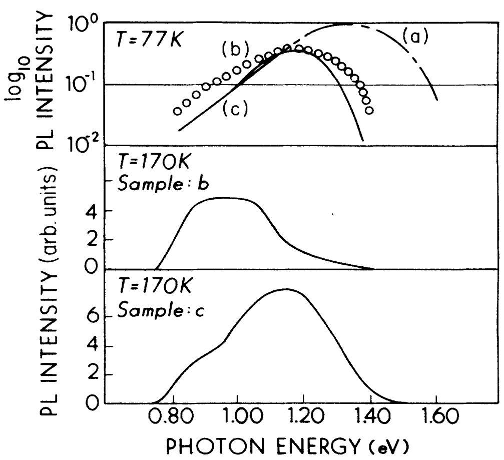

FIG. 6. PL spectra in various alloys in the system a-$Si_{1-x}Ge_x$:H at 77 K (top portion of figure) and 170 K (middle and bottom portions). Top: curve (a), PL spectra for glow-discharge-produced (Ref. 5) and magnetron-sputtered a-Si:H normalized to the same peak value (dashed line); curve (b), PL spectrum for magnetron-sputtered (Ref. 8) a-$Si_{0.7}Ge_{0.3}$:H (circles); curve (c), PL spectrum for glow-discharge-produced (Ref. 5) a-$Si_{0.65}Ge_{0.35}$:H (solid line). Note the semilog scale in this portion of the figure. Middle: PL spectrum for magnetron-sputtered (Ref. 8) a-$Si_{07.}Ge_{0.3}$:H Bottom: PL spectrum for glow-discharge-prepared (Ref. 5) a-$Si_{0.65}Ge_{0.35}$:H.

even where there is no resolved structure present. The first feature is that the half-width of the PL spectrum at low temperatures (< 100 K) does not decrease significantly with increasing Ge content as has sometimes been observed.[9,10] The magnetron-sputtered samples of Fig. 6 also show this behavior [cf. curves (a) and (b) of this figure]. It will become apparent from the discussion below that this situation occurs because the measured half-width is an apparent width which encompasses the contributions of two distinct, but not necessarily resolvable, PL bands. In contrast to this behavior, other workers[5,11] have observed PL linewidths which decrease rapidly with Ge concentration at essentially the same rate as that of the band gap. We believe this behavior represents the case when only the high-energy PL process is important.

The second feature which indicates that a second PL process is important in the observed PL line shape is that the measured peak of the PL spectrum shifts rapidly toward 0.8—0.9 eV as the temperature approaches 300 K. This rapid shift is due to the fact that as the temperature increases the low-energy PL becomes relatively more important than the high-energy PL. Such behavior has been observed by several authors.[1,4,9,12] As we shall see the shift of the PL peak with temperature is much more gradual when only the high-energy PL process is important.

This situation becomes clearer as we consider in more detail the temperature dependence of the present series of alloys prepared by the glow-discharge technique. In Fig. 7 are plotted the integrated intensities for the two components of the PL spectra in two selected samples where $x = 0$ and 0.38. The two contributions are easily separable in these two cases. For the case of pure a-Si:H ($x = 0$) a

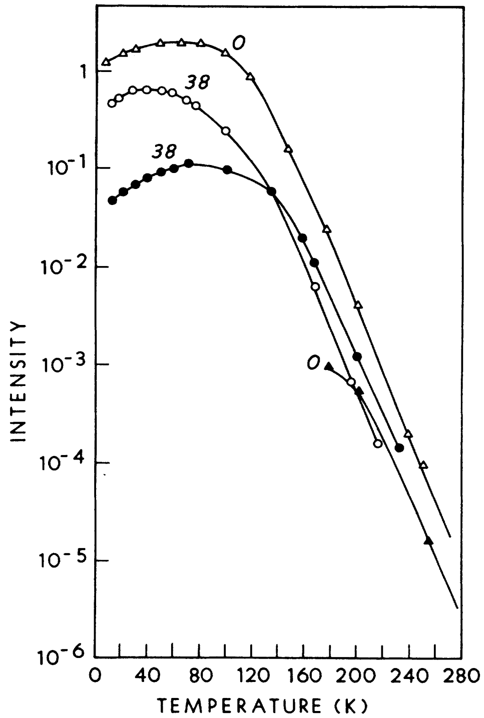

FIG. 7. Integrated PL intensity for the high-energy (open circles and triangles) and low-energy (solid circles and triangles) recombination processes as a function of temperature for two alloys in the system a-$Si_{1-x}Ge_x$:H. The labels represent the Ge content in percent (100x).

resolved peak at 0.8 eV occurs only at higher temperatures ($T > 160$ K) and the low-energy tail of the high-energy PL can readily be subtracted from this feature. Similarly, in the sample with $x = 0.38$ (middle trace of Fig. 3), two resolved features are readily apparent.

In pure a-Si:H at low temperatures the low-energy PL is about three orders of magnitude less intense than the high-energy PL. On the other hand, in a-$Si_{0.62}Ge_{0.38}$:H these two PL processes differ by only an order of magnitude at low temperatures. At high temperatures the high-energy PL decays more rapidly than the low-energy PL in both samples. There is an abrupt break in the dependence of the amplitude of the low-energy PL with x at around $x = 0.35$. This fact is demonstrated in Fig. 8 where only the low-energy PL is plotted for various alloys. It can be seen from this figure that at low temperatures the intensities of the low-energy PL fall into two groups depending on whether x is less than or greater than about 0.35. This behavior is the second example of an abrupt change in PL properties around $x = 0.35$. The first example was the departure from the universal behavior of the low-energy tail as shown in Fig. 5. Both examples occur for the same general reason, the emergence of the low-energy PL process as an important radiative recombination mechanism for $x > 0.35$.

There exists a useful empirical method for estimating the importance of the low-energy PL process in a-$Si_{1-x}Ge_x$:H alloys. We illustrate this method for the case of a-Si:H ($x=0$) in Fig. 9. Figure 9 shows the peak of the measured PL in a-Si:H (x's) as a function of temperature for samples as grown and for samples purposely degraded by annealing at 500 °C for 20 min. In the good quality material the PL peak decreases with temperature slightly faster than the band gap as one can see by comparison of the x's at the top of Fig. 9 with the dashed line. On the other hand, in the annealed sample, the peak of the PL spectrum changes much more rapidly at higher temperatures and approaches the peak of the low-energy PL at the highest temperatures (hexagons in the middle of Fig. 9). Although the low-temperature PL efficiency of the annealed sample is only marginally less than that of the standard sample ($\sim 30\%$ decrease), the low-energy PL is orders of magnitude more important and actually determines the peak of the PL spectrum at high temperatures. In addition, the annealed sample no longer falls on the universal tail shown in Fig. 5, and the PL intensities at low energies ($h\nu < 1$ eV) are actually greater than those in the standard sample. There is, however, no resolved structure at 0.8 eV in this particular annealed sample, although resolved structure has been observed by others.[13] (See Fig. 10 in the next section.)

The important information to be gained from Fig. 9 is that, at least in our samples, one may estimate whether the low-energy PL in a given series of samples will fall on a universal curve by whether or not the peak of the PL spectrum asymptotes to 0.8 eV as the temperature approaches 300 K. This fact is illustrated dramatically in Fig. 9 where the PL peaks for several alloys in the a-$Si_{1-x}Ge_x$:H system are also plotted. The distinct change from the universal behavior observed near $x=0.30$ in Fig. 5 is reproduced as a distinct break in the high-temperature asymptotes in Fig. 9. Thus the peak of the PL spectrum as T approaches 300 K can be used effectively to predict the behavior of the low-energy PL line shape at low temperatures.

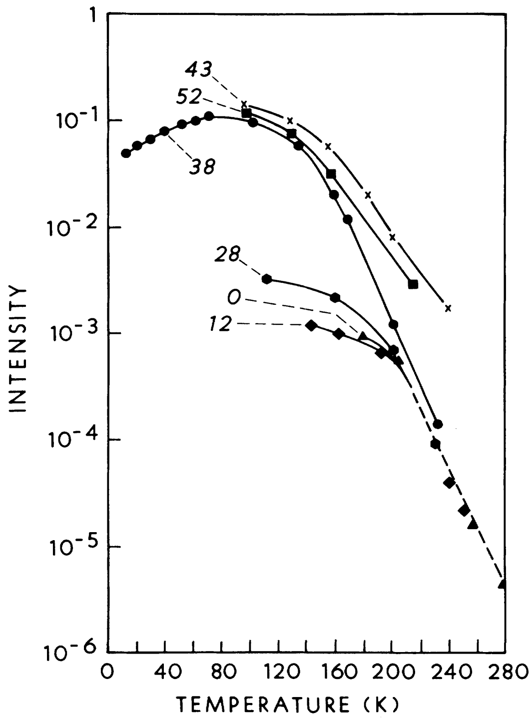

FIG. 8. Integrated PL intensity for the low-energy (0.85 eV) process as a function of temperature for alloys in the system a-$Si_{1-x}Ge_x$:H. Labels represent the Ge content in percent (100x).

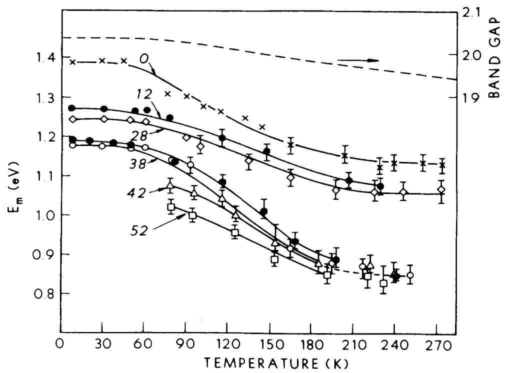

FIG. 9. Position of the peak of the PL spectrum as a function of temperature for alloys in the system a-$Si_{1-x}Ge_x$:H. The labels refer to the Ge content in percent (100x). Note the qualitative difference between the curves for $x<0.35$ and those for $x>0.35$. The x's at the top of the figure are data for a-Si:H as grown and the hexagons in the middle of the figure are data on the same sample after annealing at 500 K for 20 min. The dashed line at the top represents the variation of the optical gap (right-hand scale).

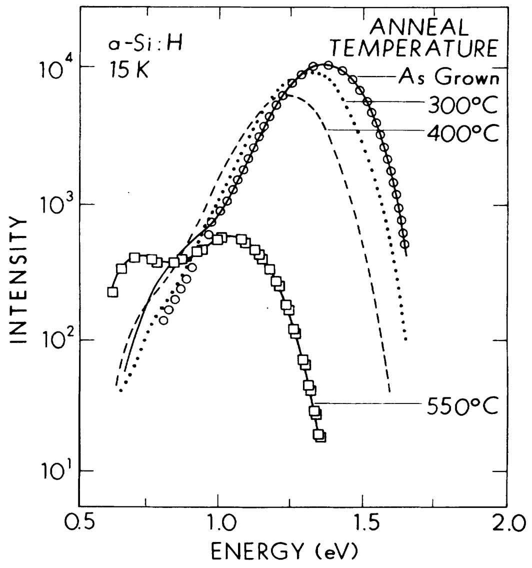

FIG. 10. PL spectra at 15 K in a-Si:H as a function of annealing temperature on a semilog scale. The solid line represents a sample grown at a substrate temperature of 250 °C as reported by Wilson *et al.* (Ref. 13). The circles are the data of Gal *et al.* (Ref. 5) normalized at the peak. The additional curves are spectra obtained by Wilson *et al.* (Ref. 13) after annealing at the temperatures indicated.

IV. DISCUSSION

The universal behavior of the PL at low energies is not restricted to the a-Si$_{1-x}$Ge$_x$:H alloys system. Similar behavior has also been observed in a-Si:H when the hydrogen content is varied.[13] Figure 10, after Wilson *et al.*,[13] illustrates the situation for a-Si:H prepared by the glow-discharge method and annealed at various temperatures to lower partially the hydrogen concentration. The circles in Fig. 10 are the data from Gal *et al.*[5] which are the same as those for a-Si:H shown in Figs. 5 ($x=0$) and 6 [curve (a)]. The data have been normalized to those of Wilson *et al.*[13] at the peak of the PL spectrum. Note that the low-energy tail is essentially constant in this series of alloys and that the peak shifts to lower energy with decreasing H content. There is a departure from this behavior only when a new PL peak near 0.78—0.8 eV appears. This peak is particularly apparent in the curve after annealing at 550 °C in Fig. 10. Thus also in the a-Si:H system there is evidence for a universal tail to the PL spectrum provided that only one PL process is dominant.

We must mention at this point that some of the PL line shapes reported by others do not appear to exhibit the "universal" character.[14,15] Although all researchers commonly observe essentially the same low-energy dependence for the PL as exhibited in Figs. 5 and 6, not all have observed that the PL efficiency at a given energy is independent of x as shown in Figs. 5, 6, and 11. On the other hand, we have found that the highest efficiency photovoltaic grade materials exhibit the "universal" low-energy tail in the PL spectrum.

We have also performed annealing experiments on the film of a-Si:H whose PL is exhibited in Figs. 3, 5, and 6. The qualitative behavior is the same as that displayed in Fig. 10 for the samples of Wilson *et al.*[13] In our case, however, there is no evidence for any structure near 0.8—0.9 eV in either the unannealed or annealed sample. The annealing data are shown in Fig. 11. Note that although there is no resolved structure in any of the PL spectra in Fig. 11, the intensity of the PL in the annealed sample is actually greater near 0.8—0.9 eV than it is in the unannealed case. The data of Figs. 10 and 11 provide convincing evidence that one can actually increase the low-energy PL efficiency in material whose electrical properties indicate a greater density of defects within the energy gap.

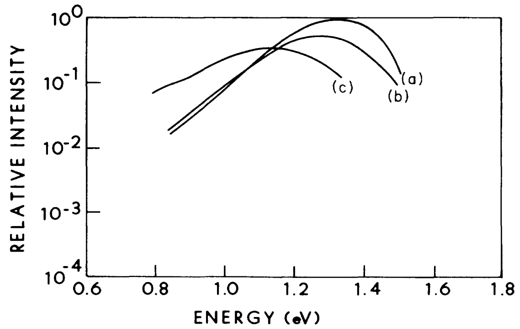

FIG. 11 PL line shape of a-Si:H at 77 K showing the effect of annealing. Curve (a), before annealing, curve (b), annealed at 300°C for 20 min curve (c), annealed at 450 °C for 20 min

It has often been suggested that the appearance of a low-energy PL peak is indicative of material with a large number of electronic states in the gap. The implication has been that no PL processes can be very efficient in these materials because the increased densities of electronic states in the gap provide many nonradiative paths for the recombination. In a-Si:H this conclusion may be valid to the extent that the integrated PL intensity on films with strong low-energy PL never exceeds the integrated high-energy PL intensity in the best quality films.

On the other hand, the PL intensity in the vicinity of 0.8—0.9 eV will actually increase when the low-energy PL is strong. In addition to the annealing experiments shown in Figs. 10 and 11, one example has already been given. In curve (b) of Fig. 6 it can be seen that the alloy a-Si$_{0.7}$Ge$_{0.3}$:H exhibits PL intensities below about 1.1 eV which exceed those of pure a-Si:H [curve (a)] and also those of a sample of a-Si$_{0.65}$Ge$_{0.35}$:H [curve (c)]. In fact the total integrated PL intensity in sample b actually exceeds that in sample c. This situation is often the case in the narrower gap materials where the high-energy PL is weaker.

At present one can only speculate concerning the microscopic origin of the low-energy PL efficiency in a-Si:H and a-Si$_{1-x}$Ge$_x$:H alloys. The usual explanation, which invokes recombination of electrons in conduction band-tail states with holes in the valence band tail, has some difficulty fitting naturally with the observed behavior. For this mechanism one would expect the PL to shift to lower energies with Ge concentration, but one would not necessarily expect a decrease in the PL efficiency just such that the low-energy PL is independent of Ge concentration.

The position of the low-energy PL peak at 0.8 eV is independent of Ge concentration as shown in Fig. 4. Because this peak also occurs in pure a-Si:H and is the dominant band in films with high defect densities, the PL peak has been associated with radiative recombination through silicon dangling bonds. In particular, it has been suggested that the PL transition is from an electron in the conduction band tail into a silicon dangling-bond state.[16] As Ge is added to a-Si:H it is the edge of the conduction band which decreases in energy while the valence band remains relatively constant in energy.[17] It is therefore unlikely that the low-energy PL is due to a transition from the conduction band into a silicon dangling-bond state because the energy of the silicon dangling bond with respect to the valence band is probably essentially independent of Ge content. If the PL which peaks near 0.8 eV results from a transition which involves a silicon dangling bond, then the transition may be from the dangling bond to the valence band.[18]

ACKNOWLEDGMENTS

The authors gratefully acknowledge R. D. Wieting and ARCO Solar, Inc. for supplying most of the samples used in this study. Some samples of magnetron-sputtered material were kindly supplied by G. Lucovsky and R. A. Rudder of North Carolina State University. We acknowledge B. A. Wilson for kindly allowing the data on annealed films to be reproduced in Fig. 11. R. Carius is gratefully acknowledged for several very useful suggestions. This research was supported by the Solar Energy Research Institute under subcontract No. XM-5-05009-2.

---

[*] Present address: Department of Physics, University of New South Wales, Kensington, P.O.B.: 1, Sydney, Australia 2033.

[1] R. A. Street, Adv. Phys. **30**, 593 (1981).
[2] D. J. Dunstan, Philos. Mag. **46**, 579 (1982).
[3] T. M. Searle, T. S. Nashashibi, I. G. Austin, R. Devonshire, and G. Lockwood, Philos. Mag. B **39**, 389 (1979).
[4] R. A. Street, in *Hydrogenated Amorphous Silicon,* Vol. 21B of *Semiconductors and Semimetals,* edited by J. I. Pancove (Academic, New York, 1984), p. 197.
[5] M. Gal, J. M. Viner, P. C. Taylor, and R. D. Wieting, Phys. Rev. B **31**, 4060 (1985).
[6] R. A. Street, Phys. Rev. B **23**, 861 (1980).
[7] R. A. Rudder, J. W. Cook, Jr., J. F. Schetzina, and G. Lucovsky, J. Vac. Sci. Technol. A **2**, 326 (1984).
[8] R. A. Rudder, J. W. Cook, Jr., and G. Lucovsky, Appl. Phys. Lett. **45**, 887 (1984).
[9] R. W. Collins, M. A. Paesler, G. Maddel, and W. Paul, J. Non-Cryst. Solids **35& 36**, 681 (1980).
[10] K. D. Mackenzie, J. R. Eggert, D. J. Leopold, Y. M. Li, S. Lin, and W. Paul, Phys. Rev. B **31**, 2198 (1985).
[11] D. Hauschildt, R. Fischer, and W. Fuhs, Phys. Status Solidi B **102**, 563 (1980).
[12] R. Fischer, W. Rehm, J. Stuke, and U. Voget-Grote, J. Non-Cryst. Solids **35& 36**, 687 (1980).
[13] B. A. Wilson, A. M. Sergent, K. W. Wecht, A. J. Williams, T. P. Kerwin, C. M. Taylor, and J. P. Harbison, Phys. Rev. B **30**, 3320 (1984).
[14] R. Carius and W. Fuhs (private communication).
[15] J. Eggert and W. Paul (private communication).
[16] R. A. Street, D. K. Biegelsen, and R. L. Weisfield, Phys. Rev. B **30**, 5861 (1984).
[17] C. Senemaud, B. Pitault, and B. Bourdon, Solid State Commun. **43**, 483 (1982); **50**, 643 (1984).
[18] R. A. Street, Adv. Phys. **30**, 593 (1981).