Temperature dependence of the indirect energy gap in crystalline silicon

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The photoluminescence spectra of crystalline silicon samples are measured for temperatures below 1000 K. The optical transitions are analyzed in terms of excitonic and band-to-band transitions. From the modeling of the line shape we are able to determine the fundamental indirect band gap for temperatures up to 750 K. The temperature dependence follows the Varshni equation with $E_g(0)=1.1692$ eV, $\alpha=(4.9\pm0.2)\times10^{-4}$ eV/K and $\beta=(655\pm40)$ K. © *1996 American Institute of Physics.* [S0021-8979(96)08108-4]

I. INTRODUCTION

The change of the energy gap with temperature is a result of two different processes. The first one arises from the change in bond lengths with temperature and can be related to the pressure coefficient of the energy gap through the compressibility and the thermal expansion coefficient.[1] The second contribution originates in the electron–phonon interaction. The latter dominates at elevated temperatures ($T\approx100$ K), decreasing the band-gap energy with temperature. The electron–phonon contribution can be calculated at different levels of sophistication.[1–6] At high temperatures, theory predicts a linear energy shift of the band gap with temperature, while at low temperatures the dependence is strongly nonlinear. This behavior is reflected in the semiempirical Varshni equation,[7]

$$E_g(T)-E_g(0)=\frac{-\alpha T^2}{T+\beta}, \tag{1}$$

which is widely used to fit experimental data by adjusting the parameters α and β, $E_g(0)$ is the energy gap at the temperature $T=0K$. Other approximate analytical expressions were proposed to give better fits to the data, particularly at low temperatures.[8,9]

Experimental data for the indirect band gap in Si exist in the temperature range from 1.5 to 415 K.[10–12] At these temperatures the optical properties are dominated by excitonic processes. MacFarlane *et al.*[10] measured the excitonic absorption with high optical resolution. A fine structure in the absorption edge was attributed to phonon transitions which are characteristic for indirect gap semiconductors. The excitonic transition energies were derived from a fit to the absorption curves. Bludau *et al.*[12] omitted the fitting procedure: the derivative of the free exciton (FE) absorption coefficient has a well defined singularity, which can be detected by wavelength modulation spectroscopy. In order to obtain the energy gap from the absorption data, the exciton dissociation energy and the phonon energies have to be known; both are usually assumed to be almost independent of temperature. Thurmond[13] used the Varshni equation to fit the experimental band gap data. Although the experimental data were only available in a limited regime the Varshni expression for the Si band gap was also used at much higher temperatures. Absorption measurements at 1.152 μm at temperatures up to 1140 K strongly support however the validity of Thurmond's fit.[14]

To obtain experimental data for the energy gap, we performed an elaborate study of the high-temperature photoluminescence (PL) in Si. Preliminary data were already published in Ref. 15. A detailed model for the recombination processes at elevated temperatures is developed, and a complete analysis of the experimental line shapes derived. In this letter, we concentrate on the derivation of the temperature dependence of the band-gap energy. The properties of the PL lines and the modeling of the line shape is presented in a separate publication.[16]

II. EXPERIMENT

Measurements below room temperature (RT) are performed by placing the samples in a He exchange gas cryostat (Oxford), which allows to stabilize and control the temperature from 10 K to room temperature with high accuracy. Above RT, the samples are mounted on a quartz sample holder in a quartz tube oven. The entire quartz tube is evacuated and then purged with He or Ar gas to avoid deterioration of the sample surface. The temperature is measured by a NiCr/Ni thermocouple, which is in close contact with the sample.

The sample is excited by an unfocussed Ar^+ ion laser ($\lambda=514$ nm, 100 mW). The PL signal is detected by a cooled Ge detector (Northcoast) and analyzed in lock-in technique. A grating monochromator ($f=0.25$ m) with large aperture is used for spectral resolution. The optical path has to be carefully aligned to avoid saturation of the detector due to unmodulated light of the black body radiation.

The PL intensity at RT depends strongly on the surface recombination and is almost independent on shallow dopants (P and B doped, 4000–0.1 Ω cm or growth conditions, floating zone or Czochralski). Several differently doped samples are studied, best PL intensities resulted from samples with surfaces which are passivated by a thick ($\approx$100 nm) thermal

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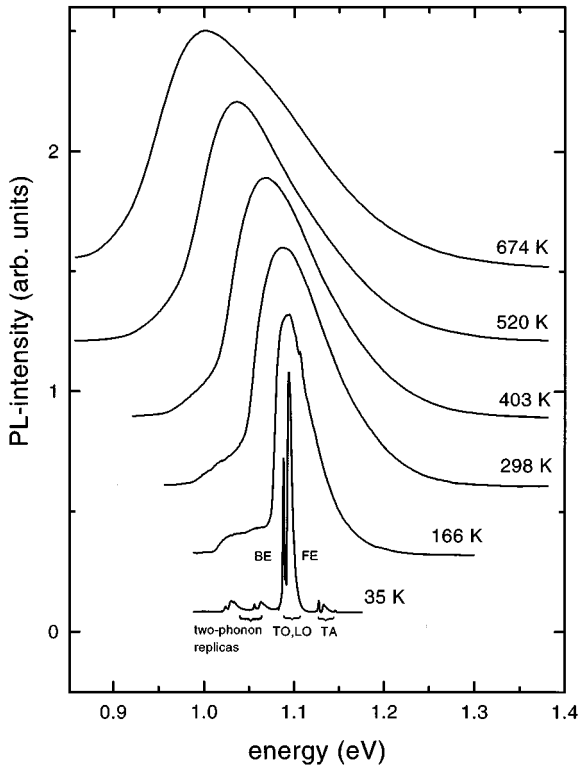

FIG. 1. Normalized photoluminescence spectra of a 0.5 Ω cm boron doped Si sample with surface passivation by a 100 nm thermal oxide, recorded at different temperatures.

oxide. Details of this behavior will be published in Ref. 16.

All spectra are corrected for the spectral response of the setup. According to simple models,[28] self absorption of the PL should drastically affect the line shape of the band-gap PL. We measured the absorption of our samples up to 900 K. We find in agreement with the discussion in Ref. 18, that self-absorption of the PL is much weaker than expected from the measured absorption coefficient. Under the experimental conditions described in Ref. 16 we can neglect the self-absorption.

In Fig. 1, typical PL spectra at different sample temperatures are presented. At 35 K the spectrum exhibits the well-known features of the near band-gap PL in Si. The exciton bound to be boron acceptor (BE) and the free exciton (FE) in different phonon replicas are clearly resolved. For details of the assignment see Ref. 19. With increasing temperature a smooth change in the PL features occurs and there is an increasing broadening of the different lines, which results in only one broad PL band above around 100 K. A pronounced shift of the broad PL band with temperature is a direct indication for the reduction of the energy gap.

III. DISCUSSION

The measured PL intensity, which is proportional to the emitted energy flux $j(E)$, is analyzed according to the theory of indirect excitonic emission presented in Ref. 18. According to the theory of detailed balance, whose validity in the indirect case was shown by Würfel,[17] $j(E)$ is given in Maxwell–Boltzmann approximation by

$$j(\hbar\omega)\sim\frac{(\hbar\omega)^3}{\exp\left(\frac{\hbar\omega}{kT}\right)}\,\alpha(\hbar\omega). \tag{2}$$

Introducing the excitonic absorption coefficient from Ref. 20 yields

$$j(\hbar\omega)\sim\omega^2\,\exp\left(\frac{-\hbar\omega}{kT}\right)\sum_b\sum_{\text{abs./em.}}a_{\text{abs./em.}}c_b \times\left(\sum_n\frac{1}{n^3}\sqrt{\hbar\omega-E_g-\frac{E_{\text{exc}}}{n^2}\pm k\Theta_b}\otimes G(\sigma_1) + r\mathfrak{T}(\hbar\omega-E_g-E_{\text{exc}}\pm k\Theta_b)\otimes G(\sigma_2)\right). \tag{3}$$

The first expression in the sum accounts for the absorption into bound states of the FE with main quantum-number n, whereas the integral $\mathfrak{T}$ takes care of the absorption into unbound exitonic states. The transitions due to these continuum states are sometimes referred to modified band–band transitions. The explicit form of the integral $\mathfrak{T}$ is given in Ref. 20; for large energies it has the same proportionality on energy as is obtained by neglecting Coulomb interaction. The sum extends over all phonon replicas b with energies $k\Theta_b$, which are weighted by c_b. Only the LO and TO phonon replicas are included in the analysis with a relative intensity ratio of 0.11.[21] The TA phonon replica is too weak to be of any importance in the line shape ($TA/TO=0.03$).[22] The second summation is for the phonon absorption and emission processes. The convolution with the Gauss functions G with half widths σ_1 and σ_2 accounts for the different intrinsic as well as experimental broadening mechanisms. The exciton binding energy E_{exc} increases with temperature, due to the change of the effective masses.[26] The increase is, however, only a few meV, which is too small to have an influence on our band-gap energies. We therefore used the low-temperature value $E_{\text{exc}}=14.7$ meV in our line shape analysis.[23] The temperature dependences of the near-infrared refractive index[24] and the phonon energies[25] are small, hence neglected in our analysis. Two-phonon emission or absorption processes are also not included in the fit, they are weak and modify only the low-energy part of the spectra.

We perform least-squares fits of Eq. (3) to our PL spectra. The fitting procedure involves five free parameters: (1) the energy gap E_g, (2) the broadening $G(\sigma_1)$ of the absorption into the bound states of the FE, (3) the broadening $G(\sigma_2)$ of the absorption into the unbound states of the FE, (4) the ratio $a_{\text{abs./em.}}$ of the phonon absorption and emission processes, and (5) the ratio r of the relative strength of the unbound/bound FE processes. Parameters (4) and (5) can be determined, in principle, theoretically, however we find in our fitting process no agreement with the theoretical predictions. The theory of spontaneous and stimulated phonon transitions (analogous to the one for photons) gives directly the ratio of the phonon absorption and emission processes (see, for example, Ref. 29) $a_{\text{abs./em.}}\approx\exp(-\Theta/T)$.[20] The experimentally determined ratio r of the recombination from bound to unbound FE states deviates also from the calculated

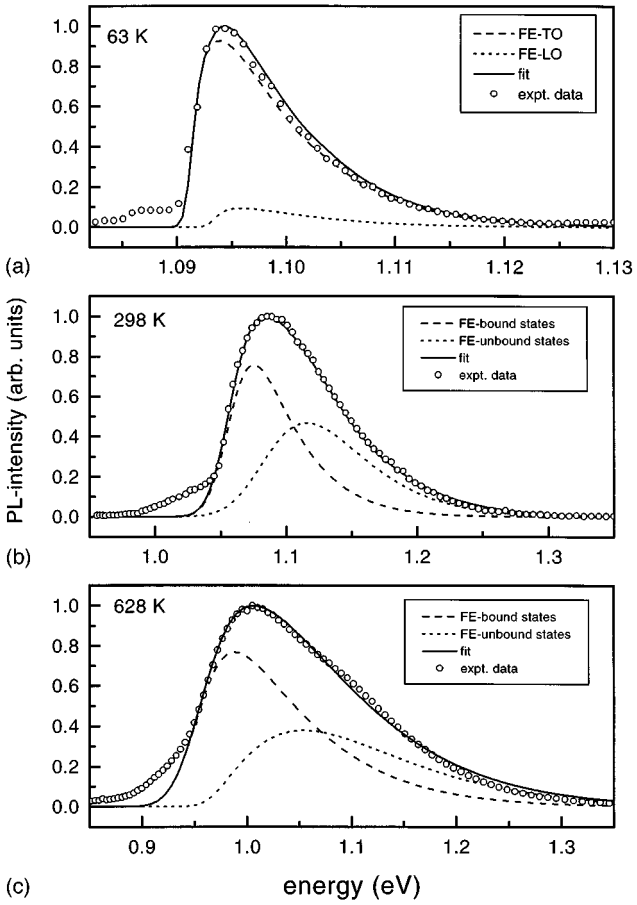

FIG. 2. Typical PL spectra at three different temperatures, (a) $T=63$ K, (b) $T=298$ K, (c) $T=628$ K. The least-squares fits according to Eq. (3) are shown along with the different recombination processes contributing to the line shape.

value.[26] The deviation is far too strong to be explained by assuming a temperature-dependent FE binding energy, as was suggested in Ref. 26.

Figure 2 gives three typical PL spectra at various sample temperatures along with the least-squares fits according to Eq. (3). At low temperatures ($T \leqslant 100$ K), the PL line shape is exclusively formed by the TO and LO phonon replicas of the FE (bound states). At higher temperatures ($\approx RT$) the modified band–band transitions in the TO and LO phonon replicas have to be included in the fitting process. No phonon-absorption process could be detected at these temperatures. The applicability of a pure excitonic recombination even at 600 K with an excitonic binding energy corresponding to only 150 K is justified by the calculations of Schlangenotto *et al.*:[26] The enhancement factor of recombination via excitonic states to the unmodified band–band transition is

$$4\sqrt{\pi}\sqrt{\frac{E_{\mathrm{exc}}}{k_B T}}\left[1+2\frac{E_{\mathrm{exc}}}{k_B T}\sum_{n=1}^{\infty}\frac{1}{n^3}\exp\left(\frac{E_{\mathrm{exc}}}{n^2 k_B T}\right)\right]\approx 7 \quad (4)$$

at 600 K. Furthermore, the unmodified band–band transition has a similar spectral dependency as the unbound excitonic recombination and their influence can be incorporated in the parameter r.

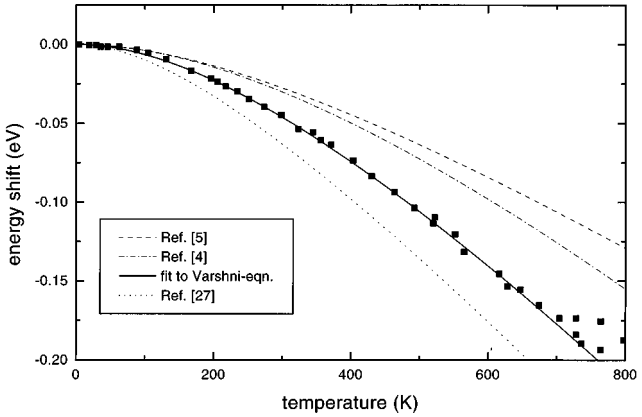

FIG. 3. Experimental values for the band-gap energy at elevated temperatures and the corresponding Varshni equation are compared to theoretical predictions.

The temperature dependence of the band gap E_g, as derived from the line shape analysis of the luminescence, is shown in Fig. 3. We plot only the data from a sample with the best surface passivation, all other samples gave in principle the same results, but due to the weaker PL intensity the error in the determination of band-gap energies is larger. The Varshni Eq. (1) with $E_g(0)=1.1692$ eV, $\alpha=(4.9\pm0.2\times10^{-4})$ eV/K, and $\beta=(655\pm40)$ K gives a good description of the temperature dependence up to 750 K. At higher temperatures almost no change in the band-gap energy is found from the line shape analysis. However, we find a drastic change in the line shape above 800 K, which has to be attributed to a new recombination process at these temperatures. In that case we find our line shape analysis no longer appropriate to derive the band-gap energy. Details of the PL band at temperatures from 800 to 1000 K will be published in separately.[16]

The shift of $E_g(T)$ here reported up to 300 K agrees well with data from Bludau *et al.*[12] and the Varshni parameters α and β derived by Thurmond[13] are identical to ours within the limits of error. The preliminary data from Ref. 15, derived also from PL measurements, gave a smaller band-gap variation with temperature. The pronounced difference is due to insufficient line shape analysis, which included only the bound states of the FE. The experimental data in Fig. 3 are compared to results from different calculations. Most of the theories predict band-gap shifts, which are too small compared to our experimental data.

IV. SUMMARY

We have performed a detailed study of the band-gap PL in Si at temperatures below 1000 K. From a line-shape analysis we are able to determine the temperature dependence of the fundamental indirect band gap in the temperature range from 2–750 K.

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