Well-Resolved Band-Edge Photoluminescence of Excitons Confined in Strained $Si_{1-x}Ge_x$ Quantum Wells

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We report the first well-resolved band-edge luminescence from excitons confined in fully strained SiGe quantum wells grown on Si. At liquid-He temperatures the photoluminescence is due to shallow bound excitons, and in addition to a no-phonon line, phonon-assisted transitions involving TA phonons and Si-Si, Si-Ge, and Ge-Ge TO phonons are observed. At higher temperatures the spectra are dominated by free-exciton luminescence. Quantum-confinement effects shift the observed free-exciton edge above the bulk strained band-gap energy, and also influence the relative intensities of the three TO-phonon replicas.

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Strained $Si_{1-x}Ge_x$ alloy layers grown epitaxially on Si have recently become the subject of intense scientific and technological interest due to the promise of enhanced capabilities in a materials system compatible with standard Si processing technology. Heterojunction bipolar transistors using SiGe bases already offer improved high-frequency performance over conventional Si homojunction devices.[1] In the more distant future, considerable hope exists that SiGe/Si heterojunction technology could provide optoelectronic detector and emitter capabilities. Given the central importance of radiative recombination for such applications, it is surprising that to date there has been no observation of any readily identifiable near-band-gap photoluminescence (PL) features from strained (or unstrained) SiGe quantum wells.

It has been proposed[2,3] that zone-folding effects might create a quasidirect bandgap in short-period Si/Ge atomic-layer superlattices (ALS's), leading to the possibility of efficient radiative recombination. The reported PL spectra[4,5] from such structures are very controversial, however.[6] The spectra observed by the two groups are quite dissimilar, and the PL signals of Okumura *et al.*[4] attributed to quasidirect ALS transitions appear nearly identical to the well known D_1 and D_2 dislocation-related PL bands often observed in dislocation-rich Si (Ref. 7) or in partially or fully relaxed SiGe epitaxial layers on Si.[8] The broad, asymmetric PL line shape reported by Zachai *et al.*[5] is strikingly similar to an efficient PL system recently reported by Noël *et al.*[9] in a variety of thick SiGe alloy layers and SiGe/Si multiple quantum wells (MQW's), none of which should have any zone-folding effects. Northrup, Iyer, and Wolford[10] have reported depth-profiling results which suggest that the PL signal observed by Zachai *et al.* may have originated from dislocations in the SiGe alloy layer upon which the ALS was grown, rather than from the ALS itself.

Well-resolved free-exciton (FE) and bound-exciton (BE) PL has been observed in relaxed, bulk SiGe alloys by several groups, culminating in the comprehensive work of Weber and Alonso.[11] The lack of sharp, identifiable PL transitions from strained SiGe heterostructures has led to studies of deep-defect PL in strained SiGe layers by the introduction of recombination centers whose properties are well known in Si, but such results unfortunately reveal little about the energy levels or perfection of the SiGe layers.[10,12] Very recently Terashima, Tajima, and Tatsumi[13] have reported FE and BE PL from a thick layer containing only 4% Ge, which may have been partially relaxed, as well as BE PL from a thick layer containing 20% Ge which appeared to be fully relaxed.

In this Letter we report the first well-resolved near-gap PL features from fully strained SiGe quantum wells grown on Si. The spectra are dominated by shallow donor or acceptor BE's at liquid-He temperatures, and by FE's at higher temperatures. The spectra are remarkably similar to those previously reported[11] for relaxed, bulk SiGe, except of course for energy shifts due to the strain in our SiGe layers, and to a lesser extent, due to quantum-confinement effects. We observe linewidths which are comparable to the best previous results for relaxed, bulk alloys.[11,14] In addition to no-phonon (NP) transitions, we observe phonon-assisted transitions involving transverse acoustic (TA) phonons and three transverse optical (TO) replicas for Si-Si, Si-Ge, and Ge-Ge modes whose energies are in excellent agreement with the bulk values.[11] The PL spectra have been stud-

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ied over a wide range of excitation densities and sample temperatures, and in addition photoluminescence decay-time measurements and photoluminescence excitation spectroscopy (PLES) were used to verify our assignments.

The samples were grown by a combination of rapid thermal processing and chemical-vapor deposition (RTCVD) on (100) silicon substrates. After a high-temperature hydrogen clean and silicon buffer layer (~1000 °C), a $Si_{1-x}Ge_x$/Si multi-quantum-well structure was grown. The silicon was grown at 700 °C, using dichlorsilane in a hydrogen carrier (6 torr) to give a growth rate of ~30 Å/min. The $Si_{1-x}Ge_x$ layers were grown at 625 °C by adding a germane-hydrogen mixture to the above gas flows, yielding a nominal growth rate of 80 Å/min. In between the growth of each layer, the wafer temperature was directly switched from 625 to 700 °C (or vice versa) at a ramp rate of 20 K/s, but a total of 10–15 s was allowed for temperature stabilization and complete gas purging between each layer. The silicon wafer was heated without a susceptor by tungsten halogen lamps outside of the reaction tube, and the wafer temperature was continuously probed *in situ* (for feedback control of the lamp power) by the infrared transmission technique.[15,16]

Two 4-in. wafers (No. 416 and No. 489) were grown, and each was measured at two separate locations on the wafer (locations labeled 416 and 416-1B, 489 and 489-4). (Because of nonuniformities in the wafer temperature, the rate of the CVD reaction and thus the layer thicknesses vary across the wafer.) At each measured location, photoluminescence, x-ray diffraction (XRD), and cross-section high-resolution transmission electron microscopy (HRTEM) were performed on samples all from within 5 mm of each other. The thicknesses of the Si and SiGe layers at each point were obtained from the HRTEM measurements (Table I). This information was combined with the XRD data of the average superlattice peak to arrive at the composition of the $Si_{1-x}Ge_x$ layers in each sample. In all cases, a composition between 0.17 and 0.19 (±0.03) was found. Because all samples were grown under nominally identical conditions of temperature and gas flows, a single composition of 0.18 was used for all subsequent analysis. The misfit dislocation spacing was > 10 μm in all cases, so that the samples can be considered fully strained. The threading dislocation density was ~10^3 cm^{-2}.

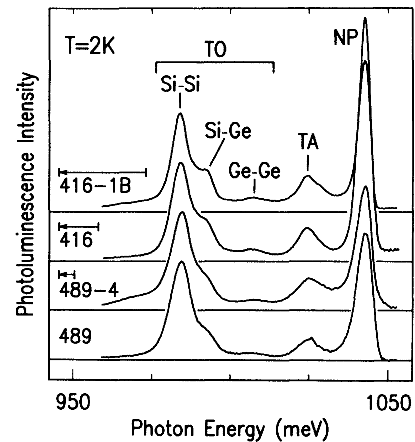

FIG. 1. Photoluminescence spectra of the four samples taken at 2 K. The energy scale is appropriate for the bottom spectrum (sample 489); the other spectra have been shifted up in energy so as to align the no-phonon (NP) transitions, as indicated by the arrows.

The PL spectroscopy was performed on a Bomem DA3.02 Fourier-transform interferometer. Excitation was provided by Ar-ion laser light at power densities ranging from 10^{-2} to 10^3 W cm^{-2}, but most PL measurements were taken at ~5 W cm^{-2}. Low-temperature PL was obtained from samples immersed in superfluid He and mounted in a strain-free manner. PL was also collected from 10 to 150 K with samples glued to a temperature-controlled Si block in a flowing-He-gas Super Varitemp Dewar. Photoluminescence excitation spectra were collected with the same dispersive spectrometer and a tunable optical parametric oscillator as the source.[17]

All four samples showed strong PL from the SiGe/Si MQW's, with integrated intensities equal to or greater than those of the lightly doped Si substrates. The MQW luminescence of all samples remained very strong to 77 K, and was still readily observable to 150 K. Low-temperature PL spectra of the four samples have been superimposed in Fig. 1 to emphasize their overall similarity. The spectra have a no-phonon transition as the

TABLE I. Summary of structural measurements, photoluminescence data, and calculations of quantum-confinement effects.

	TEM+XRD analysis					Photoluminescence			Calculations	
	Thickness (nm) ±0.3			No. of		BE_{NP}	x_{ph}	$E_{FE}-$	E_{conf}	
Sample	SiGe	Si	SiGe+Si	periods	x	(meV) ±1	±0.01	E_{conf}	(meV)	x_{eff}
489	2.3	2.3	4.4	50	0.18±0.03	1042.6	0.135	1001	47	0.130
489-4	2.5	2.3	4.7	50	0.19±0.03	1037.5	0.15	1000	43	0.135
416	2.9	5.4	8.3	10	0.17±0.02	1030.0	0.165	995	40	0.160
416-1B	3.4	6.5	9.9	10	0.18±0.02	1014.9	0.165	988	32	0.166

highest-energy component, followed by momentum-conserving phonon replicas involving TA phonons and three distinct TO replicas due to Ge-Ge, Si-Ge, and Si-Si modes. The observed phonon energies of these four modes are, respectively, 17.8 ± 0.5, 35 ± 1.5, 50.5 ± 1, and 58.2 ± 0.5 meV, in agreement with previous results for relaxed bulk alloys.[11] The energies of the NP transitions are summarized in Table I under the heading BE_{NP}.

It is expected that the PL spectra of high-quality SiGe MQW's will be dominated by shallow BE's at liquid-He temperature, since this is the case in Si even for very low donor or acceptor concentrations ($>10^{13}$ cm^{-3}). At low temperatures, BE luminescence dominates the PL spectra of previous studies[11,14] of bulk, relaxed alloys, as well as the spectra of Terashima, Tajima, and Tatsumi.[13] The full width at half maximum (FWHM) of the NP lines in Fig. 1 is ~ 5 meV, and at low excitation a FWHM of only 3.7 meV was obtained, comparing well with the best previous results.[11,13,14] Confirmation of the shallow-BE origin of the transitions shown in Fig. 1 was obtained from a careful study of the PL with increasing sample temperature. Some typical examples are given in Fig. 2. Below ~ 10 K, the spectra are relatively independent of temperature, but at 18 K (Fig. 2, curve *b*) a high-energy shoulder appears on the BE_{NP} line, becoming stronger than the BE_{NP} at 24 K (Fig. 2, curve *c*) and dominating the spectrum at 60 K (Fig. 2, curve *d*). This behavior, and the Maxwell-Boltzmann line shape evident at 60 K, reveals the higher-temperature PL process to be due to free excitons in the SiGe wells.

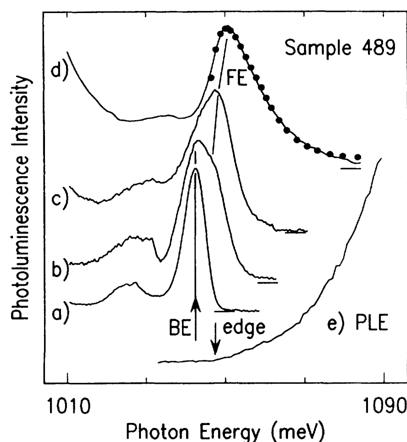

FIG. 2. Curves *a*–*d* show the NP photoluminescence of sample 489 at $T=4.2$, 18, 24, and 60 K, respectively, under identical excitation conditions. At 4.2 K only a single symmetrical bound exciton (BE) transition is observed, while at 18 and 24 K a higher-lying free exciton (FE) shoulder grows in intensity. At 60 K the FE dominates the spectrum, revealing its asymmetrical, Maxwell-Boltzmann line shape. The solid circles show the best fit to the 60-K data obtained by fitting a Maxwell-Boltzmann function, convolved with the low-temperature BE line shape to account for alloy broadening. This fit was obtained for a temperature of 59.2 K and a FE edge (at 60 K) of 1043.75 meV. Curve *e* shows the photoluminescence excitation spectrum of the TA replica of the BE luminescence taken at 2 K. Note the absence of any response at the BE NP energy, and the absorption edge at 1047.3 ± 1.5 meV.

To further support this assignment, we have measured the photoluminescence excitation spectrum of the TA-phonon PL replica of sample 489 at 2 K, as shown in Fig. 2, curve *e*. Note that, unlike the case for direct-gap heterostructures, in indirect-gap systems such as this the PLE spectrum of the FE does not show peaks but rather an absorption edge below which the response is zero and above which the response climbs monotonically. In Fig. 2, curve *e*, note the complete absence of any response at the position of the low-temperature BE PL line (BE absorption is extremely weak in indirect-gap materials), and a clearly defined absorption edge at 1047.3 ± 1.5 meV. This absorption edge is in good agreement with the location of the FE PL component in Fig. 2, curves *b* and *c*, and results in a value of 5 ± 2.0 meV for the binding energy of the shallow BE which dominates the spectrum at low temperatures. This is in good agreement with shallow-BE binding energies in Si (Ref. 18) and in relaxed SiGe alloys.[11,14] Furthermore, PL lifetime measurements of the NP lines in samples 489 and 416 at 2 K yielded decay times of 375 ± 40 and 420 ± 50 ns, respectively. These are in good agreement with shallow-BE lifetimes previously observed in Si,[18] but are much too short to be the radiative lifetimes of FE's trapped in alloy fluctuations.[14]

Since the SiGe layers are thin, the band gap is increased by quantum-confinement effects, predominantly due to the large valence-band offset (~ 140 meV). This is supported by the fact that within each wafer, the sample with the thicker layers had lower observed photoluminescence energies. The structural data of Table I was then used to compute the quantum-confinement shift of the valence-band edge by calculating the ground state of the valence-band superlattice. These results were then subtracted from the observed free-exciton energy to yield an extracted band gap (Table I). The results from the two locations on each wafer are the same within 7 meV in the worst case. The average computed band gaps from the two wafers differ by ~ 9 meV (992 vs 1001 meV). This could be caused by a difference in composition of the $Si_{1-x}Ge_x$ layers in the two wafers of $\Delta x = 0.01$, which is within the error of our structural measurements. Note that these band gaps are in good agreement with those measured by Lang *et al.*[19] using absorption spectroscopy for $x = 0.2$.

Another interesting feature which can be observed in Fig. 1 is the differences in the relative intensities of the Si-Si, Si-Ge, and Ge-Ge TO-phonon replicas between

samples. Weber and Alonso[11] have shown that these relative intensities can be related to x in bulk alloys. We have calculated the relative intensities of the Si-Si and Si-Ge components for each sample, and converted these ratios to a "phonon" x (x_{ph}) using the relationship given by Weber and Alonso. These results are summarized in Table I. In qualitative terms, when the alloy layers are thick (compared to an exciton Bohr radius, e.g., ~ 4 nm), the exciton wave function is confined fully within the alloy layers and $x_{ph}=x$. As the quantum wells are reduced in thickness, the exciton wave function increasingly penetrates into the Si barriers, and $x_{ph}<x$. An accurate theoretical prediction of x_{ph} is complicated by our lack of knowledge concerning the conduction-band offset, which is thought to lie in the range of $+20$ to -20 meV. We have calculated an effective x seen by the exciton, labeled x_{eff} in Table I, based on the reasonable assumption that the electron-hole overlap within the quantum wells versus that in the barriers is determined solely by the hole wave function, and that the electron wave function is not affected by the relatively small conduction-band discontinuity. The results are seen to be in good agreement with the measured x_{ph}.

In conclusion, we have observed the first strong, well-resolved band-edge luminescence from fully strained SiGe MQW's grown on Si. The spectrum is dominated by shallow BE's at low temperatures and by FE's at higher temperatures. These strong, sharp transitions will be of great use in studying the physics of this prototypical indirect-band-gap heterostructure system, and in perfecting the growth technology. We have also shown that the phonon replicas can be used to calculate an "effective" alloy composition sampled by the exciton wave function, which differs from the actual quantum-well alloy composition for thin wells such as those studied here. This can provide useful information in addition to the transition energies.

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