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Photoluminescence in implanted and doped silicon near room temperature

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Key words Silicon, photoluminescence, indirect, phonon assisted
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Photoluminescence in implanted and doped silicon at room temperature is measured, and the observed structures are assigned as intrinsic-phonon-assisted indirect allowed transitions. The temperature of photoexcited carriers, which are higher than the bath temperature, is estimated. For confined carriers produced by boron implantation the temperature dependence of the effective temperature of the excited carriers is same for the different samples, but an enhancement of the photoluminescence is observed.

1 INTRODUCTION

Investigations on semiconductors have shifted to topics related to nanotechnology recently. The development of detectors in the near-infrared region have stimulated the investigation of the basic optical properties of Si near room temperature. There have been almost no detailed measurements of the temperature dependence of photoluminescence (PL) in Si crystals, exhibiting an indirect optical transition at high temperatures (around room temperature), because of the weakness of the PL. Recently, electroluminescence (EL) was observed by Homewood \textit{et al.}\textsuperscript{[1]}, and PL was investigated by Prins \textit{et al.} \textsuperscript{[2]} and by Ishibashi \textit{et al.}\textsuperscript{[3]} in boron implanted Si. Photoluminescence enhancement in EL devices was explained as follows: near the boron-implanted surface of Si, the dislocation loops introduce a local strain field, that modifies the band structure and provides spatial confinement of charge carriers in the non-defective region near the surface. It is considered that this spatial confinement allows room temperature EL at the band-edge owing to the very clean surface region of Si. Such devices are highly compatible with ULSI (ultra large scale integration) technology, as boron ion implantation is already routinely used in silicon device fabrication.

In this B-implanted Si, and n(p)-type doped Si, we observe PL spectra that we attribute to phonon-assisted recombination of free excitons. Thorough investigations of PL for indirect forbidden transitions was reported in thallous halides \textsuperscript{[5, 6]} but for Si it has so far proved difficult to measure PL at high temperatures. In this paper, we observe intrinsic phonon-assisted photoluminescence, an enhancement in the phonon-assisted indirect transitions in p- and n-type doped Si, and an abnormal increase in electron temperature and PL intensity of photoexcitation especially in B-implanted Si.

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2 EXPERIMENTS

Commercial n- and p-type Si as a substrate and B-implanted Si[1] are used for PL observation. Excitation light for PL are focused on the Si surface, at wavelengths of 488 nm or 514.5 nm from a 30 mW Ar ion laser. The PL is collected on a 25 cm monochromator and a photomultiplier (Hamamatsu Photonics R5509-41) sensitive to 1.4 µm radiation. The sensitivity of the system is calibrated using black body radiation. At low temperatures PL intensities have been observed to increase at the absorption edges ‘2a’ and ‘1a’[4]. We observe no impurity-associated PL in n- and p-type commercial Si above 20K.

At higher temperatures PL spectra are decomposed into three components for phonon-assisted indirect transitions as in the following Eq.(1):

\[ I \propto \sum_i B_i(T) \sqrt{E - E_i} \exp\left(-\frac{(E - E_i)}{k_B T_e}\right). \]  

The threshold ‘2e’ of the PL corresponds to ‘2a’ in the absorption spectra, and the lower energy thresholds ‘3e’ and ‘4e’ of the PL correspond to the absorption edges ‘3a’ and ‘4a’ of Ref. [4], as shown in Fig. 3. The line shape of the absorption is fitted by this equation. Here \( T_e \) is the thermalized temperature of the excited electrons near the band edges of the conduction and valence bands, and \( B_i(T) \) is a slowly varying function of temperature. The agreement between the observed and calculated line shapes is very good, and typical examples of both spectra are shown in Fig.2.
In Fig. 3 solid lines show the threshold energies of phonon-assisted absorption spectra [4], and the broken lines correspond to phonon emission processes and phonon absorption processes at high temperatures [4]. Symbols labeled as n-, p- and B- indicate the threshold energies corresponding to the different Si sample, and the labels ‘e’ and ‘a’ refer to phonon emission and absorption, respectively. At low temperatures, PL thresholds are observed at four absorption thresholds ‘1e’, ‘2e’, ‘3e’, and ‘4e’, whose temperature dependences are plotted in Fig. 3. The intensities of all PL peaks decrease with increasing temperature below 180K for n- and p-Si. Above 200K, the PL with the threshold at ‘2a’ increases with temperature, following the increase in phonon creation probability. This increase is smaller than that observed for the PL of B-implanted Si. Thus the thresholds labelled as 1, 2, 3 and 4 correspond to different phonon emission processes in PL. The labels ‘a’ and ‘e’ respectively indicate the phonon absorption and emission processes for both absorption spectra and PL. The labels ‘a’ and ‘e’ for PL and absorption threshold energies are opposite for the same energy.

3 DISCUSSIONS

The temperature dependence of PL intensity is fitted by the following equation for the phonon emission process:

\[
B_i(T) \propto \frac{1}{1 + a \exp \left( \frac{-\Delta E}{k_B T_e} \right) \left[ n(h\omega_i) + 1 \right]}
\]  

Here \( n(h\omega_i) \) is the population of phonons with energy \( h\omega_i \), \( \Delta E \) is the barrier height for transitions from excited states to nonradiative centres, and \( T_e \) is the temperature of thermalized carriers in excited states. Here the determined parameters \( \Delta E/k_B \) and \( a \) using Eq.(2) are, respectively, 260K and 350 in p-Si and 200K and 130 in n-Si. But the observed enhancement for B-implanted Si is...
Fig. 3 Threshold energies of the absorption spectra (lines [4]) and of the PL spectra (see key for the symbols corresponding to p-type Si, n-type Si and B-implanted Si.). Open symbols, closed symbols, and the others correspond to p-type Si, n-type Si, and B-implanted Si for phonon emission processes, respectively.

more than twice that calculated by Eq.(2). This temperature dependence is related to the increase in the lifetime [7]. High carrier temperatures are much higher than the bath temperature (dotted straight line), but the temperatures of excited carriers are almost the same for all the different types of Si, as shown in Fig.4. The excited carriers are not thermalized with the lattice. Further, the thermalized temperature of the excited carriers is almost independent of the intensity of optical excitation. These results indicate that the excess energy of excited electrons corresponds to the difference $|\Delta E_g|$ between the energy gap at temperature $T$ and at absolute zero. The detailed mechanism for the temperature dependence of the PL intensity is not known. As is clear from Fig. 5, PL intensities increase a little near room temperature for commercial n- and p-Si following Eq.(2) for phonon-assisted indirect transitions. But the PL enhancement is very large in the case of B-implanted Si compared to the ratio 1.1 calculated from Eq.(2) for the corresponding transition, in accordance with the change in phonon creation probability between 50K and 300K. The temperature dependence of the threshold ‘2e’ of the PL thresholds is the same as the threshold ‘2a’ previously observed [4]. Likewise for the estimated positions at low temperatures for the other absorption thresholds, as shown in Fig. 3. The observed PL line shape coincides with the EL spectra previously observed [1], as shown in Fig. 1 by the open squares. The EL threshold energies are the same as the thresholds of our PL spectra. This indicates that the lifetime only becomes longer in B-implanted Si at high temperatures. In Fig. 5 an enhancement of the intensity above that expected from the variation in phonon creation probability near room temperature is observed only in B-implanted Si, whereas an enhancement according to the variation of the phonon population alone is sufficient to explain the data for the other samples. The internal
**Fig. 4** Effective electron temperature. The straight line indicates the same temperature. The symbols indicate the carrier temperatures calculated using Eq.(1) in the line shape fitting. The curved line indicates $|ΔE_g|/k_B + T$. Here, $|ΔE_g|/k_B$ is the change of the energy gap with respect to 0 K. The agreement between the curved line and the calculated effective electron temperature variation indicates that this change in energy gap corresponds to the excess energy (under energy relaxation of excited carriers to the bottom of the band) expressed in Kelvin, and that the excited carriers are not thermalized with the lattice except for the case of the EL of B-implanted Si.

Quantum efficiency can be written as

$$η_i = \frac{R_{BB}}{(R_{SRH} + R_{BB} + R_{Auger})},$$

where $R_{BB}$ is the radiative recombination rate, $R_{Auger}$ is the Auger recombination rate, $R_{SRH} = Δn/τ_{SRH}$ is the multiphonon recombination rate owing to deep levels in the band gap. Here $τ_{SRH}$ is increased as the temperature increases, and $η_i$ becomes larger when $τ_{SRH}$ becomes longer [7]. In B-implanted Si, $τ_{SRH}$ is promoted by the gathering action of the implanted boron as in the case of phosphorous [7] and the PL enhancement is larger than that expected from the variation in the phonon creation probability.

**4 CONCLUSION**

The temperature dependence of the PL spectra in differently doped and implanted Si sample is observed from room temperature to low temperatures $\sim 20$ K. Near the absorption edge, the various structures in the PL spectra can be assigned to different phonon creation and annihilation indirect transitions. The temperature of the thermalized excited carriers is higher than the temperature of the heat bath by an amount equal to the excess energy, which is almost same as the energy difference $|E_g(T = 0) − E_g(T)|$ from the indirect gap of Si estimated from optical absorption data.
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