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Excitonic photoluminescence from Si-capped strained $Si_{1-x}Ge_x$ layers

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High-quality fully strained $Si_{1-x}Ge_x$ layers with $0\% < x < 22\%$ grown on Si(100) by rapid thermal chemical vapor deposition have been analyzed by photoluminescence spectroscopy. We report a well-resolved near-band-gap excitonic transition observed in SiGe layers. These transitions make it possible to determine directly the fundamental band gap of such strained $Si_{1-x}Ge_x$ alloys. The results show that high surface recombination in very thin films prevents the observation of radiative recombination, while demonstrating the striking effectiveness of a Si epitaxial capping layer in eliminating surface recombination.

Strained $Si_{1-x}Ge_x$ layers grown on Si substrates have recently become the subject of intense scientific and technological interest because they provide an opportunity to engineer the band gap in a material compatible with Si technology. Research on devices such as heterojunction bipolar transistors,[1] modulation doped field effect transistors,[2] and internal photoemission heterojunctions[3] is very active and requires the growth of high-quality SiGe/Si heterostructures. Given the central importance of knowing the fundamental band gap and measuring the radiative recombinations for such applications, photoluminescence (PL) measurements appear to be very well suited. However, to our knowledge, there have been no observations of any readily identifiable near-band-gap PL features from such strained films.

Bound-exciton and free-exciton luminescences have been measured in bulk SiGe alloys and recently reviewed by Weber and Alonso.[4] In SiGe films, PL lines near the band gap have been reported by Terashima, Tajima, and Tatsumi,[5] but the films, grown by molecular-beam epitaxy (MBE), were either thick when $x=4\%$ or fully relaxed when $x=20\%$. Only recently, Sturm *et al.*[6] have observed excitonic lines in fully strained SiGe quantum wells grown on Si.

In this paper, we report a well-resolved near-band-gap PL feature from fully strained high-quality SiGe layers grown on (100) Si. The results show that free excitons can be well confined by a Si capping layer. Furthermore, they allow direct and highly accurate determination of the fundamental band-gap energy.

The samples were grown by a combination of rapid thermal processing and chemical vapor deposition (RTCVD). The machine used (Jipelec FUV4) is a 4-in. single-wafer reactor that employs radiant energy, operates at reduced pressure, and is equipped with a load lock. The reaction chamber comprises a stainless-steel water-cooled chamber with a water-cooled quartz window. Both chambers have a base pressure of around 10^{-7} mbar. The sample is heated through the quartz window by a bank of high power halogen lamps and the temperature is monitored *in situ* by a pyrometer. Two series of samples were grown: The first, named EPI, consists of fully strained $Si_{1-x}Ge_x$ layers, in the composition range 0%–22%, grown on Si; in the second series, named BL, an additional capping Si layer, 100-nm thick, was grown above the SiGe layer in order to obtain a coherent, strained SiGe buried layer. Each sample, 4-in. Czochralski *n*-type (100) Si wafer, was chemically cleaned prior to loading and subsequently hydrogen baked *in situ* at 1020 °C for 30 sec. An intrinsic Si buffer layer was then grown at 900 °C. After this buffer layer, the strained SiGe layer and possibly the Si capping layer (in the BL series) were grown at 800 °C. The silicon layers were grown using silane in a hydrogen carrier gas, yielding a nominal growth rate around 100 nm/min. The SiGe layers were grown by adding a germane-hydrogen mixture to the above gas flows. In between the buffer layer and the SiGe layer, the temperature was switched from 900 °C to 800 °C in approximately 2 sec. The germane-hydrogen-mixture flow was simply switched off between the SiGe layer and the Si cap.

Before the PL study, high-resolution x-ray diffraction (HRXRD), transmission electron microscopy (TEM), and Rutherford backscattering (RBS) measurements were performed on the samples, all in the central part so as to avoid any problem of nonuniformity. The thickness of the SiGe layers taken from cross-sectional TEM images ranged from 100 nm to 25 nm depending on the Ge content (0%–22%). The thicknesses used were far below the critical thickness at each composition in order to have the films completely strained. The strain as well as the crystalline quality were verified by HRXRD, and cross-sectional TEM observations which showed no misfit dislocations at the interfaces or dislocations in the films were found. In order to compare our results with the literature in terms of fundamental gap energy, the Ge content was carefully measured by RBS in conjunction with HRXRD with an estimated accuracy better than $\pm 0.5\%$.

The PL measurements were carried out using the 514.5-nm line of a cw argon-ion laser with power densities ranging from 1 to 50 W/cm^2. The samples were mounted

on a copper block in a strain-free manner and placed in a variable temperature He gas steady-flow cryostat allowing PL measurements from 5 K to room temperature. The PL signal passed through a high-resolution grating monochromator (Jobin Yvon-type 11R52) and to a liquid-nitrogen-cooled high-sensitivity Ge *p-i-n* detector (Applied Detector Corporation).

Figure 1 shows the PL spectra of 70-nm-thick $Si_{0.85}Ge_{0.15}$ films at 6 K. Spectrum (a) corresponds to a strained SiGe layer on Si (EPI series). All the lines observed are attributed to the substrate. The superscript NP indicates the no-phonon transition and TA (TO) indicate the transitions assisted by the transverse-acoustic (optical) phonon. The assignment of these lines has been well established in the literature.[7] Along with these lines, additional PL lines are observed in spectrum (b), which corresponds to the PL of the buried layer (BL series). These lines, which are attributed to the SiGe layer, have an integrated intensity comparable to those of the silicon (substrate and cap) and remain strong up to 90 K. The energy difference between the lines labeled $X^{TO_{SiSi}}$ and X^{NP} is 58 meV. This value is almost the same as the TO phonon energy in Si or SiGe.[8] Consequently, they are associated with the radiative recombination of excitons. The X^{NP} line is assigned to no-phonon transitions, the X^{TA}, $X^{TO_{GeGe}}$, $X^{TO_{SiGe}}$, and $X^{TO_{SiSi}}$ lines to the phonon assisted transitions involving a TA phonon and three transverse optical replica for SiSi, SiGe, and GeGe modes, respectively. The measured energy of the four modes are, respectively, 16, 34, 50, and 58 meV, in agreement with results for relaxed alloys[4] and superlattices.[6]

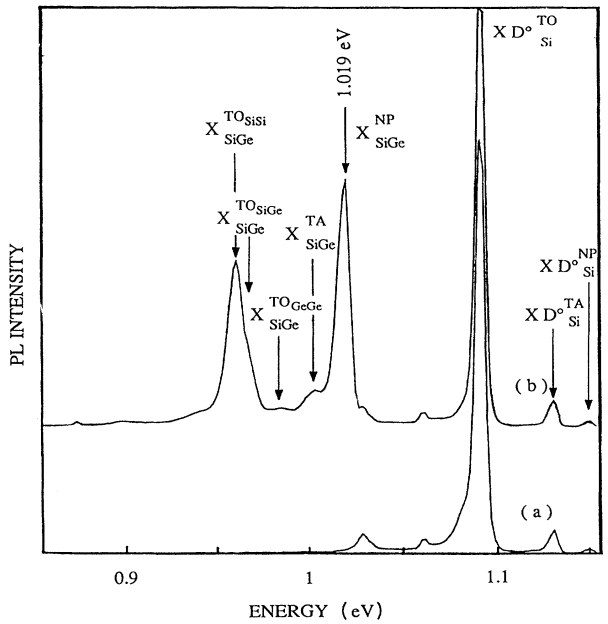

FIG. 1. Near-band-gap photoluminescence spectra at 6 K of 70-nm-thick strained $Si_{0.85}Ge_{0.15}$ layers grown on Si(100); (a) without a silicon capping layer and (b) with a 100-nm-thick silicon capping layer. The 1.019-eV line followed by its phonon replica corresponds to the heavy-hole excitonic transition in strained $Si_{1-x}Ge_x$ alloy.

The obvious difference between the PL of the two series of samples, EPI and BL, which is well illustrated in Fig. 1, has been systematically found for all compositions. The intense excitonic lines emitted by the BL are the consequence of an accumulation of excitons in the SiGe layer due to their confinement by the double heterojunction structure. Since the valence-band discontinuities make the SiGe layer a "hole box," the exciton confinement is supposed to result mainly from the interaction between holes and the valence band. Note also that additional excitons generated in the Si cap or substrate can diffuse toward and accumulate within the SiGe layer, thus contributing to the PL lines. In the EPI samples, the excited species (electron-hole pairs, excitons, etc.) are assumed to be lost at the surface via nonradiative or deep-level-assisted recombinations. This clearly explains why excitonic PL is easily observed in bulk materials and thick films where some generation occurs far from the surface, and in quantum wells where confinement occurs.

The excitonic peak labeled X^{NP} has been investigated in order to follow its dependence on temperature and excitation power. When the temperature is increased from 5 to 90 K the lines widen and take the shape characteristic of free-exciton recombination. The line shape can then be fitted by the well-known expression:

$$I(h\nu)\sim(h\nu-E_{gx})^{1/2}\exp[-(h\nu-E_{gx})/kT]\,, \qquad (1)$$

where $I(h\nu)$ is the luminescence intensity at photon energy $h\nu$, E_{gx} the excitonic band gap, and T the temperature. The line shape does not change with increasing laser power, and the line intensity increases almost linearly with the laser power without any saturation effect. These observations are typical to free excitons. Note that the excitonic NP luminescence is greatly increased in SiGe alloys compared to Si, since the statistical distribution of the Si and Ge atoms can act as momentum-conserving scattering centers;[9] and the free nature of excitons can be correlated to a very low doping level in our samples.

The observed lines make it possible to obtain the excitonic band gap E_{gx} of strained SiGe alloys without correction and thus with great accuracy. In addition, the fundamental gap E_g can be deduced from the former by adding the dissociation energy of the free exciton. The free-exciton (FE) band gap was obtained by fitting Eq. (1) to the free-exciton no-phonon-transition luminescence lines measured at 90 K. As did Mitchard and McGill[10] we estimated the FE dissociation energy for each Ge composition by a linear interpolation between the FE dissociation energies in Si and Ge, which are 14.7 and 4.15 meV respectively. Figure 2 presents the fundamental band gap deduced from our luminescence measurements at 90 K in the Ge composition range 0%–22% (squares) compared to those calculated by Lang *et al.*[11] from photocurrent measurements on SiGe/Si strained superlattices (hatched area). It should be noted that the values given by Lang *et al.* concern the experimental band gap E_{expt}, related to the fundamental band gap E_g by $E_{expt}=E_g+E_{ph}$ where E_{ph} is the average energy of the phonon involved in the absorption process.[12] Within this uncertainty, the two sets of values are in relatively good agreement.

Since the measurement of the indirect band gap by PL

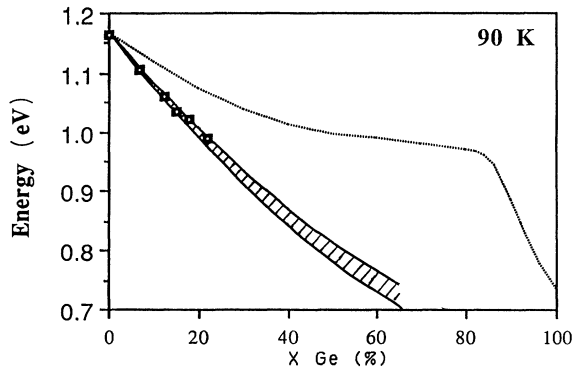

FIG. 2. Fundamental (indirect) band gap of strained $Si_{1-x}Ge_x$ alloys at 90 K vs the Ge fraction. The squares are deduced from excitonic photoluminescence measured at 90 K in the present work including the exciton dissociation energy. The hatched band is the lower-energy band of the fundamental band gap given by Lang *et al.* (Ref. 11) from photocurrent spectroscopy. The dotted curve is the fundamental indirect band gap of unstrained $Si_{1-x}Ge_x$ alloys given in Ref. 8.

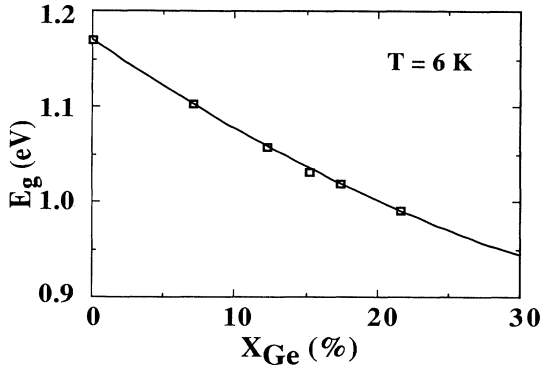

FIG. 3. Second-order polynomial fit of the fundamental indirect band gap of strained $Si_{1-x}Ge_x$ alloys measured at 6 K in the present work: $E_g = 1.171 - 1.01 \times 10^{-2} X_{Ge} + 8.35 \times 10^{-5} X_{Ge}^2$.

is more direct, we are able to provide with a good accuracy the variation of the fundamental band gap of completely strained SiGe alloys grown on Si versus the Ge composition. Figure 3 shows our experimental results together with a fit obtained by a least-squares procedure. The analytical expression is as follows:

$$E_g = 1.171 - 1.01 \times 10^{-2} X_{Ge} + 8.35 \times 10^{-5} X_{Ge}^2 , \quad (2)$$

where X_{Ge} is the Ge content as a percentage and E_g is in eV.

Another interesting fact to note is that our coherent SiGe/Si structures yield well-resolved band-edge photoluminescence peaks without the broad luminescence peaks observed by Nöel *et al.*[13] in the same kind of structures and labeled strain-localized exciton (SLE) thereafter. (i) This suggests that the SLE peaks observed by Nöel *et al.* and used in electroluminescence[14] involve defects which have not yet been identified and (ii) indicates that RTCVD yield excellent-quality SiGe epitaxies from the structural as well as chemical points of view.

In summary, this paper reports on well-resolved near-band-gap excitonic luminescence lines from fully strained SiGe layers, grown on (100) Si in the Ge composition range 0%–22%. This result has been obtained on buried layers, which demonstrates that the SiGe surface is very recombinative and that excitons are confined by a silicon cap layer. The PL spectral lines were identified as FE luminescence yielding high accuracy determination of the fundamental gap. The results suggest that PL can be a useful experimental tool for direct measurement of the fundamental gap as well as for quality assessment of thin strained SiGe/Si structures; this technique employed on our samples also leads to the conclusion that RTCVD produces SiGe/Si heterostructures of an excellent structural quality.

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