Enhancement of high-temperature photoluminescence in strained $Si_{1-x}Ge_x$/Si heterostructures by surface passivation

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The photoluminescence from strained $Si_{1-x}Ge_x$ alloy quantum wells on Si(100) has been measured from 6 to 300 K. It is shown that the high-temperature photoluminescence of $Si_{1-x}Ge_x$ quantum wells can be increased by over an order of magnitude by passivation of the top silicon surface. Through experiments and a model, it is clearly demonstrated that the decay of the $Si_{1-x}Ge_x$ photoluminescence at high temperature is controlled by surface recombination, not by an intrinsic property of $Si_{1-x}Ge_x$. By applying proper conditions, nearly constant $Si_{1-x}Ge_x$ photoluminescence can be achieved from 77 to 250 K. © *1994 American Institute of Physics.*

Recently there has been great interest in the photoluminescence (PL) of strained $Si_{1-x}Ge_x$ alloys on Si(100) substrates as materials for potential light emitters[1,2] as well as for characterization purposes.[3–6] While most work has been performed at temperatures in the range 2–10 K, lately there has been increasing interest in luminescence at higher temperatures.[7–10] This has been motivated both by the desire for high-temperature (e.g., room temperature) emitters and because luminescence at high temperature has appeared to be a more severe test of material properties. In this letter, we report clear evidence that the luminescence efficiency of Si/$Si_{1-x}Ge_x$/Si heterostructures at high temperature is controlled by surface recombination rather than by bulk $Si_{1-x}Ge_x$ or Si properties. Proper surface passivation can increase the room-temperature $Si_{1-x}Ge_x$ PL by an order of magnitude and can lead to $Si_{1-x}Ge_x$ luminescence which is essentially constant in intensity from cryogenic temperatures up to 250 K.

All samples used in this study were grown by rapid thermal chemical vapor deposition (RTCVD) on 100 mm Si(100) substrates. The $Si_{1-x}Ge_x$ layers were grown from dichlorosilane (DCS) and germane at 625 °C, and the Si was grown from DCS at 700 °C. Further details of our growth system and conditions are available elsewhere.[11] The samples initially consisted of nominally undoped strained single $Si_{1-x}Ge_x$ quantum wells on an undoped Si buffer and capped by approximately 25 nm of Si. Sample 1623 contained 30% Ge and was approximately 5 nm thick, while sample 1539 contained 20% Ge and was 15 nm thick. A piece of each sample was separately oxidized at 800 °C for 10 min in a wet oxygen ambient resulting in about 10 nm SiO_2. The samples were then cleaved, and a portion of each was stripped of oxide in dilute HF. In this way, the effect of the oxide could be experimentally separated from that of the thermal treatment. The samples with oxide will be referred to as 1623a and 1539a, while the stripped pieces will be referred to as 1623b and 1539b.

The photoluminescence spectra of each sample (1623a, 1623b, 1539a, 1539b) was measured from 6 to 300 K using a liquid nitrogen-cooled Ge detector and argon laser excitation. The pump power density was approximately 0.1 W/cm^2. Figure 1 shows the evolution of the PL spectrum from sample 1623a (30% Ge with oxide) as a function of temperature. In the 6 K spectrum, the $Si_{1-x}Ge_x$ no-phonon (NP) line and the TO and TA phonon replicas were observed, while no sub-band-gap luminescence[12] was observed. This is evidence of high quality, uniform material. Note, that only the phonon replicas are observed in the nonalloyed Si region of the spectra. Above 20 K, the luminescence was due to free excitons[4] (or an electron-hole plasma[13]). In all cases the Si PL was at least 10× lower in intensity than was the $Si_{1-x}Ge_x$ PL in this temperature range, indicating that nearly all carriers excited by the pump were collected in the $Si_{1-x}Ge_x$ well. Also note that in the 6 K spectrum, the Si TO replica has

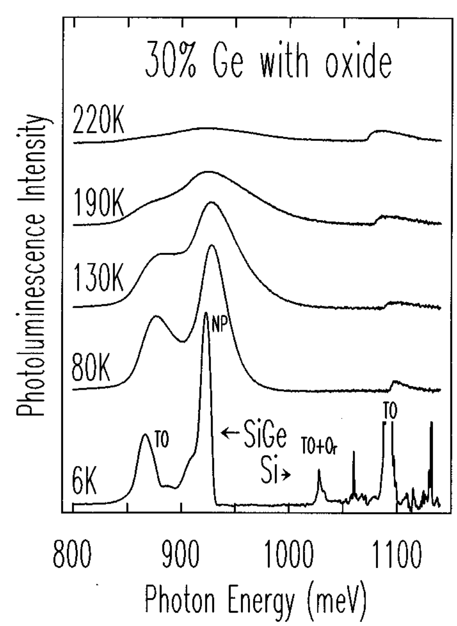

FIG. 1. Five photoluminescence spectra for sample 1623a (30% Ge with oxide). The pump power density was about 0.1 W/cm^2.

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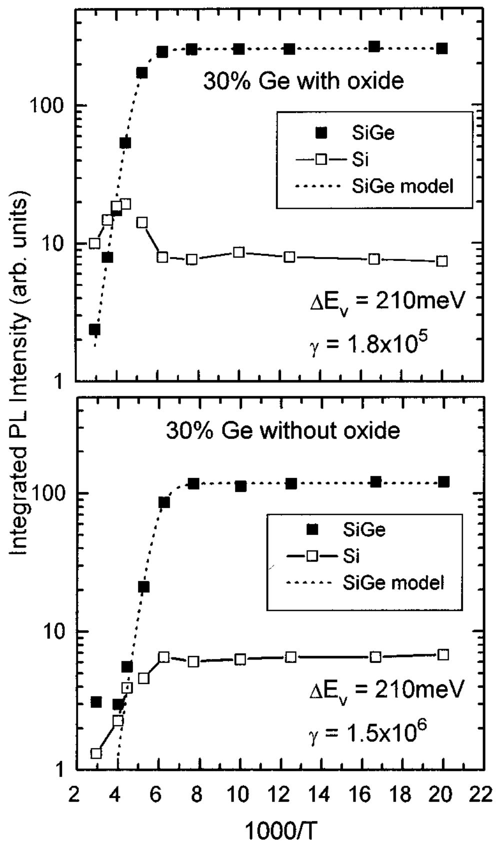

FIG. 2. Integrated photoluminescence intensity as a function of inverse temperature from samples 1623a (30% Ge with oxide) and 1623b (without oxide). The pump power density was about 0.1 W/cm^2.

been cut off so as not to obscure the other spectra.

In Fig. 2, we have plotted the integrated Si and $Si_{1-x}Ge_x$ PL intensities of samples 1623a (30% Ge with oxide) and 1623b (without oxide) as a function of inverse temperature. The most striking feature of this figure is the precipitous rolloff of the $Si_{1-x}Ge_x$ PL at elevated temperatures. The "knee" of the curve was clearly pushed to higher temperature (by ~40 K) by the oxide passivated top surface, and the $Si_{1-x}Ge_x$ PL at high temperature was 10× higher with oxide than without. The sample with its oxide removed behaved similarly to as-grown samples, showing that the surface passivation, not the thermal treatment, is responsible for the enhanced PL at high temperature.

A qualitatively similar temperature dependence of PL from as-grown $Si_{1-x}Ge_x$ quantum wells with Si caps (i.e., sharply decreasing intensity at elevated temperature) has been observed by several other groups,[7–9] and a phenomenological model of this effect has been presented in Ref. 10. The model is based on thermal equilibrium between the carriers in the Si and those in the $Si_{1-x}Ge_x$ and yields a result for the integrated intensity of the $Si_{1-x}Ge_x$ luminescence, I_{SiGe},

$$I_{SiGe}=\frac{C_1}{1+\gamma e^{-\Delta E_v/kT}}\frac{\tau_{SiGe}}{\tau_{SiGe}^{rad}}, \tag{1}$$

$$\gamma\equiv\frac{\tau_{SiGe}W_{Si}}{\tau_{Si}W_{SiGe}}, \tag{2}$$

τ_{SiGe}^{rad} is the radiative lifetime in $Si_{1-x}Ge_x$. ΔE_v is the valence band offset between Si and the $Si_{1-x}Ge_x$ alloy. τ_{SiGe} is the total lifetime in the $Si_{1-x}Ge_x$ layer (dominated by nonradiative recombination), and τ_{Si} is the effective lifetime in the Si cladding (buffer layer and cap), which is potentially lower than the bulk Si lifetime due to surface and interface recombination. W_{SiGe} is the width of the $Si_{1-x}Ge_x$ layer, and W_{Si} is the effective width of the Si over which the generated carriers can travel. The model assumes that all lifetimes are not a function of temperature.

At low temperature ($T<\sim150$ K), nearly all of the carriers are trapped in the $Si_{1-x}Ge_x$ so that the $Si_{1-x}Ge_x$ luminescence is much stronger than that of Si, and the absolute intensity is controlled by the lifetime in $Si_{1-x}Ge_x$ (a weak function of temperature). At elevated temperatures, the $Si_{1-x}Ge_x$ PL begins to decay well before a majority of the carriers are in Si because the total number of carriers in the system decreases due to the very low effective lifetime in the Si. γ is a measure of the relative lifetimes in the $Si_{1-x}Ge_x$ and the Si, and it is experimentally observed via the position of the knee in the $Si_{1-x}Ge_x$ PL intensity versus $1/T$ curves.

The $Si_{1-x}Ge_x$ data of Fig. 2 were fit to the model using $\Delta E_v=210$ meV in both cases, which is consistent with the change in band gap of 230 meV relative to Si as measured by PL at 6 K. For the oxidized piece (sample 1623a), $\gamma=1.8\times10^5$; while for the piece with its oxide stripped (sample 1623b), $\gamma=1.5\times10^6$. Of the factors in γ, only τ_{Si} could possibly be changed by stripping the surface oxide, so we can interpret these results as changes in the effective electron-hole pair lifetime in Si. Furthermore, given that the presence of oxide decreased γ by a factor of 8, we can assume that τ_{Si} is determined by recombination at the top Si surface and that the recombination velocity of the Si/oxide interface is 8 times smaller than that of the Si/air interface. Thus, we conclude that the high-temperature luminescence efficiency in high quality $Si/Si_{1-x}Ge_x/Si$ quantum wells is controlled by surface recombination.

An analogous expression to Eq. (1) for integrated Si PL intensity is

$$I_{Si}=\frac{C_2}{\gamma+e^{\Delta E_v/kT}}\frac{\tau_{Si}}{\tau_{Si}^{rad}}. \tag{3}$$

This expression predicts that the Si PL intensity will be constant at high temperature when all of the carriers are in Si and will decrease exponentially at low temperature. The measured Si intensity did not go to zero at low temperature, however, because most of the carriers were created in the Si substrate and cannot achieve their thermal equilibrium distribution instantaneously. The Si PL of sample 1623a (with oxide) did begin to increase with temperature near 170 K, but an unidentified phenomenon not included in our model appeared near 250 K and reversed this increase in intensity.

The integrated Si and $Si_{1-x}Ge_x$ PL intensities for samples 1539a (20% Ge with oxide) and 1539b (without oxide) were measured as a function of temperature. Their behavior was qualitatively very similar to that of sample

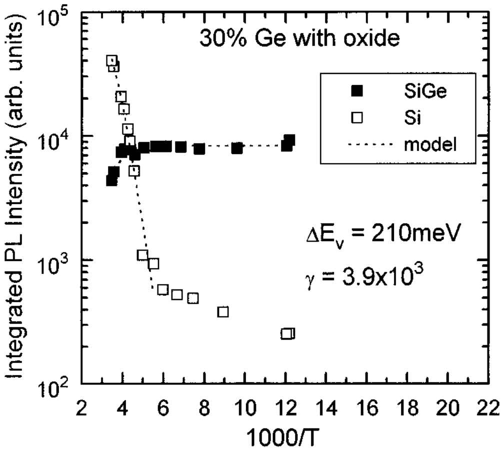

FIG. 3. Integrated photoluminescence intensity as a function of inverse temperature from sample 1623a (30% Ge with oxide). The pump power density was about 10 W/cm^2.

1623 displayed in Fig. 2. Again, the $Si_{1-x}Ge_x$ PL from the sample with oxide rolled off at a temperature approximately 40 K higher than that of the sample without oxide. Because the $Si_{1-x}Ge_x$ quantum well was less deep for the samples with only 20% Ge, the knee appeared at lower temperature, and the activation energy of the roll-off was smaller than in the case of the sample with 30% Ge. The $Si_{1-x}Ge_x$ intensities were fit to the model using $\Delta E_v = 140$ meV. Again, the parameter γ for the piece with oxide was smaller than that for the piece without (1.0×10^4 vs 2.0×10^5), indicating a passivated surface. Oxidization reduced the surface recombination velocity by a factor of 20 in this sample.

The γ values for sample 1539 are approximately one order of magnitude smaller than those of sample 1623. This is thought to be due largely to a longer $Si_{1-x}Ge_x$ lifetime in sample 1623 which was also manifested by the greater absolute intensity of its low-temperature $Si_{1-x}Ge_x$ PL. At low temperature when nearly all carriers are confined to $Si_{1-x}Ge_x$ and surface recombination is not important, the limit of Eq. (1) yields $I_{SiGe} \propto \tau_{SiGe}$ as one would expect. That the low-temperature $Si_{1-x}Ge_x$ PL of sample 1623 (30%) was 4× more intense than that of sample 1539 (20%) is consistent with a longer lifetime in sample 1623. This is not thought to be an intrinsic $Si_{1-x}Ge_x$ property, rather it is more likely due to uncontrolled variations in trace nonradiative impurities in our samples such as oxygen introduced during growth.

The PL from sample 1623a (30% Ge with oxide) was again measured as a function of temperature but at a pump power density of about 10 W/cm^2, two orders of magnitude higher than before. The temperature dependence of the integrated Si and $Si_{1-x}Ge_x$ PL intensities at high pump power density were quantitatively very different from that at low pump power density. Figure 3 shows integrated PL intensity at high pump power density from sample 1623a as a function of inverse temperature. The low-temperature behavior was similar to that at low pump power density; the $Si_{1-x}Ge_x$ PL was constant as a function of temperature and was more than an order of magnitude stronger than the Si PL. The behavior at high temperature (above 200 K), however, was strikingly different. Note that the $Si_{1-x}Ge_x$ PL knee was pushed out to 250 K and that the Si PL intensity increased exponentially between 200 and 300 K. The high pump power data for $Si_{1-x}Ge_x$ and for Si was fit simultaneously to the model with $\Delta E_v = 210$ meV as before, but with $\gamma = 3.9\times10^3$ (versus 1.8×10^5 at low pump power density). Thus it appears that the effective lifetime in Si was increased, and the surface recombination rate decreased, by a factor of 46 at high pump power density (and presumably high carrier concentration).

While the physical explanation for this dramatic reduction in surface recombination velocity is not clear, surface recombination is known to be exponentially affected by band bending at surfaces.[14] High carrier concentrations would be expected to alter the shape of the bands and, hence, could affect the surface recombination rate, which we have shown controls the effective lifetime in Si. Further work is required to determine the extent of this effect.

In conclusion, we have definitively demonstrated that the high-temperature decay of the band-edge photoluminescence from high quality $Si_{1-x}Ge_x$ quantum wells is determined by recombination at the top Si surface, not by a property of the $Si_{1-x}Ge_x$ itself, and can be dramatically increased by surface passivation. Also, we have shown that the recombination velocity of the Si/oxide interface can be reduced at high pump power densities, resulting in undiminished $Si_{1-x}Ge_x$ PL from 77 to 250 K in samples with 30% Ge. Our results suggest that this limit could be pushed to room temperature by employing higher Ge content films or by better passivating the top Si surface.

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[1] D. J. Robbins, P. Calcott, and W. Y. Leong, Appl. Phys. Lett. **59**, 1350 (1991).
[2] Q. Mi, X. Xiao, J. C. Sturm, L. C. Lenchyshyn, and M. L. W. Thewalt, Appl. Phys. Lett. **60**, 3177 (1992).
[3] K. Terashima, M. Tajima, and T. Tatsumi, Appl. Phys. Lett. **57**, 1925 (1990).
[4] J. C. Sturm, H. Manoharan, L. C. Lenchyshyn, M. L. W. Thewalt, N. L. Rowell, J.-P. Noel, and D. C. Houghton, Phys. Rev. Lett. **66**, 1362 (1991).
[5] D. Dutarte, G. Bremond, A. Souifi, and T. Benyattou, Phys. Rev. B **44**, 11525 (1991).
[6] J.-P. Noel, N. L. Rowell, D. C. Houghton, A. Wang, and D. D. Perovic, Appl. Phys. Lett. **61**, 690 (1992).
[7] S. Fukatsu, N. Usami, and Y. Shiraki, Jpn. J. Appl. Phys. **32**, 1502 (1993).
[8] M. Wachter, F. Schäffler, H.-J. Herzog, K. Thonke, and R. Sauer, Appl. Phys. Lett. **63**, 376 (1993).
[9] M. Gail, J. Brunner, U. Menczigar, Z. Zrenner, and G. Abstreiter, Mater. Res. Soc. Symp. Proc. **298**, 21 (1993).
[10] J. C. Sturm, A. St. Amour, Q. Mi, L. C. Lenchyshyn, and M. L. W. Thewalt, Jpn. J. Appl. Phys. **33**, 2329 (1994).
[11] J. C. Sturm, P. V. Schwartz, E. J. Prinz, and H. Manoharan, J. Vac. Sci. Technol. B **9**, 2011 (1991).
[12] J. C. Sturm, A. St. Amour, Y. Lacroix, and M. L. W. Thewalt, Appl. Phys. Lett. **64**, 2291 (1994).
[13] X. Xiao, C. W. Liu, J. C. Sturm, L. C. Lenchyshyn, and M. L. W. Thewalt, Appl. Phys. Lett. **60**, 1720 (1992).
[14] R. S. Muller and T. I. Kamins, *Device Electronics for Integrated Circuits*, 2nd ed. (Wiley, New York, 1986), pp. 229–231.