Near-Band-Edge Photoluminescence from Pseudomorphic $Si_{1-y}C_y/Si$ Quantum Well Structures

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Band edge related photoluminescence (PL) is observed from $Si_{1-y}C_y/Si$ multilayer structures at low temperature. High quality samples were grown pseudomorphically on Si substrates by solid source molecular beam epitaxy. A bound exciton no-phonon line and its Si-Si TO phonon replica are observed at energies which decrease linearly with increasing C content. In 52 Å thick $Si_{0.984}C_{0.016}$ alloy layers the PL redshift is about 100 meV, compared to pure Si. The PL shifts to higher energy for decreasing $Si_{1-y}C_y$ layer width due to the quantum confinement of carriers. The decrease in PL energy observed for decreasing Si barrier layer width implies that neither electrons nor holes are localized in the Si layers.

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In the last decade, extensive work has been done on the growth and characterization of $Si_{1-x}Ge_x$ alloy layers on Si substrates. The structural, electrical, and optical properties of $Si_{1-x}Ge_x/Si$ heteorstructures are investigated for fundamental physical aspects and for the improvement of SiGe-based devices, compared to conventional Si structures [1–3]. Besides some efforts concerning Sn-based heterostructures [4,5], the field of group IV alloys was broadened by the realization of commensurate $Si_{1-y}C_y$ and $Si_{1-x-y}Ge_xC_y$ alloy layers on Si [6–8]. The large lattice mismatch of 52% between diamond and Si limits pseudomorphic growth of $Si_{1-y}C_y$ alloy layers on Si substrates to a carbon content $y \leq 5\%$ or to novel C-rich ordered $Si_{n-1}C_1$ phases [9,10]. The intrinsic band gap of $Si_{1-y}C_y$ alloys was proposed to increase with the carbon content in a virtual crystal approximation which interpolates the Si, SiC, and diamond properties [11,12]. In a first principles model calculation, the intrinsic relaxation of C and Si atoms due to the very different bond lengths was taken into account. The results predict a shrinkage of the band gap and semimetal properties for $y \approx 10\%$ [13]. So far, there is some ambiguity about the band gap and the band alignment in $Si_{1-y}C_y/Si$ heterostructures. The large tensile strain in pseudomorphic $Si_{1-y}C_y$ layers on Si is expected to strongly affect the band edges.

In this Letter we present the low temperature photoluminescence (PL) properties of $Si_{1-y}C_y/Si$ multiquantum well (MQW) and superlattice (SL) structures. The luminescence lines of 52 Å $Si_{1-y}C_y$/156 Å Si MQW structures strongly decrease in energy with increasing carbon content y by about $\Delta E_{\mathrm{PL}} = -y(5.7\ \mathrm{eV})$. A no-phonon line of bound excitons and its Si-Si TO phonon replica are predominant. Weak Si-like TA and TO + O^{Γ} phonon replicas are also resolved. Two series of multilayered samples with varied $Si_{1-y}C_y$ or Si layer width reveal systematic shifts of the PL line energy. The emission is related to the effective band edge within the $Si_{1-y}C_y$ layers representing a quantum well for at least one carrier type. There is no significant localization of the other carrier type in the Si layers which would be expected for a staggered type II band alignment. The data can be well described by a finite potential well model with strong electron and weak hole confinement in the $Si_{1-y}C_y$ layers.

The samples studied here were grown by solid source molecular beam epitaxy on (001) Si substrates at a growth temperature of about 550 °C. A directly heated pyrolytic graphite filament is used for C sublimation and Si is supplied by an electron beam evaporator. At typical C and Si growth rates of 0.01 and 1 Å/s, respectively, the chamber pressure is about 1×10^{-8} mbar starting at a base value of about 10^{-11} mbar. Optimizing the C source design without hot metal components keeps the CO and CO_2 pressure low and is attributed to improve the sample quality. The active $Si_{1-y}C_y/Si$ multilayer structures are 0.5 to 0.6 μm in thickness. They are grown on a 3800 Å thick Si buffer layer and are capped by a 2000 Å thick Si layer. PL is excited by a 476 nm Kr^+ laser beam which is 5 mW in power and is focused to a sample area of about 2 mm^2. The samples are cooled in a He-flow cryostat to a temperature of about $T = 6$ K. PL is analyzed by a $f = 1$ m spectrometer and is detected by a liquid-nitrogen cooled Ge detector in standard lock-in technique.

The structural properties of the samples are determined by two-crystal high resolution x-ray diffraction (XRD) and by comparing the data with dynamical simulation results, which are based on Vegard's law and linearly interpolated elastic constants. Typical (004) reflection data of 30-period multilayer structures with different $Si_{1-y}C_y$ layer width and C content are given in Fig. 1. The good agreement of the experimental and simulated curves indicates high quality pseudomorphic growth of a well-defined layer sequence with constant layer widths and composition. A distinct 0-order SL peak is well separable from the substrate peak, even for $Si_{0.99}C_{0.01}$ layers of only 22 Å width. The C content is determined from the shift of the 0-order SL peak and the relative $Si_{1-y}C_y$ and Si layer width, which are well known from the open/close time durations of the C source shutter.

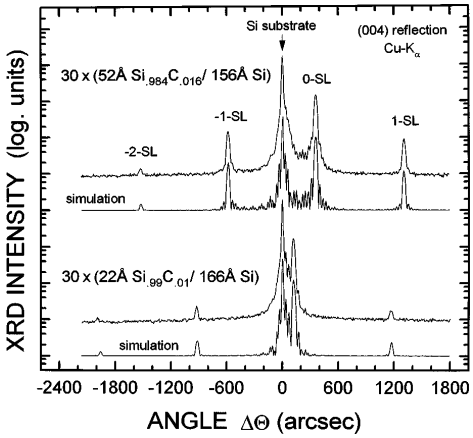

FIG. 1. (004) reflection x-ray rocking curves and dynamical simulation data of 30-period $Si_{1-y}C_y/Si$ MQW structures. The C content y and layer widths are given in the figure.

The period and actual layer widths are deduced from the higher-order SL peaks. The preproducibility of growth parameters and the accuracy in determining layer widths and C content is about 5%. The C content measured by XRD agrees well with the C deposit observed by secondary-ion-mass spectroscopy (SIMS) analysis.

PL spectra from 30-period 52 Å $Si_{1-y}C_y$/156 Å Si MQW structures with varied y are shown in Fig. 2. The Si-TA, Si-TO, and Si-(TO + O^Γ) lines at energy $E =$ 1.138, 1.099, and 1.035 eV originate from the Si substrate, buffer, and cap layer [14]. The spectra reveal two additional PL lines of comparable intensity. These lines shift to lower energy with increasing carbon content. At $y = 1.05\%$, for example, the emission lines at $E = 1.089$ and 1.032 eV are about 12 meV in width. They are attributed to the no-phonon (NP) line and the Si-Si TO phonon replica of excitons confined in the $Si_{1-y}C_y$ layers. The PL shoulder at about $E = 1.070$ eV and the weak resonance at about $E = 0.97$ eV also shift with y and may be related to Si-like TA phonon and TO plus Γ point optical phonon assisted recombination of confined carriers. The phonon energies agree well with that of momentum conserving Si phonon modes [14,15]. No transition lines related to Si-C or C-C phonon modes are resolved. For high C concentration an emission background at low energy is observed which is similar to the broad PL reported earlier from a $Si_{0.995}C_{0.005}$ layer grown by rapid thermal chemical vapor deposition [16]. The peak positions of the NP and TO phonon lines in dependence on y are given in Fig. 3. The experimental data are well fitted by a linear decrease in PL energy of about $\Delta E_{NP} = -y(5.7\text{ eV})$ and a slightly decreasing peak separation of the TO phonon replica of about $(58.5 - 2y/\%)$ eV.

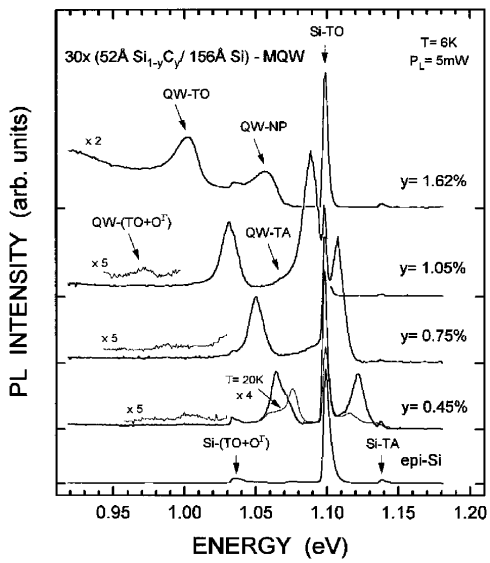

FIG. 2. PL spectra of 52 Å $Si_{1-y}C_y$/156 Å Si MQW structures with different C content y. The samples were excited by a 476 nm Kr^+ laser beam at $T = 6$ K.

In Fig. 4 typical spectra are shown from 30-period d_{SiC} $Si_{0.99}C_{0.01}$/156 Å Si structures with varied alloy layer width $d_{SiC} = 110$, 33, and 11 Å. The transition energy depending on d_{SiC} is summarized in the inset. The PL lines from the $Si_{0.99}C_{0.01}$ layers shift monotonically up to about 45 meV higher energy by reducing the layer width. This is a direct proof that the PL lines originate from quantum confined subband levels and not from any local defect states related to C incorporation. At least one type of photoexcited carrier is localized to the $Si_{1-y}C_y$ layers. The total QW emission intensity is maximum at about $d_{SiC} = 30$ Å. The ratio of NP and TO phonon line intensity increases slightly with decreasing width. PL from a set of 30 Å $Si_{0.992}C_{0.008}/d_{Si}$ Si structures with varied Si width d_{Si} is shown in Fig. 5. The PL shifts monotonically to lower energy by decreasing d_{Si} from 100 to 0 Å. The sample without confinement $d_{Si} = 0$ Å is realized by 8 periods of 400 Å $Si_{0.992}C_{0.008}$/300 Å Si. The PL redshift summarized in the inset reaches about 20 meV. It is attributed to the coupling of neighboring

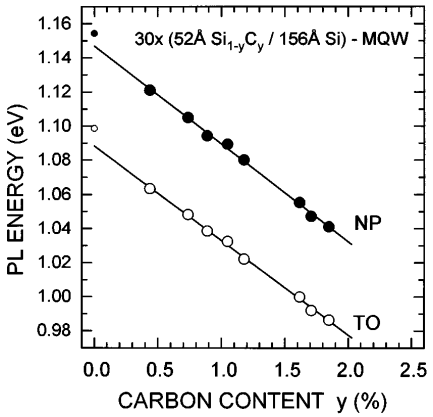

FIG. 3. Peak energy of the no-phonon line (NP) and the TO phonon replica (TP) from 52 Å $Si_{1-y}C_y$/15 Å Si MQW samples depending on y. The straight lines are linear fit results of the MQW data.

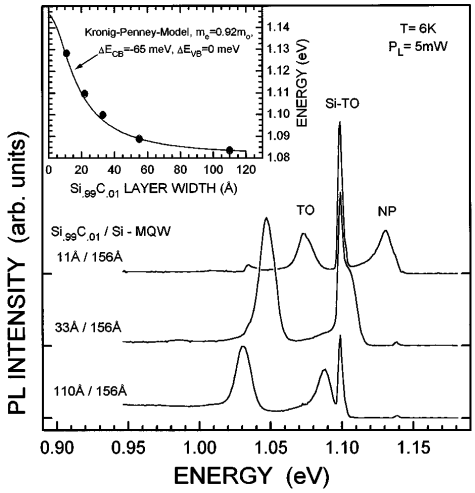

FIG. 4. Typical PL spectra of $Si_{0.99}C_{0.01}$/Si MQW structures with varied alloy and constant Si layer width $d_{Si} = 156$ Å. The experimental transition energy at $T = 10$ K depending on d_{SiC} is given in the inset by full (NP line) and open symbols (TO phonon replica, shifted by 56 meV). The curve is calculated in an effective mass approximation for a pure electron confinement $\Delta E_{CB} = -65$ meV.

$Si_{0.992}C_{0.008}$ quantum wells for thin Si barrier layers $d_{Si} \leq 30$ Å and to forming extended superlattice states of lower energy. No blueshift expected for carriers localized to the Si layers is observed. This qualitative result can be understood as a first test that no type of carrier is confined within the Si layers and that there is no staggered type II band alignment.

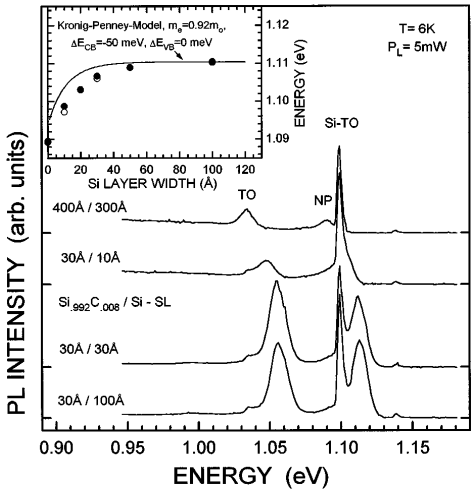

FIG. 5. PL spectra of $Si_{0.992}C_{0.008}$/Si MQW structures with varied Si and constant alloy layer width $d_{SiC} = 30$ Å. The PL peak positions of the NP line (full symbols) and TO phonon line (open symbols, energy shifted by 56 meV) observed at $T = 10$ K are given in the inset. The curve in the inset shows the calculated band gap decrease for a pure electron confinement $\Delta E_{CB} = -50$ meV, $\Delta E_{VB} = 0$ meV. The calculated values are shifted in energy to match the experimental data at $d_{Si} = 100$ Å.

In the following part, the experimental dependence of QW PL energy on C content, alloy, and Si layer width will be discussed. The linear decrease of the NP transition energy $\Delta E_{NP} = -y(5.7\text{ eV})$ in Fig. 3 reflects the shrinking optical band gap in the 52 Å $Si_{1-y}C_y$/156 Å Si MQW structures. The depth of the $Si_{1-y}C_y$ potential well is expected to be slightly larger $\Delta E(y) \approx -y(6.5\text{ eV})$, taking the carrier confinement in a 52 Å thick QW into account ($\Delta E \approx 8$ meV for $y = 1.0\%$, see inset of Fig. 4). Both of the linear fit curves extrapolate for $y = 0.0\%$ to an energy about 9 meV below the transitions of free excitons in pure Si. This additional binding energy may indicate that the QW luminescence is related to excitons which are bound to shallow impurities or the local fluctuations in C content and well width. QW inhomogeneities are also indicated by the PL linewidth of about 12 to 18 meV observed in samples of different y and layer width. The linewidth is 2 to 3 times larger than the value we estimate for local fluctuations in y for a random $Si_{1-y}C_y$ alloy, adapting the bulk $Si_{1-x}Ge_x$ result of Weber and Alonso to $Si_{1-y}C_y$ [17]. Free exciton PL may have been observed at $T = 20$ K from MQW samples with low C content. A distinct narrow emission line appears at about 12 meV higher energy than the bound exciton TO phonon replica (for $y = 0.45\%$ see the fine line spectrum in Fig. 2 at $E = 1.076$ eV). The NP line shows a weak high energy tail. At temperature $T > 35$ K the QW PL gets very weak. As a first approach to the present band structure, a $Si_{1-y}C_y$ layer will be considered as a Si layer under tensile biaxial strain of about $\varepsilon = 0.345y$, for small y. The strain situation of $Si_{1-y}C_y$ on Si is comparable to that of Si on relaxed $Si_{1-x}Ge_x$ buffer layers with $x = 8.3y$. Strain splits and reduces strongly the conduction band-edge energy. The $\Delta(2)$ electron valleys are lowest in energy and shift by about $\Delta E^{\Delta(2)} = -y(4.6\text{ eV})$, using Si deformation potential parameters. The splitting of hole states is much more complicated. Heavy holes shift linearly down in energy by $\Delta E^{hh} = -y(1.3\text{ eV})$. Light holes reveal a nonlinear behavior due to interaction with spin-orbit split holes. They represent the valence band edge at an energy which is estimated to be a few meV above the unstrained Si band edge, for $y = 1.0\%$. The band alignment caused by strain implies strong confinement of electrons and weak confinement of light holes within the $Si_{1-y}C_y$ layers. The PL redshift observed is about 30% larger than the expected band-gap reduction induced by strain. This might indicate that incorporation of C reduces the intrinsic band gap. It is in qualitative agreement with the PL blueshift observed for C incorporation in $Si_{1-x-y}Ge_xC_y$ layers, which is smaller than expected from strain compensation [8]. The trend of a decreasing $Si_{1-y}C_y$ band gap was proposed by tight binding calculations [13]. The intrinsic shift of about -30 meV observed for $y = 1.6\%$, however, is considerably smaller than the value of -170 meV calculated for the X point of the Brillouin zone.

The experimental peak energies for different layer width are compared to calculated values in the inset of Figs. 4 and 5 using a Kronig-Penney model with finite electron and vanishing hole confinement ($\Delta E_{CB} = 65$ or 50 meV, respectively, and $\Delta E_{VB} = 0$ meV). Constant effective masses for Si $m_e = 0.92m_0$, $m_{lh} = 0.20m_0$, and $m_{hh} = 0.275m_0$ are used taking the band-edge splitting due to strain into account. The PL blueshift observed for decreasing d_{SiC} (Fig. 4) is well described by a strong electron confinement in the $Si_{1-y}C_y$ layers. Although some uncertainty exists in deducing band offsets from a comparison of experimental data and simple model calculations, the weak energy increase observed by reducing d_{SiC} may also agree with a weak hole localization but it seems to contradict a strong confinement of light holes ($m_{lh} = 0.20m_0$) with energy shifts which are expected to be considerably larger. The PL redshift observed by reducing d_{Si} is qualitatively described by the decreasing electron confinement in a $\Delta E_{CB} = -50$ meV well with decreasing barrier width d_{Si} (see curve in the inset of Fig. 5). The experimental data are well matched by a curve calculated for a type I band alignment with band offsets $\Delta E_{CB} = -40$ meV and $\Delta E_{VB} = 10$ meV. The additional leaking of light hole states through thin and weak barrier layers further reduces the calculated PL transition energy for small d_{Si}. Even a weak hole confinement in the Si layers, resulting in a type II band structure, would cause a clear PL blueshift for decreasing d_{Si} from 100 to 30 Å, which is not observed. The dependence of PL energy on d_{Si} and d_{SiC} supports a band alignment with strong electron and vanishing or weak hole confinement within the $Si_{1-y}C_y$ layers. Such band offsets agree qualitatively with the expected strain-induced energy shifts. The exact band offsets are beyond the accuracy of the data and the analysis using a simple model which neglects electron hole interaction, interface roughness, impurities, and masses depending on C content and energy.

The observation of spatially direct PL from the $Si_{1-y}C_y$ layers is qualitatively supported by the layer width dependence of PL intensity given in Figs. 4 and 5. For $Si_{1-y}C_y$ layers with large $y > 1\%$ and large width $d_{SiC} > 50$ Å the PL intensity seems to be reduced by lattice defects causing nonradiative or low energy PL recombination. The QW emission, however, also decreases in intensity for small well width $d_{SiC} < 30$ Å, Si layer width $d_{Si} < 30$ Å, or C content $y < 0.5\%$. This may be attributed to the loss of electron and hole confinement and a resulting reduced PL efficiency. For spatially indirect transitions rather an increase in PL intensity would be expected in all the cases due to the increasing overlap of electron and hole wave functions at small layer widths. Further, the PL peak positions are constant within a few meV for varied excitation density. Thus no band bending expected for a type II structure is observed [18].

In conclusion, well-resolved photoluminescence is observed from pseudomorphic $Si_{1-y}C_y/Si$ multilayer structures on Si substrates at low temperature. Several PL lines are resolved which are attributed to no-phonon transitions of bound excitons and Si-like TA, TO, and TO plus Γ point optical phonon replicas. The lines shift linearly down in energy with increasing C content. The main fraction of PL redshift is attributed to the strain-induced lowering of the $\Delta(2)$ conduction band energy. QW confinement raises the PL energy by about 45 meV for reducing the $Si_{1-y}C_y$ layer width from about 110 to 11 Å. The realization of $Si_{1-y}C_y$ layers which emit intense PL provides an additional high quality material system which extends Si-based heterostructures. Large band offsets are reached already at a C content of a few percent. The presented results demonstrate that the optical properties of $Si_{1-y}C_y/Si$ structures are well comparable with $Si_{1-x}Ge_x/Si$. In ternary $Si_{1-x-y}Ge_xC_y$ alloys and in $Si_{1-y}C_y/Si_{1-x}Ge_x$ structures strain adjustment and a band structure modified by carbon open a wide field for basic research and for potential optical and electronic applications.

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