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# Lattice parameter in $Si_{1-y}C_y$ epilayers: Deviation from Vegard's rule

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The precise C content of a series of $Si_{1-y}C_y$ epilayer samples ($0<y<0.012$) was determined by resonant backscattering experiments using a $^4He^+$ ion beam at 5.72 MeV. This beam energy is more suitable for the determination of the C content than the previously used 4.265 MeV. From the correlation of these investigations with x-ray diffraction experiments, a significant deviation of the lattice parameter variation in $Si_{1-y}C_y$ from Vegard's rule between Si and diamond or $\beta$-SiC was observed, which amounts up to 30% or 13%, respectively, for $y<0.012$. This negative deviation is in agreement with recent theoretical predictions by Kelires. © *1998 American Institute of Physics.* [S0003-6951(98)01713-6]

The incorporation of carbon into Si or SiGe provides additional flexibility for the group IV-based heterostructure design. In contrast to pseudomorphic $Si/Si_{1-x}Ge_x$ structures in which the band offset occurs mainly in the valence band, it has been established that $Si/Si_{1-y}C_y$ structures have a type-I band alignment with the offset mainly in the conduction band.[1,2] Due to the huge lattice mismatch between diamond, zinc-blende type silicon carbide ($\beta$-SiC) and Si, already small amounts of substitutionally incorporated C, give rise to a substantial tensile strain in pseudomorphic $Si_{1-y}C_y$ layers on Si. This effect can be exploited for $Si_{1-x-y}Ge_xC_y$ heterostructures lattice matched to Si substrates by choosing a strain-compensating ratio of $x/y\approx 11$. However, the bulk solubility of C in Si is only about $3\times 10^{17}$ $cm^{-3}$ at the melting point. C can be incorporated into substitutional lattice sites up to a concentration of few atomic percent[3,4] only with growth techniques far from thermodynamic equilibrium, such as molecular beam epitaxy (MBE) or chemical vapor deposition (CVD).

For the determination of the Ge and C contents of $Si_{1-x}Ge_x$, $Si_{1-y}C_y$, and $Si_{1-x-y}Ge_xC_y$ epilayers x-ray diffraction (XRD) is the standard technique. By XRD, however, the lattice spacings are determined, and not directly the C and Ge contents of the epilayers. Thus the calculation of these values requires assumptions on the variation of the lattice parameters and of the elastic constants with $x$ and $y$. The lattice parameter in the $Si_{1-x}Ge_x$ system has been determined for most of the composition range experimentally,[5] and shows only minor deviations from linearity. Therefore, lacking reliable experimental data for the $Si_{1-y}C_y$ system, a linear interpolation (Vegard's rule) between the values of Si and either C (diamond) or SiC ($\beta$-silicon carbide) has commonly been assumed to be justified. Recent theoretical calculations predict, however, a deviation from Vegard's rule, even for small carbon concentrations.[6] In this letter the substitutional carbon content of pseudomorphic $Si_{1-y}C_y$ epilayers ($y<0.012$) is determined by resonant backscattering (rBS, i.e., a non-Rutherford elastic scattering). In contrast to former attempts at the 4.265 MeV resonance,[7,8] in our investigations we employed the $^{12}C(\alpha,\alpha)^{12}C$ resonance at a $He^+$ beam energy of about 5.72 MeV,[9,10] which allows a much less ambiguous C concentration profile determination. The lattice constant in the epilayers is measured by XRD rocking scans. From the comparison of the two methods a considerable negative deviation from Vegard's rule in the variation of the lattice constant with C content is observed.

The $Si_{1-y}C_y$ samples were grown by solid source MBE using *e*-beam evaporators for Si and C. Si (001) wafers were RCA cleaned[11] *ex situ* and thermally cleaned at 900 °C in the growth chamber. A Si buffer layer of ~100 nm was grown while the substrate temperature was decreased from 600 °C to the growth temperature of the $Si_{1-y}C_y$ epilayers of 500 °C. Three $Si_{1-y}C_y$ layers with adjusted thicknesses of 100, 150, and 300 nm and C/Si flux ratios of about 1.0%, 0.7%, and 0.4% were deposited at a growth rate of approximately 0.1 nm/s. Recently it has been found that under these growth conditions and C contents the carbon incorporation is fully substitutional.[12] A Si cap layer of the order of 150 nm was grown on top of the samples, which allows for a separation of the rBS signal from the surface carbon contamination and the signal from the $Si_{1-y}C_y$ epilayers. Due to the geometrical arrangement of the sources in the MBE system and because the substrate was intentionally not rotated during growth, the samples exhibit a C concentration gradient across the wafer. Three pieces from different substrate positions were cleaved from each sample giving nine specimens with different C concentrations.

Backscattering experiments have been performed at the Laboratori Nazionali di Legnaro (LNL) using $^4He^+$ beams delivered by the 7 MV CN Van der Graaff accelerator. A beam energy of 5.72 MeV was used. Around this energy a resonance in the elastic reaction $^{12}C(\alpha,\alpha)^{12}C$ occurs increasing the scattering cross section by a factor of 120–130 with respect to the Rutherford value.[9,10] The width of this resonance is much larger (±5% variation within 170 keV) than for the 4.265 MeV resonance (±5% variation within 12 keV, see inset of Fig. 1), so that a nearly constant cross section is obtained over Si thicknesses of several hundreds of

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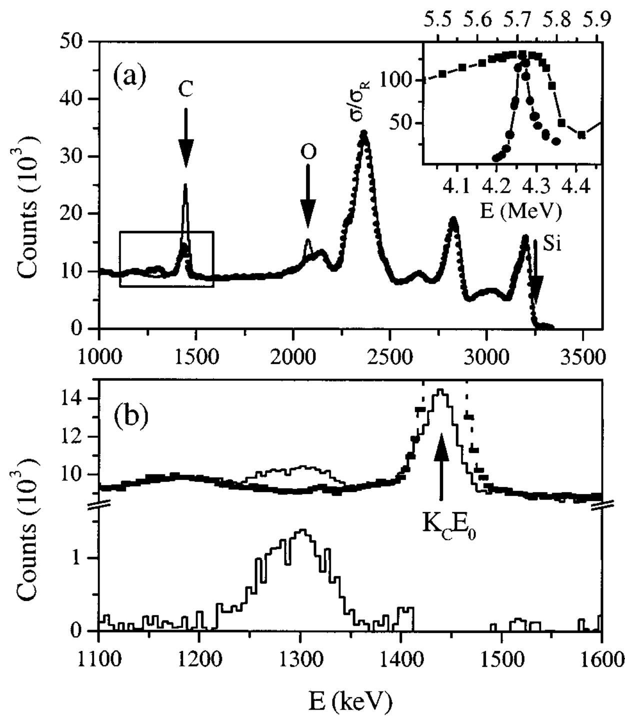


FIG. 1. (a) Backscattering spectra of the sample with C content $y = 0.0092$ (dots) and a virgin Si sample used as standard for background subtraction (solid line). (b) Magnification around the scattering energy for C atoms at the surface ($K_C E_0$) and result of the subtraction (lower signal). The peak at $K_C E_0$ stems from the surface carbon contamination. The inset in panel a shows the enhancement in scattering cross section above the Rutherford value for the resonances with maxima at 4.265 MeV (dots, energy scale at bottom) and 5.72 MeV (squares, energy scale at top), respectively.

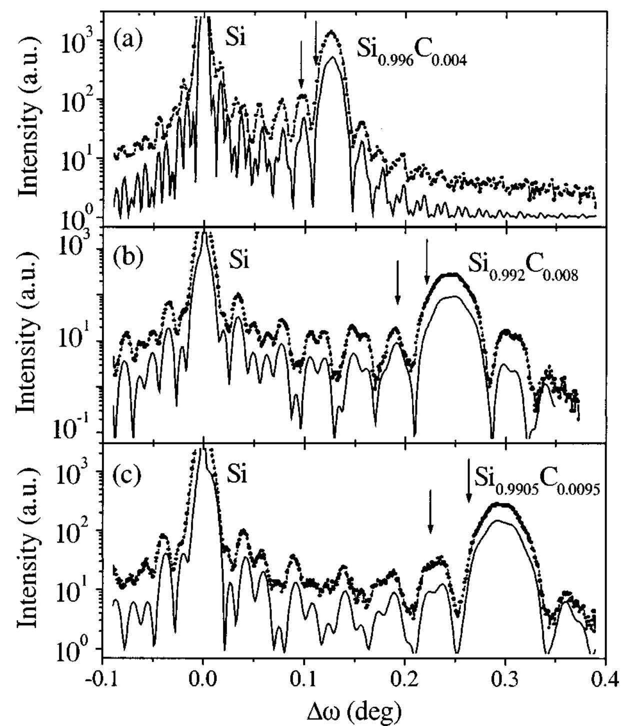


FIG. 2. XRD rocking scans around the (004) Bragg reflection of three epilayers (dots: measurements, solid lines: simulations). Arrows indicate peak positions corresponding to epilayers with the same C concentrations as given, but assuming a variation of the relaxed lattice constant according to Vegard's rule between Si and C, and between Si and β-SiC.

nm. This fact allows an easier and more accurate determination of the carbon concentration compared to experiments using the narrower 4.265 MeV resonance.[7,8] In the latter case the accuracy of C concentration determination relies on a suitable choice and the precise knowledge of many experimental parameters, such as the beam energy, sample thickness, stopping power, etc. Moreover the C lattice location measurement by ion channeling is severely affected by the ratio of the channeling to random stopping powers. This is not a problem using the 5.72 MeV resonance which is nearly depth independent. Unfortunately the silicon cross section is not Rutherford-like at a beam energy of 5.72 MeV, not even in the region in which the carbon signal is detected. In order to achieve a correct subtraction of the Si background signal, we used the so called IBM geometry[13] with a tilt of $-60°$ and glancing exit. In this way the background variation is quite smooth and the subtraction of the virgin Si spectrum can be performed very accurately (see Fig. 1). Furthermore this geometry permits to increase the depth resolution and therefore to increase the separation, due to the presence of a Si cap, between the carbon signals stemming from the $Si_{1-y}C_y$ layer and the surface carbon contamination. This experimental technique is described in more detail in Ref. 10. In order to determine the substitutional C fraction $f$, rBS spectra were taken in a ⟨112⟩ channeling configuration for the sample with the highest C content.

For all samples XRD rocking scans around the (004) Bragg reflections were recorded to measure the lattice constants in growth direction. From reciprocal space mappings around the (004) and (224) reciprocal lattice points it was verified that the samples were grown fully pseudomorphic. Figure 2 shows (004) rocking curves of three samples (dots), together with simulations using dynamical scattering theory (thin solid lines).

The strain in the epilayers, and hence the lattice constant in growth direction, $a_\perp$, can be calculated from the C content $y$ via

$$a_\perp = [a_{rel}(y) - a_\parallel] \times \left(1 + 2\frac{C_{12}(y)}{C_{11}(y)}\right) + a_\parallel,$$

where the in-plane lattice constant $a_\parallel$ is that of the substrate ($a_{Si} = 5.431$ Å). The other relevant quantities are the relaxed lattice parameter of the $Si_{1-y}C_y$ compound $a_{rel}(y)$ and the ratio of its stiffness constants ($C_{11}$ and $C_{12}$). For the latter we use a linear interpolation between the values of Si and C. Due to the small carbon concentrations in our samples ($y < 0.012$) the results are not affected whether the elastic constants are linearly interpolated to β-SiC or C, or if the Si elastic constants are used.

For the variation of $a_{rel}(y)$ with the carbon concentration we use three different assumptions. Figure 3 shows the lattice constant *in growth direction* $a_\perp$ of a $Si_{1-y}C_y$ epilayer tetragonally strained to match the Si lattice constant. The dashed line is calculated considering a linear interpolation between the Si and C lattice parameters: $a_{rel} = a_{Si}(1-y) + a_C y$, with $a_C = 3.567$ Å. The dot-dashed line corresponds to a linear interpolation between Si and SiC: $a_{rel} = a_{Si}(1 - 2y) + a_{SiC} 2y$ $a_{SiC} = 4.360$ Å. The solid line represents the calculations of $a_{rel}$ by Kelires,[6] which are approximated by $a_{rel} = a_{Si}$-$2.439y + 0.5705y^2$. The black dots represent the measurements of $a_\perp$ as obtained from the XRD rocking curves plotted against the carbon contents determined by

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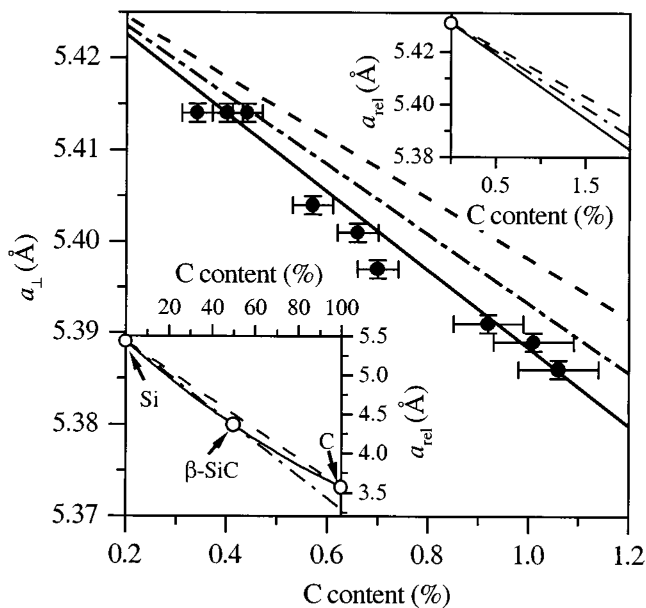


FIG. 3. Dependence of the lattice constant *in growth direction* $a_\perp$ of a pseudomorphic tetragonally strained $Si_{1-y}C_y$ epilayer. Insets show the variation of the *relaxed* lattice parameter $a_{rel}$ of $Si_{1-y}C_y$ for the full compositional range (lower left panel) and for the relevant range of small C contents (upper right panel). Dashed lines: calculated lattice parameters with $a_{rel}$ according to Vegard's rule between Si and C; dash-dotted lines: calculations using Vegard's rule between Si and $\beta$-SiC; solid lines: theoretical data according to Kelires. Black dots represent our experimental data.

rBS. The insets of Fig. 3 show the variation of the *relaxed* lattice parameter in the $Si_{1-y}C_y$-system for the three models over the full compositional range (panel at lower left corner) as well as for the relevant range of small C contents (panel at the upper right corner), the different line types are used as before.

It is obvious from Fig. 3 that the measurements are in good agreement with the theoretical predictions of Kelires.[6] If linear interpolation models between $a_{Si}$ and $a_C$ or $a_{Si}$ and $a_{SiC}$ for the relaxed lattice parameters are used to determine the C content from XRD experiments, the measured strains result in carbon concentrations 30% and 13% higher, respectively, than from our measurements. In Fig. 2 arrows indicate the position of the Bragg peak corresponding to $Si_{1-y}C_y$ epilayers with the C content as measured by rBS, but assuming a linear variation of the relaxed lattice constant with $y$ between $a_{Si}$ and $a_C$ or $a_{SiC}$.

The intrinsic uncertainties of the methods are indicated by the error bars in Fig. 3. The scattering of the data points is mainly due to the lateral inhomogeneity of our samples, as the subsequent XRD and rBS measurements might not have been performed at exactly the same position on the samples.

Another crucial point in the comparison of rBS and XRD measurements is the fraction of C that is introduced in the Si lattice at *substitutional* sites. The rBS experiments performed in channeling geometry on the sample with the highest C content confirmed that all C atoms are incorporated on substitutional sites (substitutional C fraction $f = 1.0^{+0.0}_{-0.1}$). As this sample would exhibit the largest nonsubstitutional fraction according to Ref. 12, we conclude that all samples have substitutional C fraction $f = 1$. Even if there was a significant non-substitutional C fraction, the measured negative deviation from Vegard's rule would be even larger than that predicted by Kelires.

The physical origin of the negative deviations of the lattice parameter from Vegard's rule in the $Si_{1-x}Ge_x$ and $Si_{1-x}C_x$ system has already been identified by Martins and Zunger,[14] as being caused by the charge transfer from Ge to Si or from Si to C, respectively. Whereas in the SiGe system this is a comparatively small effect, in the SiC system much larger deviations occur, in agreement with the calculations in Ref. 14.

In summary, we have performed a systematic investigation of the dependence of the lattice parameter on the C content in a series of epilayers with different C concentrations $y < 0.012$ grown pseudomorphically on Si (001) substrates. The absolute C concentration of the samples was measured by rBS using the 5.72 MeV $^{12}C(\alpha,\alpha)^{12}C$ resonance. The correlation of this C content and the lattice parameters of the epilayers obtained from XRD measurements is in good agreement with the significant negative deviation of the lattice parameter of $Si_{1-y}C_y$ compounds from Vegard's rule, as has been theoretically predicted by Kelires. The carbon contents obtained from XRD measurements taking into account this deviation are lower by about 30% and 13%, respectively, than those obtained previously under the assumption of a linear variation of the lattice constants between either silicon and diamond or silicon and $\beta$-silicon carbide.

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