Energy Transport and Size Effects in the Photoluminescence of Amorphous-Germanium/Amorphous-Silicon Multilayer Structures

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The low-temperature diffusion length of photogenerated electron-hole pairs in hydrogenated amorphous germanium and silicon has been determined from measurements of photoluminescence spectra and quantum efficiency in multilayer structures, as a function of the sublayer thicknesses. When the sublayer thickness is small compared with this diffusion length, the photoluminescence in amorphous germanium is enhanced by more than 2 orders of magnitude.

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The availability of amorphous semiconductors in the form of high-quality multilayer structures[1] has opened up the possibility of studying transport phenomena in amorphous semiconductors by cw measurements as a function of layer thickness rather than by more conventional time-resolved experiments, for which the desired time resolution (10^{-12} s) is difficult to achieve. In this Letter, we use this alternate approach to determine the diffusion length of photoexcitations in hydrogenated amorphous germanium and silicon (*a*-Ge:H and *a*-Si:H) from cw photoluminescence (PL) measurements on *a*-Ge:H/*a*-Si:H multilayer structures as a function of the sublayer thickness. We find that the PL efficiency in *a*-Ge:H is enhanced by several orders of magnitude in multilayer structures with thin *a*-Ge:H layers. This discovery should make possible a detailed study of luminescence phenomena in *a*-Ge:H, analogous to the large body of work on PL in *a*-Si:H.[2]

The multilayer structures were prepared by plasma-assisted chemical vapor deposition using pure SiH_4 for the *a*-Si:H layers and a 10:1 H_2/GeH_4 mixture for the *a*-Ge:H layers. The layered structure was formed by a rapid switching of the gas composition in the low-pressure (30-mtorr) reactor, without interrupting the plasma.[3] The existence of uniform layers with atomically abrupt interfaces was confirmed by x-ray diffraction,[1,3] transmission electron microscopy, and Raman scattering.[4] The thicknesses of the individual sublayers were determined by the flow duration of the two gases and the deposition rates (~ 0.8 Å/s) determined separately in thick *a*-Si:H and *a*-Ge:H films. The sublayer thicknesses were checked directly by x-ray diffraction and by Rutherford backscattering. All of the samples were about 0.7-μm thick and had a *a*-Ge:H to *a*-Si:H sublayer-thickness ratio of 1:1.3, with the exception of one sample with thin *a*-Ge:H layers (14 Å) for which the *a*-Si:H layers were made thicker (90 Å) to avoid interlayer coupling via tunneling.

The PL was excited by a Kr-ion laser chopped at 1 kHz, with an average incident power of about 7 mW in a line focus on the sample, which was cooled to 10 K. All of the data presented here were obtained from textured samples. The texturing, performed after deposition by ion-beam milling,[5] eliminated the interference fringes in the PL spectra and increased the apparent PL quantum efficiency by a factor of 3–6.[2]

The PL was measured in a transmission geometry with a cooled InSb detector and grating monochromator. The quantum efficiency of the detection system was nearly flat in the wavelength range of interest as determined by comparison with a standard lamp. The absolute throughput was calibrated at 1.12 μm by the collection efficiency for HeNe laser light scattered from a white surface. We estimate that the accuracy of the absolute efficiency measurements is no better than a factor of 3 and the accuracy of relative measurements to be $\pm 20\%$.

The multilayer samples with sublayer thicknesses greater than about 200 Å showed two peaks in the PL spectrum as shown in Fig. 1. We attribute the two peaks to emission from *a*-Si:H and *a*-Ge:H layers separately. The high-energy side of the *a*-Si:H emission is cut off by absorption in the lower-bandgap (~ 1.1 eV) *a*-Ge:H layers. To check for the self-consistency of this interpretation of the two peaks, we compared the ratio of the peak heights as a function of excitation energy with the relative absorbances of the *a*-Ge:H and *a*-Si:H sublayers and found that the relative emission intensities scaled with the ratio of absorbances, as expected. For illustration, we show in Fig. 1 an emission spectrum excited by light with photon energy less than the bandgap of the *a*-Si:H layers, in which the high-energy peak is absent.

The thickness dependences of the PL efficiency measured at 647–752 nm for the low-energy peak (*a*-Ge:H) and at 476 nm for the high-energy peak (*a*-Si:H) are shown in Fig. 2. The intensity of the *a*-Si:H peak drops rapidly for layer thickness < 200 Å, while the *a*-Ge:H peak increases. The drop in the *a*-Si:H emission can be explained by nonradiative tunneling of electron-hole pairs from localized states in the *a*-

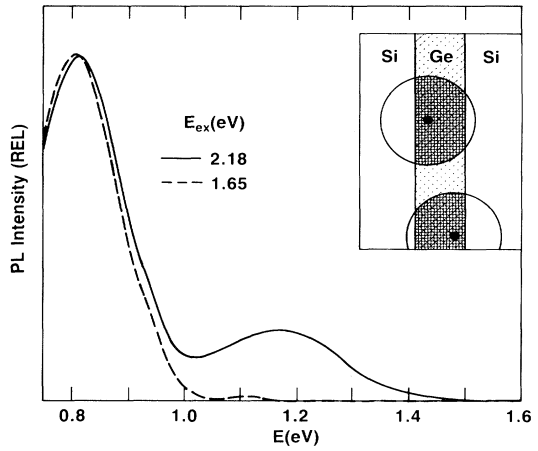

FIG. 1. Photoluminescence spectrum at 10 K for 225-Å/175-Å a-Si:H/a-Ge:H multilayer structure excited by red and green light as indicated. The inset shows the effect of a finite layer thickness on the volume of a-Ge:H accessible to photoexcited electron-hole pairs with diffusion length R_g larger than the layer thickness.

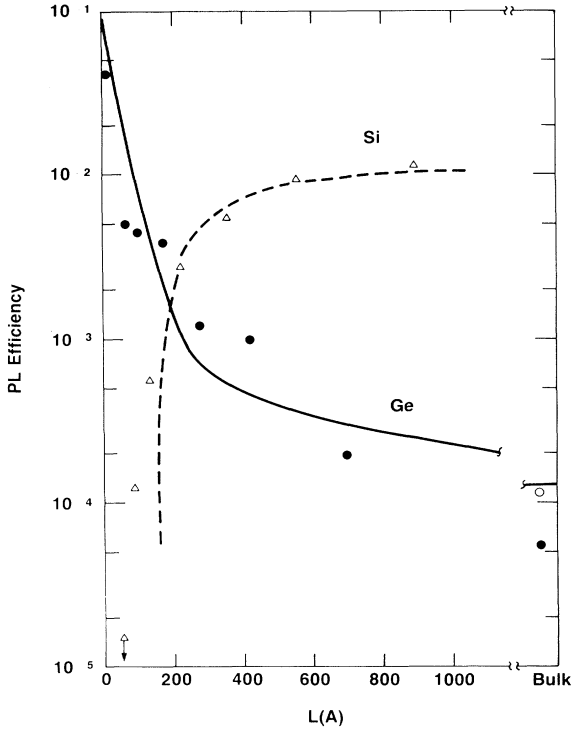

FIG. 2. Layer-thickness dependence of the photoluminescence efficiency for the a-Ge:H and a-Si:H sublayers as indicated, determined from the integrated area under the individual photoluminescence peaks in Fig. 1. The theoretical curves have been scaled by a constant factor to match the experimental data. The data point in the lower-left-hand corner is an upper limit.

Si:H layers into the neighboring lower-bandgap a-Ge:H layers when the electron-hole pairs are created close to the interface. By analogy with the model for nonradiative capture by dangling bonds,[2,6] we assume any electron-hole pair created within a critical distance $R_s = 80$ Å of an interface will tunnel into the a-Ge:H; if created farther than this distance from an interface it will recombine radiatively. The thickness dependence of the PL quantum efficiency η for the a-Si:H predicted by this model is $\eta = \eta_0(1 - 2R_s/L_s)$, where L_s is the silicon-sublayer thickness and η_0 is bulk-silicon PL efficiency; it is shown by the dashed line in Fig. 2. This model is in good agreement with the experimental data for the a-Si:H peak, except for the samples with the thinnest layers, where the model predicts zero quantum efficiency.

A discrepancy of this type must be expected, since the abrupt cut off at R_s in the model is in reality only a first approximation to a continuous transition. We expect the residual PL in thin a-Si:H layers ($L_s < 2R_s$) to be inversely proportional to the tunneling rate from localized states in the a-Si:H into the neighboring a-Ge:H layers. The tunneling rate is proportional to $\exp(-\gamma L_s)$, where γ^{-1} defines the size of the localized state wave functions. Thus we can estimate γ by a fit of an exponential to the thickness dependence of the PL for the samples in Fig. 2 with the thinnest a-Si:H layers. The resulting value of $\gamma^{-1} \sim 10$ Å is presumably the extent of the least strongly localized carrier and is in good agreement with other, indirect estimates.[2,7]

In the opposite case, when the electron-hole pairs are generated in the a-Ge:H rather than in the a-Si:H, they encounter a potential barrier at the interfaces, rather than a potential well. We do not expect the interfaces themselves to have excess defect density over that of the bulk a-Ge:H layers and be a source of nonradiative centers, since the electronic properties of a-Si_xGe_{1-x}:H alloys improve monotonically with increasing Si content.[8]

By analogy with a-Si:H, we expect the PL efficiency in a-Ge:H to be limited by nonradiative recombination at dangling bonds. It follows that the reason that PL in bulk a-Ge:H is low[8] is that the best a-Ge:H has a larger density of dangling bonds ($\sim 10^{17}$ cm^{-3}),[9] with larger capture radii, than a-Si:H. The quantum efficiency decreases exponentially with defect density N_d and capture radius R_g according to[2,6] $\eta \propto \exp(-VN_d)$, where the capture volume $V = \frac{4}{3}\pi R_g^3$ can be regarded as a sphere surrounding each electron-hole pair, such that if the sphere contains a dangling bond the pair recombines nonradiatively; otherwise, it recombines radiatively. When the luminescing layer is thinner than $2R_g$, the capture spheres are truncated and the probability that they contain a dangling bond diminishes, as illustrated schematically in the inset in Fig. 1.

The PL efficiency should increase correspondingly, in qualitative agreement with the experimental data in Fig. 2.

To make a quantitative comparison, we need to include the fact that the PL efficiency is spatially inhomogeneous in the vicinity of the interfaces. The net efficiency is a spatial average across the layer of the form

$$\eta(L)=\frac{1}{L}\int_0^L \exp[-V(x)N_d]\,dx, \quad (1)$$

where L is the thickness of the a-Ge:H sublayers, and $V(x)$ is the volume of a sphere of radius R_g with its center at x truncated at its planes of intersection with the a-Si:H/a-Ge:H interfaces.

The solid line in Fig. 2 is the efficiency as a function of L calculated from Eq. (1) with $R_g=200$ Å, $N_d=2.3\times10^{17}$ cm^{-3}, and the overall magnitude scaled to match the data. The two points on the right-hand side of Fig. 2 correspond to 1-μm-thick a-Ge:H films: The film represented by the solid circle had a 90-Å-thick a-Si:H layer on the bottom and a textured 900-Å-thick capping layer on the top; the film represented by the open circle was an uncapped sample made under similar conditions in a different reactor. The efficiency for these bulk a-Ge:H films was calculated as if the layer thickness were twice the penetration depth of the excitation light (1200 Å).

Like the PL efficiency, the peak emission energy for the a-Ge:H also decreases with increasing L as shown in Fig. 3. This decrease can be explained by the model developed in Ref. 7 to explain the emission energy for bulk a-Si:H if we incorporate the effect of the layer thickness in a similar way to that used above to explain the thickness dependence of the efficiency. According to the model,[7] immediately after being generated, the

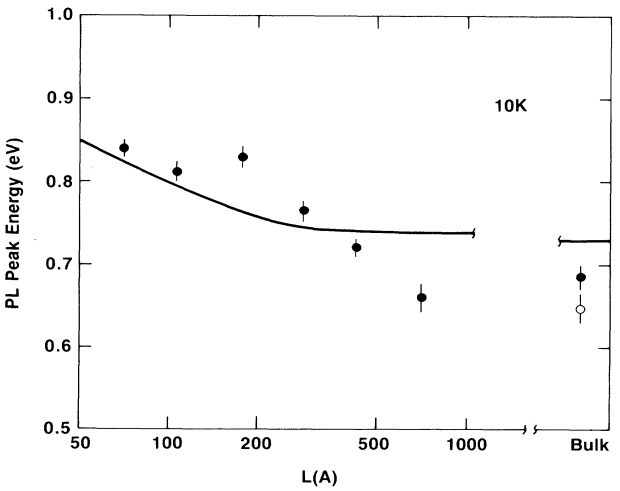

FIG. 3. Photon energy of the peak in the photoluminescence emission spectrum for the a-Ge:H as a function of the a-Ge:H layer thickness.

electrons and holes begin thermalizing down through localized states in the band tails, by phonon-assisted tunneling to progressively lower-energy states. The lowest-energy states reached by the holes and electrons before radiative recombination then determine the energy of the PL emission.

For simplicity, we assume that the typical tunneling distances for electrons and holes are the same and equal to the nonradiative capture radius R_g discussed above for dangling bonds. The lowest-energy states accessible within this radius then determine the PL emission energy. This energy can be calculated from the density of states in the band tails determined, for example, from ESR measurements.[9] These measurements show that the densities of states fall off exponentially into the bandgap with characteristic energies $E_c=32$ meV and $E_v=50$ meV, for the conduction- and valence-band-tail states, respectively.

It follows that the lowest-energy level that can be reached by a typical electron is the energy level at which there is just one band-tail state, on the average, in a volume equal to the capture sphere V. This is equivalent to the energy in the conduction-band tail, where the density of states drops to $(E_cV)^{-1}$, which in turn is equal to an energy $\Delta_c=E_c\ln(VN_c)$ below the conduction-band mobility edge, where N_c (cm^{-3}) is the density of states at the conduction-band mobility edge. The same argument can be used to obtain Δ_v, the thermalization energy for holes. The PL emission energy E_{PL} is then equal to $E_g-(\Delta_c+\Delta_v)$, where E_g is the mobility gap. However, as discussed above in connection with the efficiency, the capture volume V, and hence also Δ_c and Δ_v, are functions of position in the vicinity of the interfaces. The net emission energy will then be an efficiency-weighted average of Δ_c and Δ_v as follows:

$$E_{PL}(L)=E_g-\frac{1}{L\eta(L)}\int_0^L \exp[-V(x)N_d]\times[\Delta_c(x)+\Delta_v(x)]\,dx. \quad (2)$$

The solid line in Fig. 3 is a plot of E_{PL} calculated from Eq. (2) with $E_c=32$ meV, $E_v=50$ meV, $R_c=200$ Å, and $N_c=N_v=10^{19}$ cm^{-3}. The mobility gap E_g is taken equal to the low-temperature optical gap in a bulk a-Ge:H (1.18 eV) as determined from an extrapolation of $(\alpha E)^{1/2}$ to the photon energy E, where the absorption coefficient α is zero. The individual layers in all of the samples in Fig. 3 were too thick (>70 Å) for quantum shifts to be significant ($\Delta E_g>0.01$ eV). The solid line in Fig. 3 is derived from experimentally determined constants and contains no adjustable parameters other than the densities of states N_c and N_v, which determine only the overall position of the E_{PL} relative to the E_g, and not the thickness dependence. The agreement between the model and the

data is satisfactory in view of the simplifying assumptions involved in the model.

In summary, we have discovered that PL in *a*-Ge:H is enhanced by more than 2 orders of magnitude in *a*-Ge:H/*a*-Si:H multilayer structures with thin *a*-Ge:H layers (< 50 Å). The decrease in both the emission energy and the efficiency with increasing layer thickness is attributed to a geometrical effect in which the number of accessible localized states decreases when the layer thickness becomes comparable with the diffusion length of photoexcited electron-hole pairs. This effect, together with the high quality of the *a*-Ge:H/*a*-Si:H interfaces, opens up new opportunities for understanding luminescence phenomena in *a*-Ge:H in particular, and energy transport processes in amorphous semiconductors in general.

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