Type II Band Alignment in $Si_{1-x}Ge_x/Si(001)$ Quantum Wells: The Ubiquitous Type I Luminescence Results from Band Bending

M. L. W. Thewalt, D. A. Harrison, C. F. Reinhart, and J. A. Wolk*
Physics Department, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

H. Lafontaine
Institute for Microstructural Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6

(Received 4 February 1997)

We present experimental verification of type II band alignment in a coherently strained $Si_{0.7}Ge_{0.3}/Si(001)$ quantum well by studying photoluminescence energy shifts under external strains. A recent determination of type I band alignment from a similar experiment is shown to result from band-bending effects due to high excitation. In high quality samples, the type II luminescence can be observed in the absence of external stress by using extremely low excitation. The type II luminescence differs from the well known type I spectrum in a dramatic but as yet unexplained change in the relative intensities of the phonon replicas. [S0031-9007(97)03558-8]

PACS numbers: 73.20.Dx, 78.55.–m, 78.66.Db

The growth and properties of strained $Si_{1-x}Ge_x$, and more recently $Si_{1-x-y}Ge_xC_y$ heterostructures on (001) Si has attracted intense interest, not only because of the technological promise of combining band gap engineering with a materials system compatible with standard Si processing, but also due to the fact that this is the prototypical indirect band gap heterostructure system. Until recently, little was known about the optical properties of such structures, compared to the exhaustively studied direct gap heterostructures, but the discovery of well-resolved near-gap photoluminescence (PL) [1,2] led to a speedy adaptation of PL as a standard assessment tool, and to a rapid increase in our understanding of the physical processes involved [2–7]. As in bulk, relaxed, $Si_{1-x}Ge_x$ alloys [3], the PL of typical samples is dominated by impurity-bound excitons (BE) at liquid He temperatures, and "free" excitons (FE) at higher temperatures [2], remembering that these FE move in a random potential due to alloy disorder whose width exceeds kT at low temperatures. Related to this, localized excitons (LE) associated with local band gap minima have been discovered and shown to have much higher PL quantum efficiency and longer lifetimes than BE (dominated by Auger recombination [4,5]). While most descriptions of the now ubiquitous PL spectra of these systems limit discussion to the BE/FE species, the long carrier lifetimes make it easy to reach high excitation conditions in the quantum well (QW), and the importance of biexcitons and electron-hole plasmas in the PL processes under normal excitation conditions has been demonstrated [6,7].

One of the remaining contentious issues regarding the physics and optical properties of these systems involves the band-edge alignments. While it was known early on that the majority of the band gap difference was taken up in the valence-band (VB) discontinuity, the only certainty regarding the conduction band (CB) edge was that the discontinuity was small. Theoretical studies have predicted both type I band alignments [8,9], with electrons (e), and holes (h) localized in the $Si_{1-x}Ge_x$, and type II alignments [10,11], with h localized in the $Si_{1-x}Ge_x$ and e in the Si. Some PL studies claimed evidence for type I behavior, using line shifts [12] and hydrostatic pressure effects [13], respectively. Optically induced band-bending effects resulting in excitation intensity dependent shifts of PL energies were cited by Baier *et al.* [14] and Wachter *et al.* [15] as evidence for type II alignment. However, studies of the effects of compressive [001] uniaxial stresses by the same group produced results which were only consistent with type I alignment, although that conclusion was not explicitly stated [16]. More recently Houghton *et al.* [17] extended that approach and, based on $Si_{1-x-y}Ge_x/Si(001)$ QW PL shifts under applied [110] and [100] uniaxial stresses, concluded that the band alignment was indeed type I. A surprisingly large CB discontinuity of at least 10 meV for $x = 0.15$ was quoted, based on the absence of any indication of a turnover to type II PL up to the highest [110] tensile stresses studied.

We have carefully reexamined this situation, and come to the surprising conclusion that the band alignment of $Si_{1-x}Ge_x$ on unstrained (001) Si is, in fact, type II, *even though PL observed in all of the previously published literature is type I.* Band bending produced by type II charge separation makes it energetically favorable to move e into the $Si_{1-x}Ge_x$ above a given excitation level. Because of long recombination times inherent in a structure which is indirect in both k space and real space, significant band bending (enough to overcome a small type II CB offset) can occur at remarkably low excitation levels. The effects of [110] uniaxial and (001) biaxial tensile stress should be to increase the type II CB offset, and thus to increase the excitation level at which the PL switches from type I to type II. We have verified this for several samples, and seen clear evidence for type II PL at zero external stress in one very high quality sample. This can only be explained by a type II band alignment, since for zero CB offset the energy will be minimized by having both *e* and *h* in the QW. An interesting and unexplained detail is a dramatic increase in the intensity of the TA phonon replica for type II PL, which in hindsight can be seen in the PL spectra of separate-confinement heterostructures engineered to have type II transitions [18].

The 3 nm wide $Si_{0.7}Ge_{0.3}/Si$ single QW which formed the focus of this study was grown on (001) Si using a new ultrahigh vacuum chemical vapor deposition (UHV-CVD) system [19]. PL results at 1.6 K were obtained on either a BOMEM DA8 Fourier transform interferometer or a 0.75 m monochromator in conjunction with a LN_2 cooled Ge photodiode array (EG&G). The (001) biaxial tensile stress experiments used a novel wafer bending apparatus [20]. To facilitate direct comparison with the earlier findings of Houghton *et al.* [17], PL measurements under [110] uniaxial tensile stress were also performed using their linear bending method.

Our results are summarized in Fig. 1, which shows the energy shifts of the $Si_{1-x}Ge_x$ no phonon (NP) line vs stress for a wide range of excitation intensities, as measured relative to the position of the NP line at zero external stress and the lowest excitation level used. The inset shows schematically, for zero CB offset, the type I/II transitions (solid arrows) for zero external strain, in which case the transition energies are equal, barring small excitonic corrections which will lower the type I energy. Tensile [110] uniaxial or (001) biaxial strain reduces the band splittings in the QW while removing the band degeneracies in the Si (dashed horizontal lines), thus raising the energy of type I transitions while lowering those for type II (dashed arrows). Note that for the type I transitions the stress effects on both the CB and VB add to produce a large blueshift, while for the type II transition the redshift is due to the difference between the large decrease in the Si CB edge and the smaller increase in the VB energy in the QW.

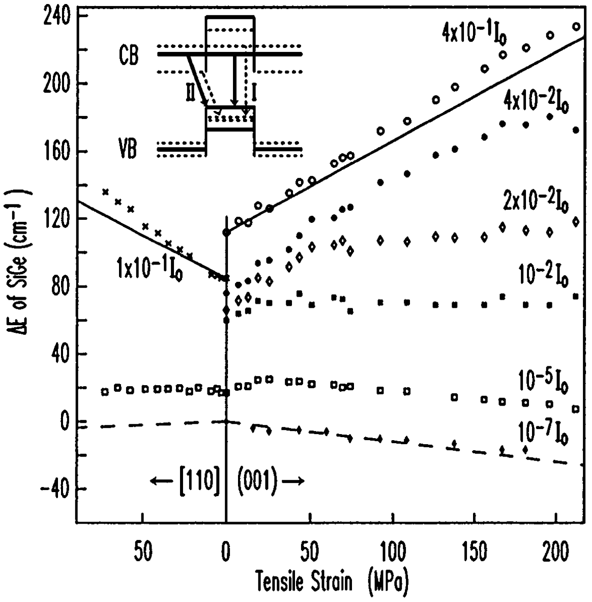

FIG. 1. Energy shift of the SiGe NP line over a wide range of excitation densities versus applied tensile strain. Energies are relative to the NP line at zero external strain and illumination with $10^{-7}I_0$, ($I_0 = 10\ \mathrm{W/cm^{-2}}$). Solid (dotted) lines are theoretical predictions for the strain dependence of type-I (II) transition energies for a $Si_{0.7}Ge_{0.3}/Si(001)$ QW. The inset illustrates the effects of external strain on type I/II transitions.

The results of our detailed calculations of the strain dependence of the type I/II transition energies are shown in the body of Fig. 1 as solid and dashed lines, respectively. Our values were obtained following Laude *et al.* [21], using deformation potentials and elastic constants interpolated from literature values for Si and Ge [22–25]. Note that only the slopes of the lines are significant; the type I and type II curves were shifted vertically to match the high and low excitation data, respectively. For both types of stress, the high excitation data shows good agreement with the blueshift calculated for type I transitions, which also is in agreement with the results reported in Refs. [16] and [17] and is consistent with the relatively high excitation levels used in those earlier studies. However, as the excitation level, and thus the charge accumulation, is lowered, we observe a strong deviation from type I behavior above some characteristic stress which decreases with decreasing excitation. This signals the changeover from type I to type II PL. The $10^{-5}I_0$ data shows a type I blueshift only at very low stress, and then shifts down in energy as predicted for type II PL. At $10^{-7}I_0$ the PL is redshifted for all nonzero stresses, which strongly suggests that the actual band alignment is type II.

The excitation level dependence of the transition energy at fixed strain seen in Fig. 1 is exactly what would be expected for a band-bending induced changeover from type II to type I PL in a system having a type II CB offset which increases with increasing stress. Considering the behavior at high (001) stress, we see that at low excitation the energy is not strongly dependent on the excitation level, since the electric fields are still small. Then, as the type II/I changeover is approached, the energy rises rapidly for small increases in excitation, and levels off again when we are in the type I regime. This is because of the much smaller band bending once extra *e* are allowed to enter the QW, together with much shorter lifetimes for the type I situation. We have verified that when we observe type I PL (with or without strain), the PL lifetime is in the μs to sub-μs region, as is typical for Si BE and normal $Si_{1-x}Ge_x$ QW PL. However, when type II PL dominates, the observed PL decay time was in the ms region, up to 10 ms at the lowest excitation. These very long experimental PL decay times emphasize the need for extremely low excitation levels in order to avoid the effects of band bending—with a 10 ms lifetime, and assuming 100% carrier collection into the QW, only 4 μW cm^{-2} are required to produce an e-h pair density of 10^{11} cm^{-2}, which can cause substantial energy shifts [14,15].

Figure 2 shows spectra at an (001) biaxial tensile strain of 180 MPa for different excitation levels. The two highest excitation spectra, which still fall on the type I curve, are typical $Si_{1-x}Ge_x$ PL spectra, indistinguishable in their features from the zero stress spectra of this sample at all but the very lowest excitation levels. By "typical" we refer to the small amplitude of the TA replica relative to the TO, and the splitting of the TO into three features characteristic of Si-Si, Si-Ge, and Ge-Ge modes. In decreasing the excitation a factor of 10 from I_0 we see very little change in the spectrum. In going from $10^{-1}I_0$ to $10^{-2}I_0$, however, there is a dramatic downshift, and, in fact, two components can be seen in the $10^{-2}I_0$ spectrum, which may reflect a charge accumulation which is not completely uniform across the sample. Below this excitation level the PL again shows little shift or change over a very large range of excitation density.

What is also seen in the lower excitation, type II PL spectra in Fig. 2 is a pronounced change from the typical PL seen in the high excitation type I regime. The TA phonon replica sharpens and its intensity is remarkably enhanced compared to the NP and TO transitions (we note that this "enhanced" TA replica is not being confused with the NP LE transition seen in thicker QW at low excitation [4,5], since there is no evidence for an LE TO replica at the appropriate energy). At present we have no explanation for the TA enhancement, other than to suggest it must be related to charge separation across the $Si/Si_{1-x}Ge_x$ interface present in type II recombination. Also evident in the type II spectra of Fig. 2 is a change in the TO replica, which is now almost solely composed of the Si-Si mode. This is readily understood if the momentum-conserving phonon transitions predominantly involve scattering due to e, rather than h. In the type I regime the recombining (x, y valley) e are in the QW, and except for leakage of their wave functions into the Si, they sample the distribution of Si-Si, Si-Ge, and Ge-Ge bonds in the alloy. In the type II regime the e wave functions are predominantly in the Si (note that while the CB offset for the x, y valleys may be quite small, the offset for the z valleys is much larger, due to their high energy in the $Si_{1-x}Ge_x$), and hence the TO replica is dominated by the Si-Si mode.

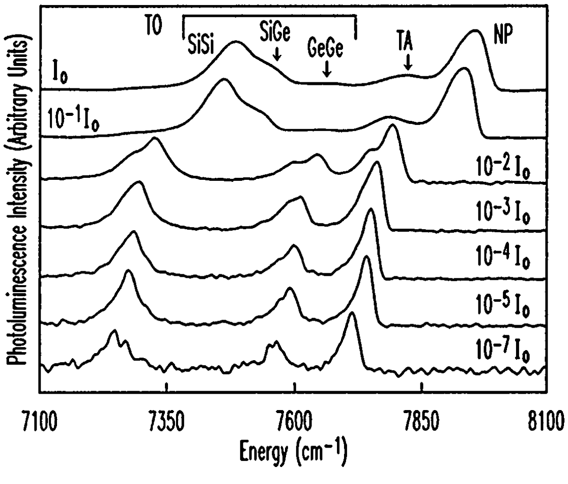

FIG. 2. PL spectra at 1.6 K from a $Si_{0.7}Ge_{0.3}/Si$ QW under a biaxial tension of 180 MPa. The NP, TA, and 3 TO phonon replica transitions are labeled in the high excitation spectrum ($I_0 = 10$ W/cm^2). At this stress, the type I to type II PL changeover occurs near $10^{-2}I_0$.

The type II band alignment at zero external strain suggested by the lowest excitation results of Fig. 1 is strongly supported by the observation of these same characteristic PL changes in the unstrained sample, shown in Fig. 3. The solid and dashed curves correspond to excitation levels of $10^{-2}I_0$ and $5 \times 10^{-8}I_0$, respectively. Also shown is the PL spectrum from a 36 nm $Si_{0.75}Ge_{0.25}/Si$ QW grown by conventional CVD (dotted line). To assist in visual comparison of the spectra, the $10^{-2}I_0$ and 36 nm QW spectra have been downshifted to align all three NP lines. It is immediately obvious that the $5 \times 10^{-8}I_0$ spectrum shows all of the features of type II PL, namely, a strongly enhanced Si-like TA replica, and suppressed Si-Ge and Ge-Ge TO replicas. The $10^{-2}I_0$ (type I) spectrum looks more typical of previous $Si_{1-x}Ge_x$ spectra, but its

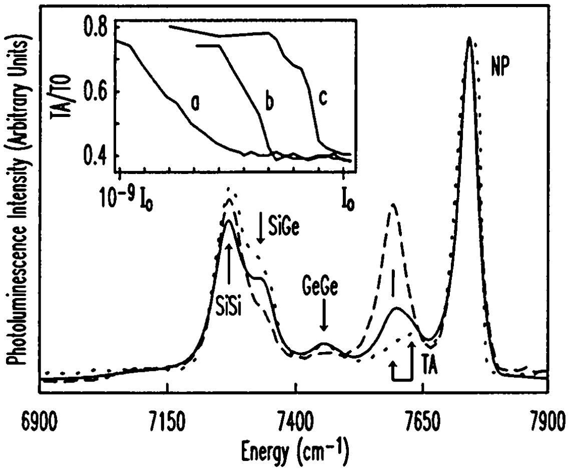

Fig. 3. PL from the $Si_{0.75}Ge_{0.25}/Si$ QW at two different excitation densities without external strain. The —— (- - -) curve corresponds to an excitation density of $10^{-2}I_0$ ($5 \times 10^{-8}I_0$). The dotted curve displays typical SiGe PL from a thick (36 nm) $Si_{0.75}Ge_{0.25}/Si$ QW grown by conventional CVD. The $10^{-2}I_0$ and thick QW spectra have been downshifted to align the three NP peaks. The inset shows the intensity ratio of the TA peak to the Si-Si TO peak over a wide range of excitation densities. Curves a, b, and c correspond to zero, 90, and 170 MPa of external (001) biaxial tensile strain, respectively.

TA replica differs significantly from that of the 36 nm QW. Analysis of the TA replica for the thin QW in the type I regime reveals two distinct components, one at the energy of the strong TA replica seen in the type II spectrum, and the other at the energy of the TA replica in the thick QW. These energies are readily understood: The 153 cm^{-1} component, the only one seen in the type II spectrum, corresponds exactly to the TA energy of pure Si, demonstrating that it is due to the scattering of e whose wave functions are in the Si, and excluded from the QW. The $10^{-2}I_0$ (type I) spectrum shows both this Si-like TA component, as well as the 123 cm^{-1} TA replica typical of $\mathrm{Si}_{0.7}\mathrm{Ge}_{0.3}$ [3]. This alloy TA replica is all that is observed for the thick QW, since there band bending ensures that both e and h are well localized within the QW. For the thin QW, even at high excitation, there is substantial penetration of the electron wave function into the Si since the only confining potential is the electrostatic field of the confined h, and thus a Si-like TA replica is also observed. The TA/TO intensity ratio can be used as an indicator of the band bending induced type I/II PL change, as shown in the inset of Fig. 3, which plots that ratio versus excitation density for zero strain and two nonzero strains.

At this point we consider why, even with our sensitive PL apparatus, it has been so difficult to find samples showing clear type II PL in the absence of an external strain enhancement of the CB offset. We emphasize that the type II behavior has been observed for other samples with external strain, and that one other multi-QW sample showed signs of type II PL without strain at the lowest excitation for which PL could still be observed. It seems likely that the type II PL will be very difficult to observe in thicker QW, since there the band bending at a given carrier density is much larger, and so even lower excitation would have to be used (also in thick QW at low excitation h are not even free to collect near the interfaces, and tend to become trapped at local minima in the random alloy fluctuations throughout the QW [5]). As well, if the Si is even weakly p-type, there will be band bending due to the transfer of h from acceptors in the Si into the QW, even in the absence of excitation, which may easily be sufficient to overcome a small type II CB offset. A rough estimate shows that for a background boron concentration in the Si of only 10^{14} cm^{-3}, a hole concentration of 2×10^{10} cm^{-2} will accumulate in the QW. In any case, it is not necessary that all samples have observable type II PL without external strain to prove that the band alignment is type II; it is enough that the very high quality UHV-CVD samples do so.

In conclusion, we have clearly shown that the band alignment of $\mathrm{Si}_{0.7}\mathrm{Ge}_{0.3}$ on unstrained (001) Si is type II, and that the ubiquitous type I PL from this system in all previous studies results from the cancellation of the small CB offset by band bending resulting from charge accumulation in this long-lifetime system. An interesting and unexplained characteristic of the type II PL is a large enhancement of the TA phonon replica relative to the TO. This merits further study, and we note that we have preliminary evidence that the NP/TA/TO intensity ratios are significantly different for PL emitted either perpendicular to or in the growth plane, and that for PL emitted in the growth plane, the ratios are polarization dependent. Thus while the band alignment controversy has been settled, interesting physics remains to be sorted out.

The support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged, and we thank S. Fukatsu for samples of separate confinement heterostructures, and J. E. Huffmann for high quality conventional CVD MQW samples.

---

*Present address: Lawrence Berkeley National Laboratory, Mailstop 2-200, 1 Cyclotron Road, Berkeley, California 94720.

[1] K. Terashima, M. Tajima, and T. Tatsumi, Appl. Phys. Lett. **57**, 1925 (1990).
[2] J. C. Sturm *et al.*, Phys. Rev. Lett. **66**, 1362 (1991).
[3] J. Weber and M. I. Alonso, Phys. Rev. B **40**, 5683 (1989).
[4] L. C. Lenchyshyn *et al.*, Appl. Phys. Lett. **60**, 3174 (1992).
[5] L. C. Lenchyshyn *et al.*, Mater. Res. Soc. Symp. Proc. **298**, 79 (1993).
[6] T. W. Steiner *et al.*, Mater. Res. Soc. Symp. Proc. **298**, 15 (1993).
[7] T. W. Steiner *et al.*, Solid State Commun. **89**, 429 (1994).
[8] R. People and J. C. Bean, Appl. Phys. Lett. **48**, 538 (1986).
[9] C. G. Van de Walle and R. M. Martin, Phys. Rev. B **34**, 5621 (1986).
[10] Ch. Zeller and G. Abstreiter, Z. Physik B **64**, 137 (1986).
[11] M. M. Reiger and P. Vogel, Phys. Rev. B **48**, 14 276 (1993).
[12] S. Fukatsu and Y. Shiraki, Appl. Phys. Lett. **63**, 2378 (1993).
[13] G. A. Northrop *et al.*, J. Vac. Sci. Technol. B **10**, 2018 (1992).
[14] T. Baier *et al.*, Phys. Rev. B **50**, 15 191 (1994).
[15] M. Wachter *et al.*, Thin Solid Films **222**, 10 (1992).
[16] U. Mantz *et al.*, in *Proceedings of the 22nd ICPS*, edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1994), Vol. 2, p. 1556.
[17] D. C. Houghton *et al.*, Phys. Rev. Lett. **75**, 866 (1995).
[18] N. Usami, Y. Shiraki, and S. Fukatsu, J. Cryst. Growth **157**, 27 (1995).
[19] H. Lafontaine *et al.*, J. Vac. Sci. Technol. B **14**, 1675 (1996).
[20] D. A. Harrison *et al.*, in *Proceedings of the 23rd ICPS*, edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), Vol. 1, p. 381.
[21] L. D. Laude, F. H. Pollak, and M. Cardona, Phys. Rev. B **3**, 2623 (1971).
[22] J. C. Hensel and G. Feher, Phys. Rev. **129**, 1041 (1963).
[23] J. C. Hensel and K. Suzuki, Phys. Rev. B **9**, 4219 (1974).
[24] I. Balslev, Phys. Rev. **143**, 636 (1966).
[25] W. A. Brantley, J. Appl. Phys. **44**, 534 (1973).