High quantum efficiency photoluminescence from localized excitons in $Si_{1-x}Ge_x$

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We report a new photoluminescence process in epitaxial $Si_{1-x}Ge_x$ layers grown on Si by rapid thermal chemical vapor deposition which we attribute to the recombination of excitons localized at random alloy fluctuations. This luminescence is characterized by saturation at very low excitation densities ($\simeq 100\ \mu W\ cm^{-2}$), very long decay times (>1 ms), and high quantum efficiency at low excitation. We have directly measured an external photoluminescence quantum efficiency of $11.5 \pm 2\%$.

Recent progress in the epitaxial growth of high quality strained layers of $Si_{1-x}Ge_x$ alloys or Si/Ge superlattices on Si has rekindled hope for Si-based optoelectronic devices. While claims of quasidirect photoluminescence (PL) resulting from zone folding in Si/Ge short period superlattices have been made,[1] the PL mechanisms in these and other SiGe structures grown by molecular beam epitaxy (MBE) remain in debate. Recently, however, there have been a number of reports of well-resolved near-band-gap PL from fully strained SiGe epilayers grown both by chemical vapor deposition (CVD)[2–4] and MBE.[5–8] After accounting for the relevant energy shifts due to alloy composition, strain,[3] and quantum confinement,[9] these features are readily identified with well known no-phonon (NP) and phonon replica transitions of free excitons (FE) and shallow bound excitons (BE) previously observed in relaxed SiGe alloys.[10,11]

We have observed a new PL process in a variety of single and multiple quantum wells of fully strained $Si_{1-x}Ge_x$ grown on ⟨001⟩Si by the previously described[2,12] rapid thermal CVD (RTCVD) method. We assign this PL to an intrinsic process in which FE become localized on random fluctuations of the alloy composition which are purely statistical in nature. Such localized excitons (LE) have been extensively studied in other semiconductor alloy systems,[13–17] but it has heretofore not been recognized that this process can lead to high luminescence quantum efficiencies (QE) in spite of the indirect band gap and very low oscillator strengths. This high QE results simply from the elimination of the predominantly nonradiative Auger recombination at shallow donors and acceptors, which even in the highest purity Si dominates over intrinsic recombination due to the long radiative lifetime of the FE ($\simeq 1$ ms[18]). In semiconductor alloys at low temperatures, the LE can become immobilized many kT below the alloy mobility edge, and even in moderately impure material, the probability of there being a defect within the radius of a given LE is negligible. Thus, the majority of the LE are expected to decay radiatively, albeit with a very long decay time. We have directly measured an external QE of 11.5 $\pm 2\%$ for the LE process in one sample, which is a remarkably high value given that for Si the QE is normally below 10^{-4}.

While many samples, including single quantum wells, multi-quantum wells and superlattices, were studied and found to show the LE band under similar conditions, the work reported here was done on a sample consisting of a single 10 nm $Si_{0.75}Ge_{0.25}$ well, with 50 nm thick linearly graded Ge ramps on either side increasing from $x=0$ at 50 nm from the well to $x=0.13$ at the well edges. We note that the LE band is observed in samples having alloy thickness below the critical value for strain relaxation, so that misfit dislocations are not thought to play any role. The methods of sample preparation and PL measurement were as described previously.[2,12] Figure 1 shows five PL spectra of this sample at different excitation levels. Figure 1(a), taken with 3.2 W cm^{-2} of excitation at 488 nm is a typical PL spectrum of $Si_{0.75}Ge_{0.25}$, showing the BE NP line, its TA phonon replica, and the three TO-phonon replicas resulting from Si-Si, Si-Ge, and Ge-Ge modes.[2] However, as the excitation density is reduced, a new broader and more asymmetrical PL system appears, whose NP peak emerges from beneath the BE TA replica. At very low excitation levels the SiGe BE lines vanish (as do the Si substrate PL lines), leaving only the NP and TO replica of the new process, which we label LE_{NP} and LE_{TO}. The peak of the LE_{NP} line at low excitation lies $\simeq 20$ meV below the BE_{NP} line position. In other samples, covering $x=0.14$ to $x=0.25$, the LE_{NP}-BE_{NP} separation was found to vary anywhere from 12 to 25 meV. It is unclear whether this LE process is related to the L-band sometimes observed in relaxed, bulk SiGe alloys.[10,11]

The dependence of the LE_{NP} line shape on excitation density is shown in Fig. 2. A semi-log plot is used to emphasize the fact that the line shape results from excitons filling a density of states which is an exponentially decreasing function of energy, in agreement with an LE model.[13–17] The relatively sharp high energy edge of the line shifts upwards with increasing excitation level as fluctuations of lesser depth become increasingly populated.

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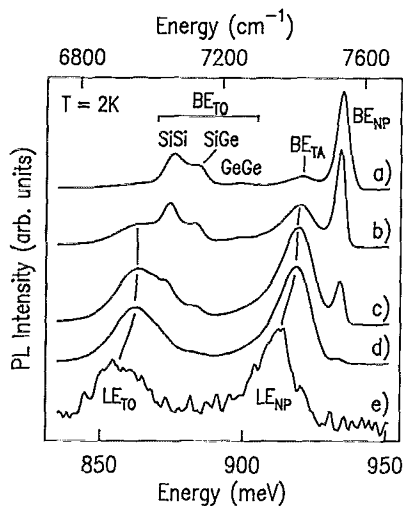

FIG. 1. PL spectra at excitation densities of (a) 3.2 W cm^{-2}, (b) 0.32 W cm^{-2}, (c) 30 mW cm^{-2}, (d) 2.3 mW cm^{-2}, and (e) 2.4 μW cm^{-2}. Typical SiGe BE_{NP} and phonon replica PL is seen at high excitation density (a). As the BE PL drops in intensity with decreasing excitation density, the LE NP and phonon replicas become apparent.

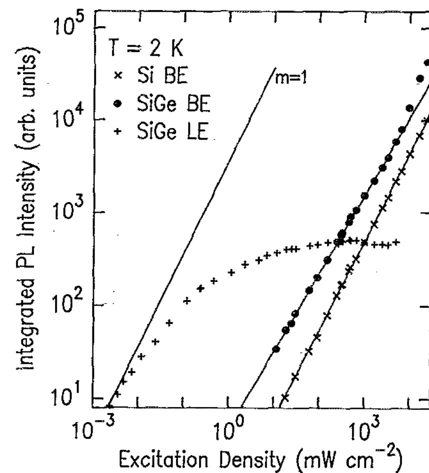

FIG. 3. Integrated PL intensity as a function of excitation density for the Si substrate BE ($\times$), SiGe BE (o), and SiGe LE (+). Intensity depends on excitation density^m, with $m \simeq 0.95$ for the Si BE and 0.84 for the SiGe BE. The LE PL follows the $m=1$ line at very low excitation density, but begins saturating at about 10 μW cm^{-2}.

Note that the LE_{NP}/LE_{TO} intensity ratio is essentially identical to that of the BE_{NP}/BE_{TO} and the FE_{NP}/FE_{TO} processes in the same alloy, as is expected given the rather shallow and diffuse nature of the potential wells responsible for the LE band. We have found the PL decay of the LE line to be nonexponential, in agreement with results for other similar systems,[13,17] with an initial $1/e$ decay of $\simeq 3$ ms stretching to tens of ms at later times.

The strong excitation dependence of the PL intensities evident in Fig. 1 is shown in more detail in Fig. 3. The BE PL from the Si substrate and the SiGe quantum well show the usual slightly sublinear dependence, PL $\propto$ excitation density^m, with $m \simeq 0.95$ for the Si and 0.84 for the SiGe. The LE intensity on the other hand shows strong saturation at very low excitation densities, and only approaches a linear dependence at the very lowest excitation levels we could investigate, $\leqslant 10$ μW cm^{-2}. This is consistent with our LE model, since at low excitation levels each fluctuation contains at most one exciton, and the recombination is expected to be radiative. However, as the excitation density is increased, the chances of having more than one exciton in a fluctuation increases, so that Auger recombination will dominate over radiative recombination. A similar effect has been observed for an isoelectronic BE in Si which can bind one or more excitons.[19]

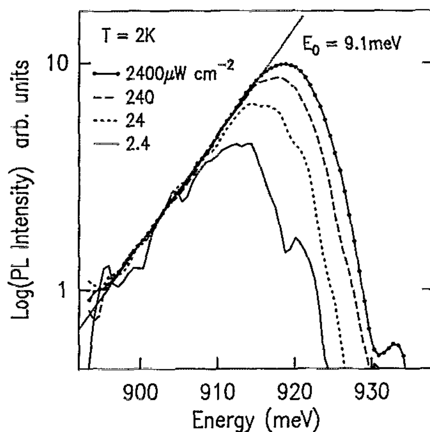

FIG. 2. SiGe LE_{NP} line shape dependence on excitation density. The PL amplitudes were normalized to give equal intensity in the low energy tails. The low energy edge is found to decrease exponentially as a function of energy, with a $1/e$ slope of 9.1 meV as indicated.

It is evident from Fig. 3 that at a low enough excitation density the LE process will have a QE $\simeq 10^3$ times that of the Si or SiGe BE processes. To investigate this interesting possibility, the external PL QE of the sample was measured using a gold-coated integrating sphere immersed in superfluid He. The sample was illuminated with 12 μW cm^{-2} of collimated 488 nm light as determined by a pyroelectric radiometer (Molectron PR-200). The PL was collected through a second hole at right angles to the first, so that only the diffuse reflectance from within the sphere could enter the interferometer. A reference spectrum was also taken, with a known power density (i.e., measured with the same radiometer) of filtered incoherent light of the same wavelength as the LE PL, entering the sphere in exactly the same arrangement as before. After correcting for the sample reflectivity, we calculate that for every 488 nm photon absorbed by the sample under these conditions 0.115 ± 0.02 photons were emitted from the sample in the LE PL band. This is a remarkable result given that not all the excitons, created predominantly in the Si, were likely to be collected by the SiGe well. Although the QE is impressive, admittedly the LE band is at present of little practical importance since it saturates at extremely low power levels and becomes thermally quenched above a few tens of K. The saturation power could be increased by increasing both the number of binding centers and the radiative rate. These goals could in principle be achieved by a system in

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which the fluctuations were no longer statistical but rather driven by some other process.

Something of this nature may be responsible for the broad, intense, and relatively efficient PL band observed ≈ 100 meV from the expected alloy band gap, in MBE samples grown under certain conditions.[5,8,20] We have measured the PL QE of a MBE sample studied previously[20] and obtained an external QE of $1.9 \pm 0.35\%$. Although this is lower than the value reported earlier, which was obtained less directly, the sample efficiency appears to have degraded by up to a factor of two over time. Despite the lower QE of the MBE sample, it can emit much more PL since it saturates at higher pump power than does the RTCVD LE band. The appearance of the MBE PL band has in fact been correlated with the presence of small platelets, platelets, possibly regions rich in Ge, in transmission electron micrographs.[8] There is also a considerable amount of evidence for compositional inhomogeneities which can arise during MBE growth in the Si/Ge system.[21–24]

It is clear that while the emission process involved in the MBE band may also involve compositional fluctuations, the nature of the binding centers is quite distinct from those responsible for the LE band. In addition to the much larger energy shift from the average alloy band gap, we also note that the MBE process is predominantly no-phonon,[20] whereas the LE band has nearly the same ratio of phonon replicas to no-phonon processes as do the shallower processes in the same alloy. The MBE band was also found to have a considerably shorter PL lifetime ($\simeq 30$ μs). This all points to a much deeper and shorter range potential associated with the MBE band.

In conclusion, we have demonstrated that high PL QE can be achieved in the SiGe system by the effective elimination of nonradiative channels, rather than through an increase in the radiative rate. An external PL QE of 11.5 $\pm 2\%$ was demonstrated in a single fully strained $Si_{0.75}Ge_{0.25}$ quantum well. A related process may explain the broad, shifted, relatively efficient PL band often observed in MBE grown SiGe layers.

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