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Photoluminescence mechanisms in thin $Si_{1-x}Ge_x$ quantum wells

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Photoluminescence spectra were obtained from thin $Si_{1-x}Ge_x$ quantum wells grown by molecular-beam epitaxy and rapid thermal chemical-vapor deposition. The effect of excitation power density is compared with recent results for thick quantum wells, in which a high-quantum-efficiency localized exciton luminescence band was observed under conditions of low excitation. The separation between the usual near-band-edge luminescence and the localized exciton feature is found here to decrease from 20 to ~0 meV when the quantum-well thickness is decreased from 83 to 12 Å. In the very thin quantum wells (10–15 Å) the spectral line shape and position change very little with excitation density changes of over six orders of magnitude. However, the dependence of the luminescence intensity on excitation power and the very long decay time (~750 μsec) at low excitation lead us to propose that a localized exciton process is also important in the very thin quantum wells grown by both techniques.

Advances in the last three years in epitaxial growth of Si-based heterostructures have made it possible to begin characterizing this materials system by photoluminescence (PL) spectroscopy. Such studies are crucial in effectively designing heterostructure electronic devices, as well as in investigating the possibility of optoelectronic applications. Observations of band-edge luminescence have been reported for strained $Si_{1-x}Ge_x$ layers grown by chemical-vapor deposition[1,2] (CVD) and more recently by several groups using molecular-beam epitaxy (MBE).[3–8] The band-edge PL has heretofore been thought to arise from the recombination of either free excitons (FE) or bound excitons (BE) associated with shallow impurities, such as boron or phosphorus. However, many questions remain as to the exact nature of these and other PL processes in $Si_{1-x}Ge_x$/Si heterostructures.

$Si_{1-x}Ge_x$ grown by MBE has been associated with a strong broad PL feature, centered roughly 120 meV below the expected $Si_{1-x}Ge_x$ band edge, which seems to occur more strongly in layers with weak or no observable band-edge luminescence.[4,5,8] This especially seems to pose a problem in growing $Si_{1-x}Ge_x$ layers thicker than 4–10 nm (depending on x).[5] While the mechanism which gives rise to this band is not clear, recombination of excitons bound to a strain field created by Ge platelets has been proposed by Noël *et al.*,[5] while Glaser *et al.*[8] maintain that a donor-acceptor pair process is responsible. On the other hand, there has been some success in growing thick $Si_{1-x}Ge_x$ layers by MBE which show dominant near-band-gap PL features identified as BE or FE, but the differences in growth conditions which select between the near-band-gap or deeper PL for thick MBE layers are not yet understood.[3]

Other features have been observed in CVD $Si_{1-x}Ge_x$ under conditions of low excitation density, which were identified with the recombination of localized excitons[9] (LE). The excitons are thought to be localized by regions of higher than average Ge content that arise simply from the random nature of the alloy. Similar localized exciton luminescence peaks had earlier been observed in other semiconductor alloys (see, for example, Fried, Ron, and Cohen,[10] or Lai and Klein[11]). Because free excitons in $Si_{1-x}Ge_x$ have the long radiative lifetimes typical of an indirect gap material, the localization leads in this case to increased luminescence efficiency by reducing recombination by nonradiative channels, such as the Auger recombination which dominates for BE. The quantum efficiency for this PL process was in fact measured to be over 10%.[9] However, the LE PL was only observable at low excitation density since it was found to saturate at very low power levels (100 $\mu W\,cm^{-2}$) and so is usually hidden by the BE or FE lines. In MBE $Si_{1-x}Ge_x$, Denzel *et al.*[12] also recently observed a broad no-phonon (NP) line and its TO replica (labeled $A1$ and $A2$) at low excitation power density. Although these transitions have not been studied in any great detail as yet, their appearance only at low power densities and their energy relative to the band-edge PL suggests that these peaks are also due to LE recombination.

In this paper we discuss PL spectra, taken under various excitation conditions, of thin $Si_{1-x}Ge_x$ quantum wells grown by CVD and MBE. The dependence of the PL spectral features on excitation power density, including the overall intensity and time decay, leads us to propose that a localized exciton process is responsible for the PL in these thin quantum wells at moderate to low excitation density.

The CVD samples were grown by the technique of rap-

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id thermal chemical-vapor deposition (RTCVD), as described previously by Sturm *et al.*[13] A series of single quantum-well samples were grown with Ge fraction $x=0.2$ and well thickness decreasing from $L_z=83$ to 33 Å. The nominal Ge fractions and thicknesses were confirmed in a few samples by x-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). A very thin single quantum-well sample with a Ge fraction of $x=0.35$ and a nominal thickness of 15 Å was also grown by RTCVD. Note that the $Si_{1-x}Ge_x$-Si interface abruptness is estimated to be of the order of 5–10 Å, so that the thin 35% well cannot be regarded as having sharp well sides.[13] The MBE samples were grown using conventional solid source MBE, as described by Noël *et al.*[5] Although similar results were found in several other MBE samples, the data presented here concentrate on a 10-period nominal 10-Å $Si_{0.6}Ge_{0.4}$/200-Å Si multiple quantum well. XRD and HRTEM indicated that the quantum wells were 12 Å thick and had $x=0.38$. Both the CVD and MBE samples had Si caps and were below the critical thickness for strain relaxation.

The PL data were collected by Fourier transform photoluminescence spectroscopy using a Bomem DA8.02 interferometer with an $In_xGa_{1-x}As$ detector. An argon-ion laser was used to excite the samples, which were immersed in superfluid (2 K) or boiling (4.2 K) liquid helium. The time-resolved data were obtained by pulsing the Ar laser with an acousto-optic modulator and detecting the PL with a Varian (VPM159A3) photomultiplier tube operated in photon-counting mode and coupled to a $\frac{3}{4}$-m double spectrometer.

Figure 1 compares sets of PL spectra taken with high (I_0) and low excitation power density ($10^{-3}I_0$) for each

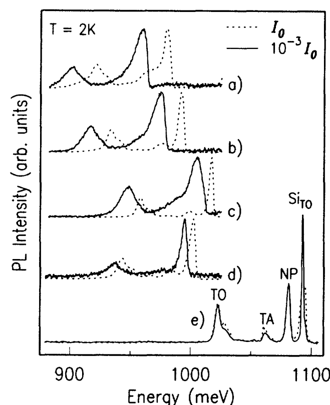

FIG. 1. PL spectra for CVD $Si_{0.8}Ge_{0.2}$ single quantum wells with thicknesses of (*a*) 83, (*b*) 58, (*c*) 33 Å, and for the very thin quantum wells, (*d*) CVD 15-Å $Si_{0.65}Ge_{0.35}$ and (*e*) MBE 12-Å $Si_{0.62}Ge_{0.38}$. Spectra are shown under conditions of high (I_0) and low ($10^{-3}I_0$) excitation density, where I_0 is of the order of a few W cm^{-2}. The spectra have been scaled to give equal intensity for the $Si_{1-x}Ge_x$ NP peaks. The energy shifts between the high and low excitation spectra are seen to decrease from ~20 meV in (*a*) to zero in (*e*). The line labeled Si_{TO} is due to the substrate.

of the CVD and MBE samples. The top three pairs of spectra are from the $Si_{0.8}Ge_{0.2}$ CVD single-well samples of intermediate well thicknesses (*a*) 83, (*b*) 58, and (*c*) 33 Å, while the PL of the very thin quantum wells are shown in (*d*) 15-Å $Si_{0.65}Ge_{0.35}$ CVD sample and (*e*) 12-Å $Si_{0.62}Ge_{0.38}$ MBE sample. In each sample at high power (dashed curves) we observe the NP peak and phonon replicas (TO and TA) which are normally attributed to the $Si_{1-x}Ge_x$ BE or FE recombination.[1–9] The band-edge PL has shifted as expected towards higher energy with decreasing well thickness from (*a*) through (*c*) due to quantum confinement effects.[14] The value for I_0 was chosen to minimize the broadening of the features which occurs at very high excitation, and was of the order of a few W cm^{-2} in each case. At $10^{-3}I_0$ the BE PL in the intermediate thickness CVD samples (*a*)–(*c*) drops in intensity to reveal the NP and phonon replica features of the LE process. The LE and BE NP peaks were simultaneously present in the spectra of the 83- and 58-Å wells at intermediate powers (not shown). The low power spectra in (*a*)–(*c*) show the broad asymmetric line shape, with a long exponential tail to low energy, which is characteristic of LE transitions.[9] Although the spectra of the thin quantum-well samples (*d*) and (*e*) do not show a change in line shape at low power, other evidence as outlined below suggests that the features are also due to LE.

The energy separation between the LE and BE peaks in curves (*a*)–(*c*) of Fig. 1 is observed to decrease with decreasing well thickness from about 20 meV for $L_z=83$ Å to 12 meV for $L_z=33$ Å. The LE-BE separation is reduced in the thin (15 Å) CVD sample to only 7 meV. Further, in the 12-Å sample (curve *e* of Fig. 1) there was, to within 0.5 meV, no observable shift or broadening of the spectral features over a change of six orders of magnitude in the excitation power density. Since, as we will later show, the LE process still exists in this sample, the LE binding energy relative to the other near-band-gap PL must be ~0.

The decrease in the observed LE binding energy with decreasing well thickness may arise because, as the hole of the exciton becomes confined to a thinner $Si_{1-x}Ge_x$ well (neglecting any confinement of the electron), the excitons are effectively localized in the z direction and are only free to move in the plane of the $Si_{1-x}Ge_x$ layer. As the exciton is increasingly constrained to move in two dimensions rather than three, the likelihood of it hopping or tunneling to the deeper alloy fluctuations within its finite lifetime is reduced. In addition, in the thin wells there is the possibility of the hole being further localized due to short-range fluctuations in well thickness. Control in well interfaces to monolayer resolution, as in III-V heterostructures (see, for example, the review by Herman, Bimberg, and Christen[15]), would be needed to separate the effects due to the alloy disorder and the well thickness fluctuations. Note also that the situation in most other systems such as $Al_xGa_{1-x}As$/GaAs is simpler because the alloy material makes up the barrier and not the well region. For the present study we simply consider the effects of localization on the exciton recombination, without specifying which mechanism is most responsible for this localization.

Despite the difference in the spectral dependence of the thin MBE and CVD quantum-well PL on excitation power density, the variation in the overall PL intensity is quite similar to the thick-well case. This is shown in Fig. 2 where we plot the PL intensity over nearly seven orders of magnitude in power density. At extremely low powers we see an approximately linear increase in PL intensity with increasing power for the MBE and CVD thin quantum wells, and for the LE PL of the relatively thick (100 Å) CVD well studied earlier.[9] The thin-well PL intensities becomes sublinear at a very low excitation density, which is in agreement with the onset of saturation (~ 10 $\mu W\ cm^{-2}$) of the LE PL in the thick CVD sample. After this sublinear region, the PL intensity again approaches a linear dependence on power level at high excitation densities. For the thick CVD well, in which the power dependence of the LE and BE features were tracked separately, this would correspond to a linear increase in the BE intensity with the LE remaining constant at its saturated value. The sum of the intensities of the LE and BE PL in the thick well (shown by the solid curve) shows a power dependence very similar to that in the thin wells, suggesting that in the case of the thin wells the LE PL is present but is not resolved from the BE simply due to its small binding energy. Extrapolating between low- and high-power densities, the low excitation PL process in the thin wells has a PL quantum efficiency of $\sim 10^3$ times that of the high excitation process, consistent with the observed high quantum efficiency of the LE process as observed[9] in thicker layers. Similar power dependence curves were observed by Wachter *et al.*[16] for their MBE quantum wells, although not to low enough power density to observe the return to linear power dependence below the LE saturation.

Further evidence that the PL in the thin CVD and MBE wells arises from similar processes to those observed in the thicker wells is provided by transient photoluminescence decay curves. Figure 3 shows a series of PL decay curves for the MBE sample. Under conditions of low excitation density (bottom curve) the near-band-gap PL is found to decrease with a single exponential decay of 750 μs. This is several orders of magnitude longer than typical BE or FE lifetimes for Si, which for the FE case are limited by capture onto impurities. Instead, it approaches the millisecond lifetimes which were measured for the LE PL in the thick CVD wells.[9] The long LE lifetime was attributed there to the elimination of the fast nonradiative channels by the localization of the excitons, which prevents their capture by impurities. As the excitation density is increased, an additional fast component appears, whose intensity is observed to increase with increasing power, while that of the slow process saturates. Shown in an expanded time scale in the inset of Fig. 3, the fast decay is described by a double exponential with lifetimes of about 350 ns and 1.5 μs. The relative intensities of these two components were also found to vary somewhat with excitation density. However, both lifetimes are consistent with recombination processes for which nonradiative channels compete with radiative ones, and so might include BE or biexcitons. These fast decay times are comparable to those of the band-gap PL in thick CVD $Si_{1-x}Ge_x$ quantum wells, which was attributed to BE.[9] Thus, even though the PL spectrum does not appear to change, the near-band-gap PL of very thin quantum-well samples is dominated by the long lifetime, highly efficient LE process at low excitation densities and by a much less efficient, ~ 1 μs lifetime process at high excitation density.

What is the nature of the high excitation PL process? Up until now, the typical near-band-gap PL of $Si_{1-x}Ge_x$ quantum wells at liquid-He temperatures has been as-

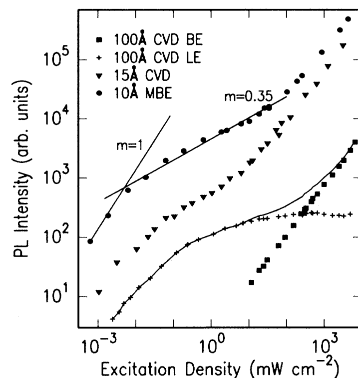

FIG. 2. Dependence of integrated PL intensity on excitation density for the MBE 12-Å $Si_{0.62}Ge_{0.38}$ sample (circles) and the CVD 15-Å $Si_{0.65}Ge_{0.35}$ single quantum well (triangles) is compared to the separate LE (crosses) and BE (squares) intensities of a 100-Å $x=0.2$ CVD sample. The linear ($m=1$) power dependence observed at extremely low power becomes sublinear ($m=0.35$) at a power density comparable to that at which the LE process in the thick quantum wells saturates. The solid curve is the sum of the LE + BE intensities for the 100-Å sample, which is seen to closely match the total PL curves for the two thin samples. The curves for the three samples have been shifted vertically for clarity.

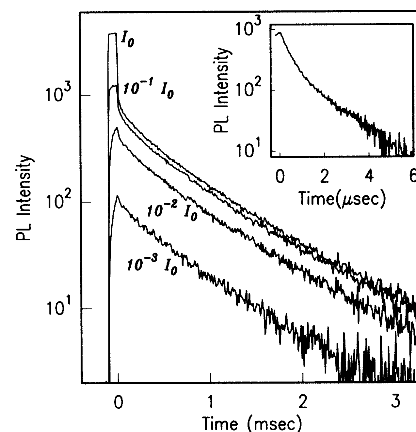

FIG. 3. Time decay of the PL from the MBE 12-Å $Si_{0.62}Ge_{0.38}$ sample. As the excitation power density is increased by a factor of 1000 the contribution from the slow component ($\tau \sim 750$ μs) is observed to saturate, while that from the fast component increases. The inset shows the double exponential dependence ($\tau \sim 350$ ns, $\tau \sim 1.5$ μs) of the fast component at high excitation density on an expanded time scale. The four decay curves have not been shifted vertically.

signed to BE and/or FE. In reality, it is questionable whether *free* excitons exist in these systems at $T \leq 4.2$ K even in the absence of impurities, since the half-width of the band-gap fluctuations due to alloy disorder, averaged over an excitonic volume, are at least a few meV, or in other words, much larger than kT. Thus in pure material at $T \leq 4.2$ K, and at low excitation density, we would have LE rather than FE. The presence of donors and/or acceptors can result in BE as well. This is clearly observed in some studies in which a double NP peak is observed,[1-3,16] with one peak due to the BE, and the other originating from LE at liquid-He temperature or FE at slightly elevated temperatures. On the other hand, a purely LE line at low T would evolve smoothly into the Maxwell-Boltzman line shape typical of FE as T is increased, without ever producing a double-peaked structure.

In fact, the 12-Å MBE sample studied here did not show a double-peaked NP line anywhere from 2 to 60 K, independent of excitation density. This raises the possibility that the high excitation PL is not predominantly due to BE, yet it is clearly different from the LE PL. Another possibility might be (localized) biexcitons, which would still be stable in the strained alloy and would have a ~1-meV binding energy relative to the LE, explaining the lack of an observable spectral shift between low and high excitation.[17] The biexciton, unlike the LE, does have a nonradiative Auger decay channel, and thus would have the necessary shorter lifetime and lower PL quantum efficiency. Both biexcitons and BE are possible explanations for the high excitation process, and the ratio of the two species will depend on the impurity concentration. It is tempting to ascribe the two different fast decay times observed in the inset to Fig. 3, namely, 350 ns and 1.5 μs, to BE and biexcitons, respectively, but further study is necessary. We are at present pursuing a spectroscopic method which is specifically sensitive to multiexciton species such as the biexciton.[17]

In conclusion, we have shown that although the near-band-gap PL spectrum of thin $Si_{1-x}Ge_x$ quantum wells does not change over a very large range of excitation density, two physically very different processes are at work at low and high excitation levels. The spectra at moderate to low excitation levels were shown to be due to localized excitons. We have also proposed that biexcitons may be important in the PL from high-purity $Si_{1-x}Ge_x$ quantum wells at moderate to high excitation levels.

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