

Growth and thermal stability of pseudomorphic $\text{Ge}_{1-y}\text{C}_y/\text{Ge}$ superlattices on $\text{Ge}(001)$

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High quality $\text{Ge}/\text{Ge}_{1-y}\text{C}_y$ superlattices with nominal carbon contents of 1.2% and 2.1% were grown by molecular beam epitaxy on $\text{Ge}(001)$. In transmission electron microscopy the layers are planar and perfectly pseudomorphic without any extended defects observable. The infrared absorption line at 529 cm^{-1} is attributed to the local vibrational mode of substitutional carbon in germanium. However, in contrast to $\text{Si}_{1-y}\text{C}_y$ alloys where almost 100% of the C is substitutional under optimized growth conditions, x-ray diffraction measurements indicate that the efficiency of carbon incorporation onto substitutional sites is only about 30% for low temperature growth at $T_S = 200\text{ }^\circ\text{C}$. It reduces further for higher growth temperatures to only about 10% at $T_S = 300\text{ }^\circ\text{C}$. Post-growth annealing experiments indicate thermal stability up to $450\text{ }^\circ\text{C}$. Annealing at higher temperature results in a reduction of substitutional carbon content. As in the case of $\text{Si}_{1-y}\text{C}_y$ alloys the built-in strain is relaxed by C diffusion and not by nucleation of misfit dislocation. © 1999 American Institute of Physics. [S0003-6951(99)02108-7]

The substitutional incorporation of small amounts of carbon into Si and $\text{Si}_{1-x}\text{Ge}_x$ is an attractive method to adjust strain, band alignments and energy gaps in Si/SiGeC heterostructures.¹⁻³ For Ge-rich $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ layers, the incorporation of carbon into the Ge matrix plays an important role. Recent experiments on $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ films indicate that growth becomes increasingly more difficult for high Ge contents, implying that C tries to avoid C-Ge bonds.⁴ Very careful optimization of the growth parameters in molecular beam epitaxy (MBE) is essential for the synthesis of $\text{Ge}_{1-y}\text{C}_y$ alloy layers, because of the even lower solubility of carbon in Ge (10^8 atoms/cm^3 at the melting point of Ge) as compared to Si, and due to the large lattice mismatch between diamond and Ge of about 59%. Previous investigations have focused on the synthesis and the material parameters of $\text{Ge}_{1-y}\text{C}_y$ layers on $\text{Si}(001)$. Since pseudomorphic $\text{Ge}_{1-y}\text{C}_y$ alloys with only a few atomic layers can be prepared on Si,⁵ most of the measurements were carried out on thick relaxed layers.⁶⁻⁸ These layers exhibit high dislocation densities which makes it difficult to measure intrinsic material parameters.

In this letter, we report on the epitaxial growth of high quality $\text{Ge}_{1-y}\text{C}_y/\text{Ge}$ superlattices (SL) with carbon concentrations up to 2.1% on $\text{Ge}(001)$ substrates. The layers are well defined and allow detailed investigation of structural properties, efficiency of the incorporation of substitutional carbon and the thermal stability of the metastable $\text{Ge}_{1-y}\text{C}_y$ alloy.

The $\text{Ge}_{1-y}\text{C}_y/\text{Ge}$ SL structures were grown by solid source MBE. The $\text{Ge}(001)$ substrates were chemically

cleaned in boiling trichlorethylene, acetone, and methanol and then oxidized in a $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ mixture. The oxide was desorbed in the MBE chamber by annealing at $550\text{ }^\circ\text{C}$ for 10 min. The growth was started at a temperature of $150\text{ }^\circ\text{C}$ to avoid the formation of islands. During a 50 nm thick buffer layer the temperature was increased up to $200\text{ }^\circ\text{C}$. At this temperature the SL structure, consisting of 30 periods alternating 10 nm Ge and 3 nm $\text{Ge}_{1-y}\text{C}_y$, and finally, a 20 nm Ge cap layer were deposited. Two structures, called A and B, were fabricated with nominal carbon contents of 1.2% and 2.1%, respectively. The growth rates were previously calibrated by x-ray diffraction (XRD) measurements of a Si/Si_{1-x}Ge_x and two Si/Si_{1-y}C_y SL. The Si/Si_{1-y}C_y samples were grown at a growth rate of $1\text{ } \text{Å/s}$ and a substrate temperature of $460\text{ }^\circ\text{C}$. The carbon content, calculated with the approach by Kelires,⁹ was 0.45% and 0.80%, respectively. The flux calibration by XRD is reasonable because former measurements with secondary-ion mass spectroscopy and XRD showed that nearly 100% of the carbon atoms were incorporated at substitutional sites for these growth conditions, which is in agreement with recent investigations by Zerlauth *et al.*¹⁰ For the deposition of germanium, we used an effusion cell and carbon was sublimated from a hot pyrolytic graphite filament. Transmission electron microscopy (TEM), double-crystal XRD, using $\text{Cu } K\alpha$

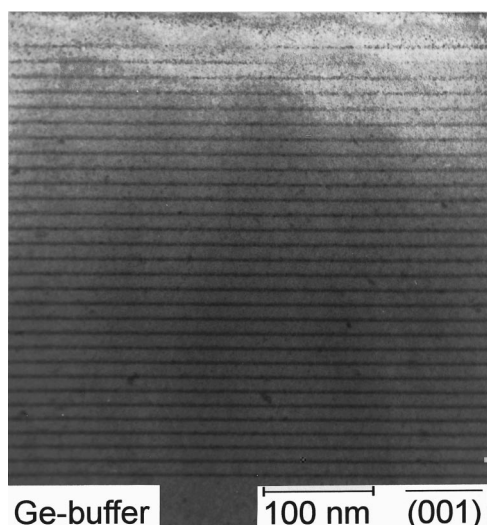


FIG. 1. Cross-sectional TEM image of 30 periods alternating 10 nm Ge and 3 nm $\text{Ge}_{0.979}\text{C}_{0.021}$. The image indicates no signs of extended C related defects or misfit dislocations.

culate the amount of substitutional carbon and the degree of relaxation of the layers.¹¹

Figure 1 shows a cross-sectional TEM image of the sample B with 3 nm thick $\text{Ge}_{0.979}\text{C}_{0.021}$ layers. The $\text{Ge}_{0.979}\text{C}_{0.021}$ layers appear as homogeneous dark lines with planar interfaces. The image does not indicate any extended defects induced by the carbon. Figure 2(a) shows XRD curves of the two $\text{Ge}_{1-y}\text{C}_y/\text{Ge}$ SL A and B described above. The main peak at $\Delta 2\theta = 0^\circ$ is the (004) diffraction from the Ge substrate and buffer layer. The zero-order peak of the SL is shifted to values of $\Delta 2\theta = +0.058^\circ$ and $\Delta 2\theta = +0.084^\circ$ for samples A and B, respectively, indicating that the average strain is tensile. Evidence of good crystalline quality is reflected in the observation of higher order SL peaks and

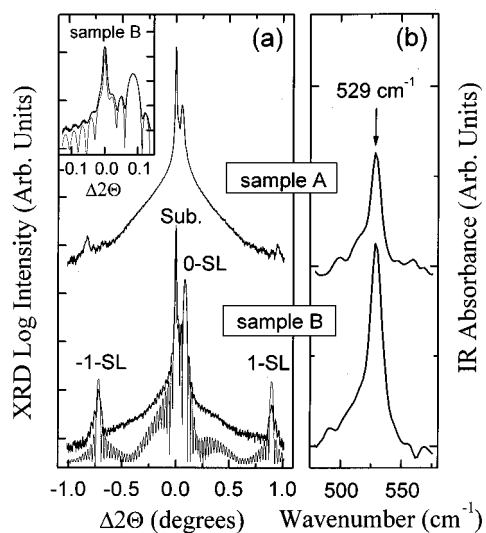


FIG. 2. Symmetric (004) x-ray diffraction rocking curves of $\text{Ge}_{1-y}\text{C}_y/\text{Ge}$ superlattices with nominal C content of 1.2% (sample A) and 2.1% (sample B), respectively and best fitted simulated curve for sample B (a). The good crystalline quality is reflected in the observation of higher order SL peaks and the observable Pendelösung fringes around the zero-order peak [see also inset of (a)]. IR absorption of the two $\text{Ge}_{1-y}\text{C}_y/\text{Ge}$ SL less a Ge reference spectra (b). The absorption line observed at 529 cm^{-1} is attributed to the local vibrational mode of substitutional C in Ge.

observable Pendelösung fringes around the zero-order peak [see inset of Fig. 2(a) for sample B]. The TEM image in Fig. 1 and the evaluation of the asymmetric (115) rocking curves demonstrate that the $\text{Ge}_{1-y}\text{C}_y$ alloy layers are fully laterally extended to match the Ge substrate (pseudomorphic growth). Figure 2(a) shows the best fitted simulated curves. The dynamical simulation uses Vegard's law, i.e. the linear interpolation between Ge and diamond, to calculate the lattice constant $a_0(y)$ of $\text{Ge}_{1-y}\text{C}_y$. A slight bowing effect in $a_0(y)$, similar to the case of $\text{Si}_{1-y}\text{C}_y$,⁹ would reduce the carbon concentration indicated in the following, but does not change the other statements. The results of the fitting procedures for the samples A and B are carbon contents of 0.5% and 0.8%, respectively. We have compared this C content with the nominal carbon flux calibrated by XRD measurements on $\text{Si}_{1-y}\text{C}_y$ SL structures. A comparison with other methods, like secondary-ion mass spectroscopy measurements, is difficult because of missing standards for $\text{Ge}_{1-y}\text{C}_y$. The comparison of the C flux with the C content of the $\text{Ge}_{1-y}\text{C}_y$ layers results in an efficiency of about 30% for the incorporation of substitutional C into Ge at $T_S = 200^\circ\text{C}$. For higher growth temperatures of 300°C , the substitutional C incorporation is reduced to only 10%. Significantly lower T_S , on the other hand, will result in increased incorporation of point defects.

Infrared absorption measurement were performed at room temperature in the frequency range of $450\text{--}4000\text{ cm}^{-1}$. An absorbance spectrum measured on a reference Ge substrate was subtracted from the sample absorbance spectra to remove any irrelevant features originating from the substrate. Figure 2(b) shows the infrared absorbance spectra of the two $\text{Ge}_{1-y}\text{C}_y/\text{Ge}$ SL. We observe an absorption line at 529 cm^{-1} for both samples. Hoffmann *et al.*¹² studied substitutional C in Ge with infrared spectroscopy and ion channeling for Ge crystals implanted with C ions. They observed a local vibrational mode (LVM) due to substitutional C at 531 and 512 cm^{-1} for Ge crystals where ^{12}C and ^{13}C have been implanted, respectively. Therefore we attribute the absorption line at 529 cm^{-1} to the LVM of ^{12}C in Ge. The 2 cm^{-1} decrease in wavenumber is due to the different temperature during measurement.¹³ The integrated absorbance of the mode at 529 cm^{-1} scales proportionally to the shift in the separation of the zero-order SL XRD peak with respect to the Ge substrate peak.

To investigate the thermal stability of the layers, the samples were annealed for 20 min at different temperatures from 300 to 850°C . After the annealing, measurements of symmetric (004) and asymmetric (115) XRD rocking curves were carried out, to determine the perpendicular and in-plane lattice constant. The layers do not relax by nucleation of misfit dislocations since no change of the in-plane lattice constant is detected within this temperature range. Figure 3 shows the angle distance $\Delta 2\theta$ between the main (004) peaks of the Ge substrate and the $\text{Ge}_{1-y}\text{C}_y$ layers. The data in Fig. 3 show that $\Delta 2\theta$ does not change up to a temperature of 450°C . At higher annealing temperatures $\Delta 2\theta$ decreases, indicating the thermal activation of C atoms located in the Ge matrix. The temperature behavior is in agreement with IR absorption and ion channeling measurements by Hoffmann *et al.*¹² which are carried out in the same temperature range.

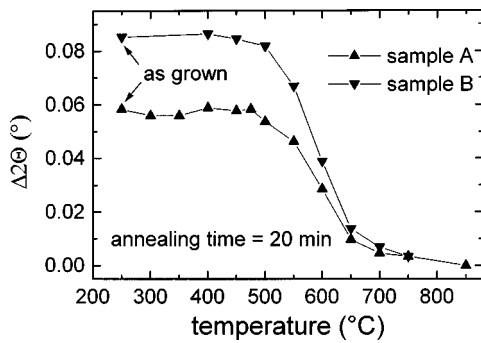


FIG. 3. Angle distance $\Delta 2\theta$ between the main (004) peaks of the Ge substrate and the $\text{Ge}_{1-y}\text{C}_y$ layers as a function of annealing temperature. At temperatures above 450 °C $\Delta 2\theta$ decreases indicating the thermal activation of substitutional C.

It indicates, that the films are likely to relax by C diffusion into precipitates and not by nucleation of misfit dislocations like in the case of SiGe/Si heterostructures. To investigate the loss of substitutional C in more detail the time dependence of the decrease of C in the SL structure is measured at different temperatures. The normalized angle distance $\Delta 2\theta(t)/\Delta 2\theta(t=0)$ in Fig. 4(a) shows that the loss of substitutional C is independent of the initial carbon content but increases with increasing annealing temperature. In the theory of phase transformations in alloys, this behavior can be described by the semiempirical rate equation $y(t) = \exp[(-k_r t)^n]$, where $y(t)$ is the fraction not transformed and k_r is the empirical rate constant.¹⁴ The empirical parameter n characterizes the model process for the growth of the precipitates. The solid lines in Fig. 4(a) are best fitted simulated curves using n and k_r as fitting parameters. We find values of $n=0.4-0.5$ for the $\text{Ge}_{1-y}\text{C}_y$ structures, almost independent of the annealing temperature and initial carbon content. In the case of $\text{Si}_{1-y}\text{C}_y$ alloys, a value of $n=1$ is found for the diffusion controlled formation of the very stable SiC phase, which dominates the formation of precipitates.¹⁵ In the Ge/C system the measured value of

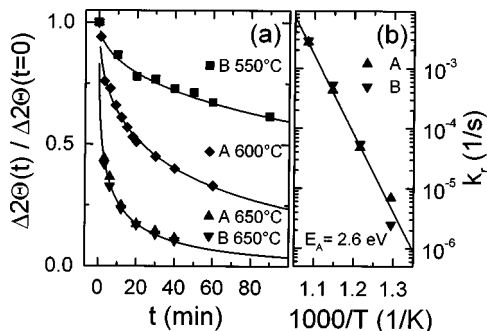


FIG. 4. (a) Normalized angle distance $\Delta 2\theta(t)/\Delta 2\theta(t=0)$ for different annealing temperatures. (b) Arrhenius plot of the rate constant k_r over $1000/T$. The straight line is a linear fit to the data.

$n=0.5$ indicates a different nature of precipitate formation. These results are in agreement with Raman measurements, which indicate the formation of amorphous and graphitic carbon clusters in $\text{Ge}_{1-y}\text{C}_y$ alloys, while no stable GeC phase is known to exist.⁷ An activation energy E_A for the loss of substitutional C can be obtained from the temperature dependence of the rate constant $k_r \sim \exp[-E_A/kT]$. Figure 4(b) shows the Arrhenius plot $\log(k_r)$ against $1000/T$ for both SL structures. The solid line is a linear fit to the data, which corresponds to an activation energy of $E_A=2.6$ eV. Kulik *et al.* report that the activation energy for the loss of substitutional carbon in $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ layers with a carbon content of about 0.8% has a maximum of $E_A=4.9$ eV for strain compensated $\text{Si}_{0.892}\text{Ge}_{0.1}\text{C}_{0.008}$ alloy on Si, and decreases for higher Ge contents.¹⁶ This is explained by an increase of the mismatch between Si-Si and Si-C bonds with increasing Ge concentration. From their results, an activation energy below 3 eV can be assumed for Ge-rich $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ layers, which is in agreement with our measurement.

In conclusion, we have shown that pseudomorphic $\text{Ge}_{1-y}\text{C}_y$ layers can be grown by MBE with carbon contents up to 0.8%. The efficiency of substitutional C incorporation at a growth temperature of 200 °C is about 30%, which is considerably lower as compared to the nearly complete incorporation of C in Si. Narrow IR absorption at 529 cm^{-1} due to substitutional carbon in Ge is observed. Annealing experiments show the stability of $\text{Ge}_{1-y}\text{C}_y$ alloys up to a temperature of about 450 °C. At higher temperatures, an activation energy for the loss of substitutional carbon of $E_A=2.6$ eV is determined.

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