

You may also like

Optical Characterization of $Si_{1-x}C_x/Si$ ($0 \le x \le 0.014$) Semiconductor Alloys

To cite this article: Hosun Lee et al 1995 Jpn. J. Appl. Phys. 34 L1340

View the article online for updates and enhancements.

THE INTERMEDIATE-MASS STAR-FORMING REGION LYNDS 1340. AN OPTICAL VIEW

Mária Kun, Attila Moór, Elza Szegedi-Elek et al.

- Self-Ordering of Cell Configuration of Anodic Porous Alumina with Large-Size Pores in Phosphoric Acid Solution Hideki Masuda, Kouichi Yada and Atsushi Osaka

- <u>Cardiac Chaotic Attractors of Ultrasound</u> <u>Echo Signals</u> Yoshihiro Yoshikawa

Optical Characterization of $Si_{1-x}C_x/Si$ ($0 \le x \le 0.014$) Semiconductor Alloys

Hosun Lee*, S. R. Kurtz, J. A. Floro, J. Strane, C. H. Seager, S. R. Lee,

E. D. JONES, J. F. NELSON, T. MAYER and S. T. PICRAUX

Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185-0601, USA

(Received June 1, 1995; accepted for publication September 7, 1995)

We have characterized the optical properties of heteroepitexial $\operatorname{Si}_{1-x} C_x/\operatorname{Si}(0 \le x \le 0.014)$ alloys grown on Si substrates by solid phase epitaxy using spectroscopic ellipsometry and photoluminescence. The measured dielectric function confirms that the samples are of good crystalline quality. The 14-K photoluminescence spectra of $\operatorname{Si}_{1-x} C_x$ /Si show several defect peaks. After hydrogen passivation, we observed a new peak near 1.15–1.17 eV which increases in energy with the incorporation of carbon. We tentatively assign this peak to the no-phonon peak of the $\operatorname{Si}_{1-x} C_x$ epi-layer. We discuss the alloy shift of the observed spectroscopic features in terms of the C-induced change in the Si indirect band gap.

KEYWORDS: photoluminescence, SiC alloys, Si substrate, spectroscopic ellipsometry, hydrogen passivation

Advances in SiGe heteroepitaxy have attracted considerable attention due to the prospect of integrating high-speed heterojunction devices with conventional Si technology.¹⁾ Si_{1-x}C_x and Si_{1-x-y}Ge_xC_y alloys with metastable concentrations of carbon in solution within the Si lattices give an additional degree of freedom for bandgap engineering in terms of varying the band gap and lattice parameter relative to those of Si. Few optical studies have been performed, however, to verify the dielectric function and band gaps of these new materials.²⁻⁴⁾ Kissinger et al.²⁾ reported the dielectric function and direct band gaps of $Si_{1-x}C_x/Si$ grown by chemical molecular beam epitaxy using spectroscopic ellipsometry and electroreflectance. Using photoluminescence, Boucaud et al.⁴⁾ measured a very broad signal of a deep level at 0.82 eV for $Si_{1-x}C_x/Si$ grown by rapid thermal chemical vapor deposition (RTCVD). In this letter, we present the dielectric functions and fitted direct gap values measured by spectroscopic ellipsometry, and report a new peak at 1.15–1.17 eV in the photoluminescence spectrum observed after hydrogen passivation, which may be the indirect band edge emission from the $Si_{1-x}C_x$ epi-layer.

 $Si_{1-x}C_x$ ($0 \le x \le 0.014$, 150 nm thick) alloy layers on Si substrates with up to 1.4 at% C were synthesized by multiple energy C ion implantation and solid phase epitaxial growth (SPE). This technique yields metastable alloys with approximately uniform substitutional C contents up to 1.4 at%. Little or no detectable β -SiC precipitation is detected by Fourier transform infrared spectroscopy (FTIR) and double crystal X-ray diffraction (DCD). We also studied an undoped Si wafer $(\rho = 1 - 10 \ \Omega \cdot cm)$ as a reference. The details of sample preparation and characterization are described elsewhere.^{5,6)} We used Si substrates grown by either the float zone (FZ) (x=0.7, 1.4%) or Czhochralski (CZ) methods (x=1.05, 1.4%). DCD indicates that all the $Si_{1-x}C_x/Si$ alloys are pseudomorphic except at the highest concentration x=1.4% on FZ Si where partial relaxation has occurred. The parallel lattice parameter of FZ $Si_{0.086}C_{0.014}$ deviated by 0.15% from that of the Si substrate. For C compositions above x=1.4%, poor epitaxial regrowth is obtained.

Spectroscopic ellipsometry (SE) data were taken at room temperature (RT) over the 1.5 to 5 eV spectral range using a J.A. Woolam spectroscopic ellipsometer. Hydrofluoric acid etching (5% in deionized water) was used to remove the native oxide layer immediately prior to the ellipsometric measurements. After etching, hydrogen termination of the sample surface prevents oxidation during the subsequent ellipsometric measurement. Photoluminescence (PL) data were taken at 14 K from 0.75 eV up to 1.8 eV using a Nicolet Fourier transform spectrometer. The excitation was provided by a Krypton laser (6470 Å) with a low laser power of 5 W/cm^2 to avoid sample heating. The excitation depth of the laser line is about $1 \,\mu m$ for $Si_{1-x}C_x$ alloys. We performed hydrogen passivation on the samples (250°C, 0.6 Torr in hydrogen plasma for 30 min) before performing photoluminescence measurements.

To analyze the ellipsometry results, standard second derivative techniques were used to enhance the structure from interband transitions and data were fitted using a modified Lorentzian lineshape formula developed by Cardona and Aspnes.^{7,8)} The lineshape formula is defined as follows,

$$d^{2}\langle\varepsilon\rangle/d\omega^{2} = -n(n-1)A e^{i\phi} (\hbar\omega - E + i\Gamma)^{n-2}, \ n \neq 0, \\ d^{2}\langle\varepsilon\rangle/d\omega^{2} = A e^{i\phi} (\hbar\omega - E + i\Gamma)^{-2}, \ n = 0,$$
(1)

where the critical point parameters are amplitude A, band gap energy E, broadening Γ , and excitonic phase angle ϕ . The exponent n is equal to (D-2)/2 for D, the dimension of the critical points. We found that the D=0 excitonic fit is the best for the E_1 gap, whereas D=2 is the best fit for the E_2 gap.

Figure 1(a) is the measured pseudo-dielectric function, $\varepsilon(E)$, as a function of the photon energy for $\operatorname{Si}_{1-x}C_x$ alloys grown on Si. Above 2.2 eV, the values of ε should be identical to those of the $\operatorname{Si}_{1-x}C_x$ layer because the probe light does not penetrate through the 150 nm thick $\operatorname{Si}_{1-x}C_x$ layer. The amplitudes of the E_1 and E_2 gaps of $\operatorname{Si}_{1-x}C_x$ alloys are comparable to those of undoped Si reference wafers. This indicates that the regrowth process results in material of high crystalline

^{*}Presently at Department of Physics, Kyunghee University, Suwon 449-701, South Korea.

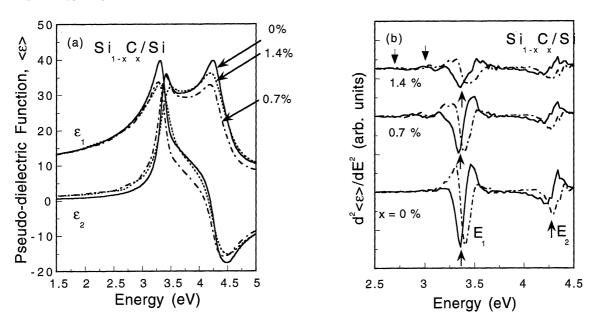


Fig. 1. (a) Plot of pseudo-dielectric functions, $\varepsilon(E) = \varepsilon_1 + i\varepsilon_2$, at room temperature where the C compositions are x = 0 (undoped Si wafer), 0.7, and 1.4%. (b) The 2nd derivative spectra, $d^2\varepsilon(E)/dE^2$, of Fig. 1(a). The real and imaginary part is designated by solid and dot-dashed lines. The arrows designate the fit peak positions of E_1 and E_2 and also unidentified peaks. The unidentified peaks at 2.7 and 3 eV are just above the noise level.

quality. The decrease of the E_1 and E_2 amplitude with increasing carbon composition matches well with Kissinger and coworkers' report.²⁾ The ' E_1 ' peak may be a triple peak of the dominant E_1 and small components of the $E_1 + \Delta_1$ and E'_0 , peak.²⁾ Figure 1(b) is the second derivative spectra with respect to the energy of the pseudo-dielectric functions, $d^2 \varepsilon(E)/dE^2$, in Fig. 1(a). We observe two unidentified peaks at 2.7 eV and 3 eV, below the E_1 gap. The intensities of the features are just above noise level and these peaks may arise from defects or C-related bands. The fitted peak positions for the E_1 gap, neglecting the other small peaks, are $(3.366 \pm 0.001) \text{ eV},$ $(3.352\pm0.001)\,\mathrm{eV},$ and (3.372 ± 0.001) eV for x = 0%, 0.7%, and 1.4%, respectively. The values of the E_2 gaps are (4.268 ± 0.006) eV, independent of C composition. As reported in ref. 5 and 6, the carbon composition is graded for 50 Å below the surface. The penetration depths of the light are about 125 Å at the E_1 peak (3.2 eV) and about 60 Å at the E_2 peak (4.25 eV). This may explain why the E_2 peak is independent of carbon composition because the light is reflected from the graded surface layer for the E_2 gap. We note that our room temperature SE-determined E_1 peak energy decreases at 0.7% and and increases at 1.4% in contrast with the monotonous increase of the E_1 gap position determined by the 80-K electroreflectance technique by Kissinger et al.²⁾ Under large biaxial strain, the strain-induced splitting of the E_1 transition $(E_{1,a} \le E_{1,b})$ is larger than the spin-orbit splitting Δ_1 and the intensity ratio is 1 to 3 according to selection rule.^{9,10)} Because the $E_{1,a}$ and $E_{1,b}$ transition is identical to the E_1 and $E_1 + \Delta_1$ gaps at zero strain, the largest peak ' E_1 ' peak is the $E_{1,a}(E_{1,b})$ transition when the strain-splitting is smaller (larger) than the spin-orbit splitting. However, for x=0.7 and 1.4%, the strain splitting is comparable to the spin-orbit splitting $(\Delta_1=30 \text{ meV})$ and the 'E₁' peak may be a mixture of two strain-split peaks of comparable intensity.⁹⁻¹²⁾

Photoluminescence (PL) spectra of the as-grown samples only exhibited peaks attributable to lattice defects. Annealing the samples at 250 °C in an H₂ atmosphere with plasma activation introduces hydrogen which passivates many non-radiative recombination channels. This procedure typically resulted in an order of magnitude enhancement of luminescence intensity and permitted observation of a peak we ascribe to the no phonon peak as well as additional defect peaks.

Figure 2(a) is the photoluminescence spectra of $Si_{1-x}C_x/Si$ alloys after hydrogen passivation, which was measured at 14 K. The dominant energy peak $(E_{\rm b}=0.92 \text{ eV})$ with a lower energy shoulder $(E_{\rm a}=0.85)$ eV) appear to be defect-related. The low energy shoulder (E_a) is independent of carbon composition whereas the dominant peak position (E_b) decrease about 8 meV from C=0% to C=1.4%. The E_a feature may come from carbon-oxygen complexes as was suggested by ref. 4 because our secondary ion mass spectroscopy analysis indicated the presence of oxygen contents of about $10^{19} \,\mathrm{cm}^{-3}$ in the C-alloved region of our FZ grown samples after SPE.⁶⁾ However, the E_b peak is observed for SPE grown pure Si and thus is inferred to be due to intrinsic defects in SPE regrown Si. Similar results were obtained by Boucaud $et \ al.$ ⁴⁾ where a broad feature near 0.8-0.9 eV was observed for $Si_{1-x}C_x/Si$ grown by rapid thermal chemical vapor deposition (RTCVD).

The most striking feature in Fig. 2(a) is the high energy peak near 1.15-1.17 eV which is clearly observed after hydrogen passivation. This feature was also observed in the as-grown Si_{0.986}C_{0.014} grown on FZ Si, and the signal was an order of magnitude weaker than that of the hydrogen passivated one. In the Fig.

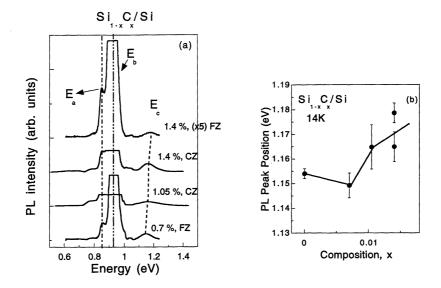


Fig. 2. (a) Photoluminescence spectra of $\operatorname{Si}_{1-x}C_x/\operatorname{Si}$ at 14 K. The dotted line designate the position of no phonon peaks (E_{NP}) of hydrogenpassivated $\operatorname{Si}_{1-x}C_x/\operatorname{Si}$ samples for x=0.7, 1.05, 1.4%. The dot(-dot-dot)-dashed lines are drawn parallel to the y axis. The peaks (E_c) are marked by arrows and are connected by a dotted line. FZ and CZ denotes that we used Si wafers grown by either Float Zone or Czhochralski method. (b) Plot of the E_c peaks which is tentatively assigned as no-phonon peaks from $\operatorname{Si}_{1-x}C_x$ layer. The error bars are estimated from the full-width-at-half-maximum of the peaks. The solid lines are a guide to the eye.

where

2(b), the peak energy increases as we incorporate more carbon, indicating that the high energy peak arises from the Si_{1-x}C_x epi-layer. The peak values are near the value of the no-phonon peak ($E_{\rm NP}$) of the Si, 1.154 eV and we do not observe any other peak up to 1.8 eV. Thus we tentatively assign the peak to the no-phonon peak of the Si_{1-x}C_x epilayer. TO phonon side bands were not detected, probably because of the weak intensities involved. Boucaud *et al.*³⁾ found a sizable no-phonon transition, but very weak TO phonon side bands in their Si_{1-x-y}Ge_xC_y/Si measurements. Other possibilities are defect-related features originating from defects in Si matrix or C-related defects of the Si_{1-x}C_x alloys. More detailed study is necessary for further clarification.

The large value of the full-width-at-half-maximum (FWHM), about 75 meV, of the $Si_{1-x}C_x$ peaks can occur mainly due to composition grading at surface and interface layer as well as local composition fluctuation. The carbon composition is graded for a 50 Å thick region at the surface, followed by 1400 Å of fairly constant composition layer, and lastly C content decreases downward over a 750 Å thick interface with the Si substrate.⁶⁾ With a penetration depth of 1 μ m, the Krypton laser light penetrates the entire implanted layer into the Si substrate. We note that the FWHM of the NP line of a pure Si is less than 0.1 meV.¹³⁾ The true band gap energy E_{g} can be estimated as $E_{g} = E_{NP} + E_{FE}$ where the free-exciton binding energy $(E_{\rm FE})$ is known to be 14.7 meV for Si.¹⁴ We assume that the carbon concentration in our range does not significantly affect the value of $E_{\rm FE}$.

Incorporation of C into Si causes misfit strain between $\text{Si}_{1-x}C_x$ layer and Si substrate. The lattice parameter of $\text{Si}_{1-x}C_x$ is known to follow Vegard's law for these low C concentrations.^{6,15)} The tetragonal biaxial strain can be expressed in Cartesian coordinates as

$$\varepsilon_{xx} = \varepsilon_{yy} = -\delta$$

$$\varepsilon_{zz} = 2c_{12}/c_{11}\delta$$

$$\delta = (a_{\rm SiC} - a_{\rm Si})/a_{\rm Si},$$
(2)

and where $a_{\rm SiC}$ and $a_{\rm Si}$ are the unstrained lattice parameters of Si_{1-x}C_x and Si, respectively.¹⁴⁾ The misfit strain was $\delta = -0.3433x$ for pseudomorphically grown samples. The misfit strain for the partially relaxed sample x=1.4% (FZ) was $\delta = -0.0033$.

The band gaps of the $\operatorname{Si}_{1-x} C_x$ alloys are expected to shift from that of Si due to misfit strain as well as alloying effects. We can estimate the strain-induced band gap shift of the pseudomorphic $\operatorname{Si}_{1-x} C_x/\operatorname{Si}$ assuming that the $\operatorname{Si}_{1-x} C_x$ ($0 \le x \le 0.014$) alloys have the same elastic constants and deformation potentials as those of pure Si. We assume that the $\operatorname{Si}_{1-x} C_x$ alloys have the Silike band structure for our small C concentration range. The degenerate valence bands are split into heavy and light hole bands, with the heavy hole band being the ground state of the in-plane valence band. The Δ_{1c} conduction bands of the $\operatorname{Si}_{1-x} C_x$ alloys are split to Δ_z and Δ_{xy} , with Δ_z being the lowest conduction band under biaxial tensile stress. The interband transition energy, E_g , between Γ_{15v} and Δ_z is expressed as¹⁶)

$$\Delta E_{g}^{strain} = \delta E_{1,c} + (1/2)(2\delta E_{h} - (1/2)\delta E_{100} + \Delta_{0}) \\ - (1/2)\sqrt{(\Delta_{0} + (1/2)\delta E_{100})^{2} + 2(\delta E_{100})^{2}}, \quad (3)$$

where the splitting of conduction band, the hydrostatic component and the shear component of the stressinduced shift of the valence bands are $\delta E_{1c} =$ $(2/3)\varepsilon_2(1+2C_{12}/C_{11})\delta$, $\delta E_{\rm h} = a(-1+C_{12}/C_{11})\delta$ and $\delta E_{100} = -2b(1+2C_{12}/C_{11})\delta$, respectively. We used the

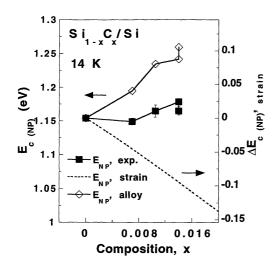


Fig. 3. The observed PL no-phonon peak positions of $\operatorname{Si}_{1-x} \operatorname{C}_x/\operatorname{Si}$ alloys (filled squares, E_{NP} , exp.), which was labeled as E_c in Fig. 2(a), are shown vs C alloy compositions. The unfilled diamonds correspond to the inferred alloy shift (E_{NP} , alloy) of unstrained $\operatorname{Si}_{1-x} \operatorname{C}_x$ alloys. The dashed line corresponds to the estimated strain shift of Si with the same amount of biaxial strain of the fully strained $\operatorname{Si}_{1-x} \operatorname{C}_x/\operatorname{Si}$ alloys. ($E_{\mathrm{NP}}^{\mathrm{strain}} = E_{\mathrm{NP}}(\operatorname{Si}) + \Delta E_{\mathrm{NP}}^{\mathrm{strain}}$). Here, left (right)-hand axis corresponds to $E_{\mathrm{NP}}^{\mathrm{strain}}$ ($\Delta E_{\mathrm{NP}}^{\mathrm{strain}}$). The sold lines connecting symbols are a guide to the eye.

value of the ratio of elastic constants of Si with C_{12}/C_{11} =0.386 from ref. 14. The values of deformation potentials for Si are a=-5.1 eV, b=-2.27 eV, and $\varepsilon_2 = -8.77 \text{ eV}$. The resulting reduction in indirect band gap of pseudomorphic Si_{1-x}C_x due to strain is plotted in Fig. 3 as the dashed line.

We infer the band gaps of unstrained $Si_{1-x}C_x$ alloys by correcting the measured band gaps of strained $\operatorname{Si}_{1-x}C_x/\operatorname{Si}$ for the strain-induced shift using eqs. (3). Figure 3 is the plot of the measured $E_{\rm NP}$ gap of strained $Si_{1-x}C_x/Si$ alloys and inferred E_{NP} gap of unstrained $Si_{1-x}C_x$ alloys with the estimated strain-induced shift, $\Delta E_{\rm g}^{\rm strain}$ (= $\Delta E_{\rm NP}^{\rm strain}$), for example, $E_{\rm NP}^{\rm alloy} = E_{\rm NP}^{\rm experiment}$ $-\Delta E_{\rm NP}^{\rm strain}$, where the exciton binding energy $E_{\rm FE}$ is assumed to be independent of strain. We also plot the expected band gap energy of strained Si under the same amount of biaxial strain of $Si_{1-x}C_x/Si$ alloys, i.e. E_{NP}^{strain} $=E_{\rm NP}({\rm Si})+\Delta E_{\rm NP}^{\rm strain}$. The values of $E_{\rm NP}^{\rm alloy}$ are the estimated values for the no phonon energy of unstrained bulk $Si_{1-x}C_x$ alloys. The estimated values of the E_{NP} gap for unstrained $Si_{1-x}C_x$ alloys are larger than those of Si by about 80 meV for x=1.4%. We deduce that the alloy shift increases quasi-linearly for $E_{\rm NP}$ as carbon composition increases in this regime. This result matches well with a linear interpolation between the band gaps of Si and C as was suggested by Soref.¹⁷⁾ This is to be contrasted with a recent band structure calculation by Demkov et al.,¹⁸⁾ where a decrease of band edge, $E_{\rm NP}$, was predicted although the C concentrations in that study (x=2%-25%) were larger than in the present work. Also they used a tight-binding method assuming Gaussian wave functions for both the s and pwave, which may not give accurate values of energies for conduction bands.

In summary, we have observed the band gaps of $Si_{1-x}C_x$ (0 $\leq x \leq 0.014$) alloys grown on Si substrates by solid phase epitaxy using photoluminescence and spectroscopic ellipsometry. The ellipsometry results confirmed the good crystal quality of the $Si_{1-x}C_x$ epilayer. Upon hydrogen passivation, we observed a new high energy peak for the $Si_{1-x}C_x$ alloys near the Si band edge. Because this highest PL peak position changes as carbon composition increases, we tentatively assign the peak to the no-phonon peak of $Si_{1-x}C_x$ epilayer. We have inferred the alloy shift of strain-free $Si_{1-x}C_x$ alloys by estimating the strain-induced shift of the band gap of the $Si_{1-x}C_x/Si$ alloys. The alloy shift of the no-phonon gap increases over the 0 to 1.4% C concentration range roughly as $\Delta E_{\rm NP} \approx 50 x \,({\rm meV/at\%})$, where $E_{\rm NP}$ is the peak position of the no-phonon peak and x is the atomic percentage of carbon composition.

Acknowledgment

This work was supported in part by the DOE contract, DE-AC04-94AL85000. The authors would like to thank Jim Sturm of Princeton University, Nigel Cave and Jon Candelaria of Motorola, and S. K. Lyo of Sandia National Laboratories for discussion, and Jim Bur and Jonathan Campbell for technical assistance.

- 1) J. C. Bean: Proc. IEEE 80 (1992) 569.
- W. Kissinger, M. Weidner, H. J. Osten and M. Eichluer: Appl. Phys. Lett. 65 (1994) 3356.
- P. Boucaud, C. Francis, A. Larré, J.-M. Lourtioz, D. Bouchier, S. Bodnar and J. L. Regolini: Appl. Phys. Lett. 66 (1995) 70.
- P. Boucaud, C. Francis, F. H. Julien, J.-M. Lourtioz, D. Bouchier, S. Bodnar, B. Lambert and J. L. Regolini: Appl. Phys. Lett. 64 (1994) 875.
- J. W. Strane, H. J. Stein, S. R. Lee, B. L. Doyle, S. T. Picraux and J. W. Mayer: Appl. Phys. Lett. 63 (1993) 2786.
- 6) J. W. Strane, H. J. Stein, S. R. Lee, S. T. Picraux, J. K. Watanabe and J. W. Mayer: J. Appl. Phys. 76 (1994) 3656, and references therein.
- M. Cardona: Modulation Spectroscopy, Solid State Physics, eds.
 F. Seitz, D. Turnbull and H. Ehrenreich (Academic Press, New York, 1969) p. 65.
- D. E. Aspnes: Handbook on Semiconductors (North-Holland, Amsterdam, 1980) Vol. 2, p. 109.
- 9) F. H. Pollak and G. W. Rubloff: Phys. Rev. Lett. 29 (1972) 789.
- 10) F. H. Pollak: Surf. Sci. 37 (1973) 863.
- 11) We can estimate spin-orbit splitting $\Delta_1 = (2/3)\Delta_0 = 0.030 \text{ eV}$ using the well known two-thirds rule for group IV and III-V semiconductors. (ref. 7)
- 12) Hosun Lee, J. A. Floro, J. Strane, S. R. Lee, E. D. Jones, T. Mayer and S. T. Picraux: to be published in Proc. Mater. Res. Soc. 1995 Spring Meet., Strained Layer Epitaxy Symp., San Francisco, CA.
- 13) N. L. Rowell, J.-P. Noël, D. C. Houghton, A. Wang, L. C. Lenchyshyn, M. L. W. Thewalt and D. C. Perovic: J. Appl. Phys. 74 (1993) 2790.
- Landolt-Börnstein, 1982, eds. O. Madelung, M. Schultz and H. Weiss (Springer, Berlin, New York, 1982) Vol. 17a.
- 15) S. S. Iyer, K. Eberl, M. S. Goorsky, F. K. Legoues and J. C. Tsang: Appl. Phys. Lett. **60** (1992) 356.
- 16) L. D. Laude, F. H. Pollak and M. Cardona: Phys. Rev. B 3 (1971) 2623.
- 17) R. A. Soref: J. Appl. Phys. 70 (1991) 2470.
- 18) A. A. Demkov and O. F. Sankey: Phys. Rev. B 48 (1993) 2207.