Line-shape model for the broad photoluminescence band from $Si_{1-x}Ge_x/Si$ heterostructures

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Photoluminescence studies on $Si_{1-x}Ge_x$ layers exceeding the critical thickness show not only dislocation-related peaks $D1, ..., D4$, but also in addition a broad band (T band), centered at $\sim$ 110 meV below the strained alloy band gap. Depth profiling studies show that the T band is due to centers in the $Si_{1-x}Ge_x$. The excitation power dependence and high quantum efficiency of the T band can be explained by assuming that it is due to an isoelectronically trapped exciton. T-band line shapes were fitted by a model based on statistical fluctuations of the Ge content and their effect on the local gap energy.

There have been many reports on the occurrence of a broad band in photoluminescence (PL) spectra of $Si_{1-x}Ge_x$ layers grown with different techniques.[1–8] Noël and co-workers[1,2] observed such a feature in layers grown by molecular beam epitaxy (MBE) at low temperatures (400 °C). Internal quantum efficiencies of up to 31% were reported. From the analysis of photoluminescence excitation (PLE) spectra the authors inferred that the high-energy edge of the broad band is due to recombination without phonon participation. Later on, electroluminescence spectra exhibiting the same broad band were reported.[3] On the basis of those studies it was concluded that the band is due to an exciton, probably isoelectronically trapped at a center involving germanium-rich complexes. Two explanations were given for the broadness of the observed band. (i) Its energy width might arise from the convolution of the no-phonon peak and individual phonon replicas, probably broadened because of Ge-content fluctuations. Such fluctuations with Ge-rich complexes are inherent to MBE material deposited at low growth temperatures by electron beam evaporation. (ii) The broad peak might arise from a convolution of individually bound exciton peaks broadened by the same mechanisms mentioned above. By means of a PL and a transmission electron microscopical (TEM) study Noël *et al.*[4] identified interstitial-type features smaller than $\simeq 1.5$ nm with an areal density up to 7×10^8 cm^{-2} as the origin of the broad PL band. The features were found in thick, fully strained layers of $Si_{1-x}Ge_x$ grown by MBE and were ascribed to Ge platelets. Furthermore, thick and partly relaxed layers of $Si_{1-x}Ge_x$ grown by rapid thermal chemical vapor deposition[8] were found to exhibit a broad PL band very similar to the one observed in MBE grown material.

The present paper reports on the observation and an interpretation of this broad T band in the PL of SiGe layers epitaxially grown by low pressure chemical vapor deposition (LPCVD). First, the evolution of the T band in the PL spectra of SiGe single layers with increasing layer thickness will be shown. Then, the spatial origin of the different PL peaks will be established by means of depth profiling experiments. Finally, evidence is collected to support the idea that the T band is due to excitons bound to an isoelectronic trap. A simple statistical line-shape model yields a good fit to the measured T band line shapes for samples with different Ge concentration.

The samples examined were grown by LPCVD (Refs. 9 and 10) on p-type ($\sim 2000\,\Omega$ cm) Si (100) wafers. The epitaxy was carried out at 700 °C and 0.1 Torr using dichlorosilane and germane. The PL was measured using a Fourier transform spectrometer equipped with a Ge detector (North Coast).[11] The samples were cooled in a continuous flow cryostat. Rutherford backscattering was used to obtain the composition and thickness of the $Si_{1-x}Ge_x$ layers; the dislocation density was obtained by counting the dislocations on plan view TEM pictures or in an optical microscope after Schimmel etching.

A series of samples, all consisting of a $Si_{0.88}Ge_{0.12}$ layer between a 70 nm Si buffer and a 4 nm Si cap layer, were grown under identical conditions. In Fig. 1 the evolution of the PL spectra is shown as the SiGe layer thickness is increased from 240 nm to 1260 nm. The spectrum at the bottom represents a SiGe layer whose thickness of 240 nm just exceeds the critical thickness for generation of misfit dislocations at a growth temperature of 700 °C.[12] The transverse optical (TO) phonon replicas of the free and bound excitons in the Si substrate show up near 1100 meV. The peaks following on the lower energy side were identified as free excitons and localized excitons[13] in the $Si_{0.88}Ge_{0.12}$ layer and their TO replicas. The very low misfit dislocation density of 0.034 μm^{-1} manifests itself by the tiny $D1$, $D2$, $D3$, and $D4$ peaks at 806, 874, 934, and 991 meV, respectively. With increasing SiGe layer thickness, the dislocation density increases as expected, and as a result the $D1$ and $D2$ and less the $D3$, and $D4$ PL peaks are enhanced strongly in intensity. In addition, the broad T band develops around 960 meV. Sauer *et al.* have attributed the $D1 - D4$ peaks at energies 807, 874, 939, and 997 meV, respectively, to certain dislocations in deformed bulk Si.[14]

A plot of the maximum intensity of the $D1$ and T peaks against the thickness of the $Si_{0.88}Ge_{0.12}$ layers (inset of Fig. 1) shows quite a similar behavior for both peaks: Above a certain critical thickness, the PL intensity increases strongly and then almost saturates as the thickness is further increased. This suggests that both

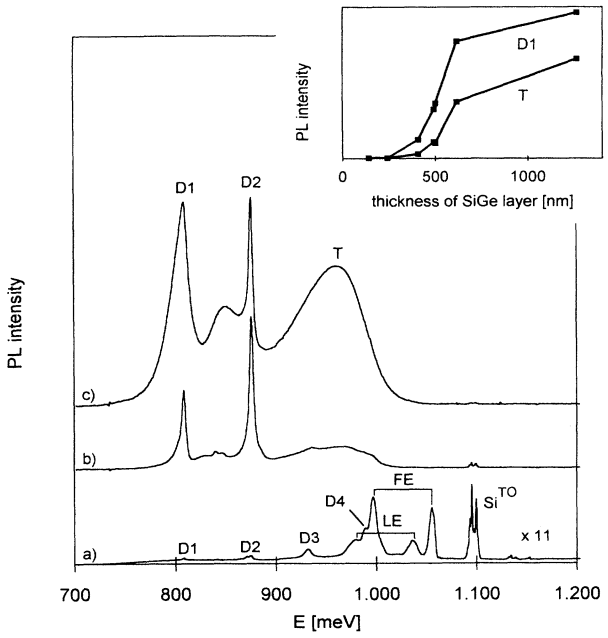

FIG. 1. PL spectra from $Si_{0.88}Ge_{0.12}$ layers measured at 11 mW/mm^2 and 3.9 K. The thicknesses of the samples (a), (b), and (c) are 240, 500, and 1260 nm with dislocation densities of 0.034, 3.4, and 10.9 μm^{-1}. Inset: Maximum intensity of $D1$ and T peaks plotted against the thickness of the $Si_{0.88}Ge_{0.12}$ layer.

the T band and the $D1$ peak are related to some mechanism which lowers the elastic strain energy stored in the SiGe layer. Thus, a similar origin both of the $D1$ peak as well as of the T band appears to be supported. Nevertheless it will be shown by depth profiling experiments that unlike the $D1$ peak the T band is not due to dislocations.

The cross section TEM picture of Fig. 2 shows a sample with a 1260 nm $Si_{0.88}Ge_{0.12}$ layer. Most dislocations are seen to be located at the Si/SiGe interface. Some penetrate quite deeply into the Si substrate. In the SiGe layer only a small number of dislocation loops can be seen near the interface while threading dislocations are not visible at all. This behavior of the dislocations was found in many other samples. The lines drawn on the TEM picture indicate the etch depth of different etching steps after which PL spectra were taken. A diluted Schimmel etch was used with an etching rate of $\sim$ 1.5 nm/s. In Fig. 3 the PL intensity is plotted against the remaining $Si_{0.88}Ge_{0.12}$ layer thickness. The T-band intensity decreases almost linearly with the reduction of the SiGe layer thickness. This implies that the centers responsible for the T-band luminescence are roughly homogeneously distributed throughout the SiGe layer. So, since the dislocations are found only near the interface, they cannot be involved in the T-band luminescence process. The $D1$ intensity, in contrast, increases as the SiGe layer is removed and then decreases again as the sample is overetched into the substrate. Knowing that dislocations are responsible for the $D1$ luminescence this result is understood as follows: As the SiGe layer is etched away, more light is absorbed near the Si/SiGe interface, and so a higher amount of carriers are able to recombine using

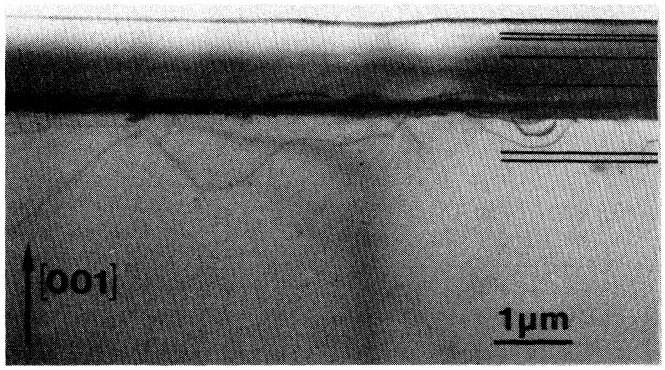

FIG. 2. ⟨110⟩ bright field cross section TEM image of the 1260 nm $Si_{0.88}Ge_{0.12}$ layer sample. The lines drawn in the micrograph represent different etching steps.

the radiative channels offered by the dislocations.

The T band was found in samples throughout the composition range of $x_{Ge} = 3 - 21\,\%$. In Fig. 4 the energetic position of the T band and its full width at half maximum (FWHM) are plotted against the alloy composition x. For comparison the excitonic energy gap of the relaxed $Si_{1-x}Ge_x$ alloy[15] and of the strained $Si_{1-x}Ge_x$ on Si substrate[16] are also plotted. Similar to the findings of Noël *et al.*,[1] our T band shifts with the strained band gap energy at a distance of $\sim$ 110 meV. The FWHM is found to increase linearly with the Ge content in the examined composition range.

PL measurements performed at different excitation power densities showed that the PL intensity of the T band responds almost linearly in the low excitation range and almost square-root-like in the high excitation range. A similar behavior was reported by Weber *et al.*[17] for a localized exciton bound to an isoelectronic trap in silicon. These authors explained the excitation power dependence on the basis of a rate equation model based on the assumption that the decay time of the exciton is very long and that the capture rates for electrons and holes at the isoelectronic center are different. The first assumption may very well be valid also in the present case, since Lenchyshyn *et al.* reported a decay time of 30 μs for MBE grown material.[13] This long decay time and also the high quantum efficiency found in our T band and for the broad luminescence band [Lenchyshyn *et al.*,

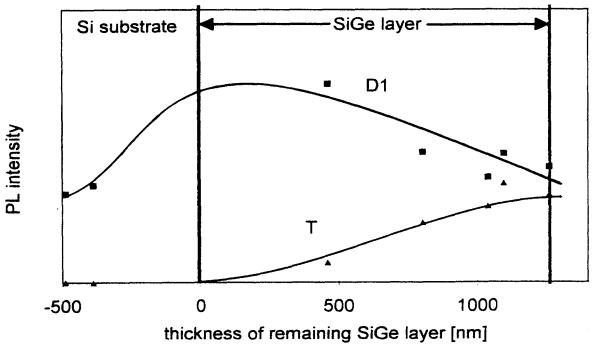

FIG. 3. Depth profiling results: PL intensity vs remaining $Si_{0.88}Ge_{0.12}$ layer thickness.

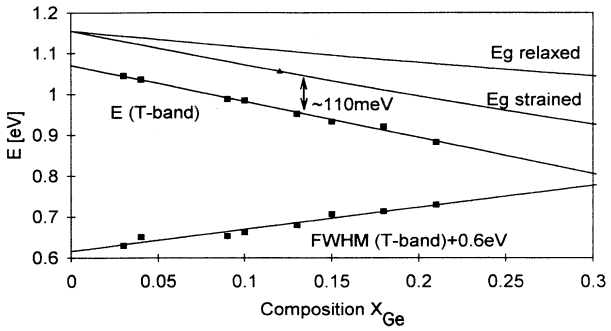

FIG. 4. Energetic position and FWHM of the T band plotted versus the Ge content x. For comparison: Band gap of relaxed (Ref. 15) and strained (Ref. 16) $Si_{1-x}Ge_x$ alloy. The point at $x = 0.12$ represents the NP free exciton peak of a strained sample with 140 nm thickness.

2%;[13] Noël *et al.*, up to 31% (Ref. 1)] of MBE grown material can be considered on its own as strong evidence for isoelectronic binding. According to Weber *et al.*,[17] the arguments are as follows: The lifetime of A^0X and D^0X excitons depends strongly on the exciton binding energy E_{BX} or, as predicted by Haynes rule, on the impurity binding energy E_i. For silicon, experimentally found dependencies $\tau \propto E_i^{-3.9}$ for donors or $\tau \propto E_i^{-4.6}$ for acceptors were reported, and were interpreted as a localized phononless Auger recombination process.[18] For example, excitons that are localized at In acceptors in silicon with $E_{BX} = 13.7\,\text{meV}$ decay rapidly with $\tau = 2.7\,\text{ns}$.[18] The exciton causing the broad band luminescence binds more strongly by a factor of ≈ 8 but nevertheless decays more slowly by a factor higher than 10^3. So the strong binding energy ($> 100\,\text{meV}$) and the long decay time of the excitons rule out the presence of a third mobile particle which would bring about short Auger determined lifetimes. Also the high quantum efficiency is then easily understood by the missing nonradiative Auger channel.

Now we will analyze whether the T band can in fact be accounted for by a model of isoelectronic centers. First, the crucial question has to be answered how an isoelectronically bound exciton (IBE) can produce the observed line shape of the broad T band. The IBE observed by Weber *et al.* in silicon was sharp, exhibiting a linewidth of less then 1 meV.[17] In contrast, the FWHM of the T band was found to vary from $\approx 35\,\text{meV}$ to $\approx 120\,\text{meV}$ with increasing x. In order to answer this question some simple considerations are made. The radius of a free exciton (FE) in $Si_{1-x}Ge_x$ was approximated by Weber *et al.* to be $a_{FE} \simeq 38\,\text{Å}$.[15] This means that the exciton volume contains $\approx 90\,000$ atoms which determine the local alloy composition seen by the exciton. The exciton binding energy is related to the exciton radius a_{ex} in the hydrogen model by the following equation:

$$E_{ex} = R_H \frac{m_r}{m_0}\frac{1}{\epsilon^2}\frac{1}{n^2} = R_H\, a_H \frac{1}{\epsilon}\frac{1}{a_{ex}}. \qquad (1)$$

R_H is the hydrogen Rydberg, a_H the Bohr radius, ϵ the dielectric constant, m_0 the free electron mass, and m_r the reduced mass of the exciton. Equation (1) can be used as a first approximation for the radius of the T-band IBE.

$$a_T \approx a_{FE}\frac{E_{FE}}{E_T} = 4.8\,\text{Å}. \qquad (2)$$

$E_T = 110\,\text{meV}$ is used for the binding energy of the IBE of the T band, $E_{FE} = 14.3\,\text{meV}$ as the FE binding energy in silicon,[19] and $a_{FE} = 38\,\text{Å}$ for the radius of the FE in SiGe. A radius of only 4.8 Å for the T-band IBE implies that this exciton samples only ≈ 170 atoms of the $Si_{1-x}Ge_x$ alloy. Thus it reflects *a very bad alloy statistics as compared with the FE.* This should lead to a strong broadening of the PL recombination peak.

A statistical line-shape model of the T band can be obtained as follows: In an alloy of average composition $\bar{x}$ the probability of finding n Ge atoms within the N_{ex} atoms contained in the exciton volume is given by the binomial distribution

$$P(n) = \binom{N_{ex}}{n}\bar{x}^n(1-\bar{x})^{N_{ex}-n}. \qquad (3)$$

So every IBE samples an area with the local composition $x = \frac{n}{N_{ex}}$ resulting in the local energy gap $E_{gap}(x)$. The luminescence intensity $I_{PL}(h\nu)$ of the T band at the energy $h\nu = E_{gap}(x) - E_T$ is proportional to the number of IBE's $N_{IBE}(x)$ that are bound in an area of local composition x. Since the number of IBE's in such an area is given by the binomial distribution [Eq. (3)], the luminescence intensity can be written as

$$I_{PL}(h\nu) \propto N_{IBE}(x) \propto P(x\,N_{ex}) = P(n).$$

Thus the binomial distribution can be used to evaluate the luminescence intensity. $E_{gap}(x)$ was taken from the least square fit of the strained excitonic energy gap by Robbins *et al.*:[16] $E_{gap}(x) = 1.155 - 0.874x + 0.376x^2$ [eV].

Using this statistical line-shape model, we are able to simultaneously fit the T-band PL spectra of samples with various Ge compositions by adjusting only one parameter, which is N_{ex} or equivalently the radius of the IBE a_T from

$$N_{ex} = V_{ex}/V_{atom}, \qquad V_{ex} = \tfrac{4}{3}\pi\langle r_{ex}^3\rangle = 10\pi a_T^3.$$

V_{ex} or V_{atom} is the volume of one exciton or atom in the crystal, and $\langle r_{ex}^3\rangle$ denotes the quantum mechanical expectation value of the exciton radius to the third power. The best fit is achieved for $N_{ex} = 108$ equivalent to a radius of $a_T = 4.1\,\text{Å}$ (Fig. 5), in reasonable agreement with the approximate value according to Eq. (2). The latest results show that T bands originating from MBE grown SiGe layers can be fitted with the same precision using our statistical line-shape model.[20]

Figure 5 shows that the main part of the T band is fitted very well by the statistical line-shape model. This implies that the main mechanism of broadening the T band is just the statistical nature of the alloy. Other broadening mechanisms, however, such as Ge-rich complexes, or convolution with unresolved phonon replicas (as proposed by Houghton *et al.*[3]), might only be necessary to explain the deviation between measurement and fit at the lower energy edge. The small contribution

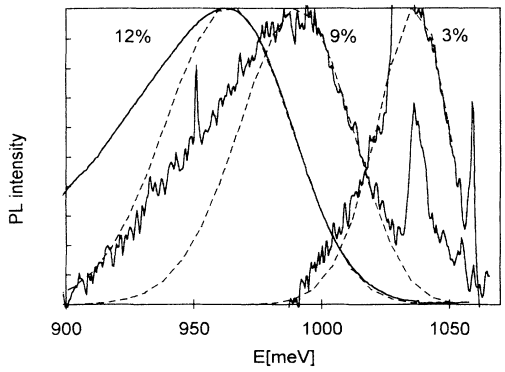

FIG. 5. T-band PL spectra from samples containing 3%, 9%, and 12% of Ge and theoretical fit (dashed curves) by the statistical line-shape model using an exciton radius $a_T = 4.1$ Å.

of phonon replicas can be understood as the exciton is strongly localized in space, and thus the k-selection rule is weakened.

A reasonable model for the neutral binding center might be as follows: The neutral binding center first captures a hole, binds it strongly at the radius of 4.1 Å, and then, as it is now positively charged, captures an electron but binds it only by the weaker Coulomb interaction with the hole. The strongly confined hole is then responsible for the sampling of the local alloy compositon. Since the conduction band offset of strained SiGe on Si is negligibly small, it is easier to believe that a deep hole energy level is more affected by the local composition than a deep electron energy level.

In conclusion, a broad PL band 110 meV below the strained band gap of SiGe was found to develop with increasing thickness of LPCVD grown SiGe layers. The centers responsible for this luminescence are roughly homogeneously distributed in the SiGe layer. By the assumption that the T band is due to isoelectronically bound excitons, it is possible to explain the high PL efficiency and the long PL lifetime observed by other authors.[13] A line-shape fit using a statistical model shows that the isoelectronic bound exciton samples only a very small volume of the alloy (radius $a_T = 4.1$ Å) which explains the broadness of the T band.

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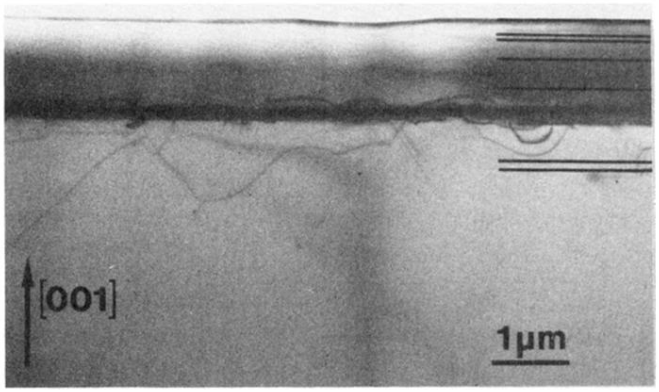

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