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Microscopic carbon distribution in $Si_{1-y}C_y$ alloys: A Raman scattering study

M. Meléndez-Lira,* J. D. Lorentzen, and J. Menéndez†
Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287-1504

W. Windl
Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

N. G. Cave, R. Liu, J. W. Christiansen, and N. D. Theodore
Materials Research and Strategic Technologies, Motorola, 220 West Broadway, Mesa, Arizona 85202

J. J. Candelaria
Semiconductor Technology Laboratory, Motorola, 3501 Ed Blustein Blvd., Austin, Texas 78721

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$Si_{1-y}C_y$ alloys grown by solid-phase epitaxy of carbon-implanted Si were investigated with Raman spectroscopy. A comparison between the experimental Raman spectrum and the spectrum predicted from *ab initio* calculations shows that the carbon distribution in these samples is more randomized than in similar alloys grown by molecular-beam epitaxy. It is argued that epitaxial, layer-by-layer growth promotes the formation of ordered Si-C structures. [S0163-1829(97)06532-6]

Epitaxial $Si_{1-y}C_y$ and $Si_{1-x-y}Ge_xC_y$ films with carbon concentrations around 1% have been fabricated recently using a variety of methods.[1–9] The films are largely defect-free, even though their carbon concentrations are three orders of magnitude higher than the solubility limit of substitutional carbon in silicon.[10] Two concurrent mechanisms have been proposed to explain the epitaxial, layer-by-layer growth of these supersaturated solutions. The stress introduced by a carbon impurity can be partially relieved near the growing surface, leading to a drastically increased solubility. For carbon near a Si surface, Tersoff estimates a surface solubility four orders of magnitude higher than the bulk value.[11] On the other hand, Rücker and co-workers computed the energy of ordered, tetrahedrally bound Si_nC structures with up to 20% carbon.[12] When these structures are epitaxially matched to a Si substrate, they find several examples in which the energy per carbon atom is lower than in the case of isolated, substitutional carbon. For example, two third-nearest-neighbor carbon atoms (3-nn) at opposite vertices of the diamond structure six-atom rings are found to have a lower energy than two isolated substitutional carbon impurities. In a subsequent paper, Rücker *et al.* propose and demonstrate an experimental probe of these carbon arrangements based on Raman and infrared spectroscopy.[13] The frequencies of the vibrational modes involving carbon atoms depend on the relative positions of these atoms, leading to a characteristic vibrational spectrum for each possible configuration. A comparison of theoretically computed Raman spectra with experimental results for $Si_{1-y}C_y$ films grown by molecular-beam epitaxy (MBE) suggest that 3-nn carbon pairs indeed appear much more frequently than expected for a random distribution of carbon atoms.[13]

The research described above leaves an important open question, namely, the extent to which the surface solubility enhancement described by Tersoff[11] is required to obtain the ordered Si-C structures predicted by Rücker *et al.*[13] In this paper, we address this issue by performing Raman experiments on $Si_{1-y}C_y$ films grown by direct carbon implantation followed by solid-phase-epitaxial regrowth (SPE).

Preamorphized CVD grown Si films on Si(100) were employed to produce the $Si_{1-y}C_y$ implanted samples for SPE regrowth. Multiples of a $1\times10^{15}C^+/cm^2$ dose at 25 KeV followed by solid-phase-epitaxy regrowth at 750 °C produced peak concentrations between 0.3 and 1.8 at. % C over 300 nm, as measured by secondary-ion mass spectroscopy. The Raman experiments were performed at room temperature in the perfect backscattering $z(x,y)\overline{z}$ configuration; x, y, and z correspond to the [100], [010], and [001] crystal directions. The 488-nm line from an Ar^+ laser was used, and a Spex 1404 double monochromator equipped with a CCD detector was employed to analyze the scattered light.

Figure 1(a) shows the Raman spectrum of implanted $Si_{1-y}C_y$ samples in the spectral region corresponding to the local mode of C in Si. Since the Raman spectrum of Si has a relatively narrow second-order feature in the same spectral range,[14] we subtracted this feature from all spectra shown here by performing identical measurements in samples without carbon. Therefore, the peaks seen in Fig. 1 are due to carbon-related vibrations only. The single peak observed at 605 cm^{-1} in Fig. 1(a) is very similar to the infrared absorption spectrum of substitutional carbon in Si for carbon concentrations below the solubility limit,[15] except that the linewidth we observe is 12 cm^{-1}, roughly twice the value determined from those infrared measurements. Figure 1(c) shows a similar Raman spectrum obtained earlier by Rücker *et al.*[13] from a $Si_{1-y}C_y$ sample grown by MBE. This Raman spectrum has a clear satellite peak near 625 cm^{-1}, which has been assigned to a higher number of 3-nn carbon pairs than expected from a random distribution of carbon atoms. No

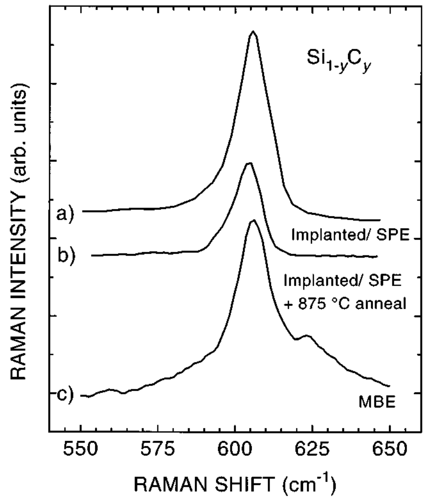

FIG. 1. First-order Raman spectrum of $\mathrm{Si}_{1-y}\mathrm{C}_y$ alloys after substraction of the silicon second-order contribution. (a) Implanted SPE sample with a peak concentration of 1.4 % at. C as grown, (b) same as (a) after 4-h anneal at 875 °C under flowing Ar gas and, (c) $\mathrm{Si}_{0.994}\mathrm{C}_{0.006}$ alloy grown by MBE (from Ref. 13). The relative scale between the implanted and MBE samples is arbitrary.

such satellite peak is observed in the samples grown by carbon implantation.

Figure 2 shows two theoretical Raman spectra for a $\mathrm{Si}_{0.986}\mathrm{C}_{0.014}$ alloy, obtained from *ab initio* calculations of the structure and vibrations of $\mathrm{Si}_{62}\mathrm{C}_2$ and $\mathrm{S}_{63}\mathrm{C}_1$ supercells.[16] The predicted Raman spectra are obtained (using a bond-polarizability model and a full width at half maximum of 6 cm^{-1} for all Raman-active vibrations) as an average of spectra calculated for different C-C configurations. The vibrational frequencies from the *ab initio* calculations are within 7% of the experimental values. The spectra shown in Fig. 2 were frequency shifted (for easier comparison) to match exactly the experimental peak at 605 cm^{-1}. The solid line in Fig. 2 corresponds to a random distribution of C-C configurations. For the spectrum shown as a dotted line, each configuration was given a weight proportional to $\exp(-E/kT)$, where is E is the energy of the configuration (shown in the inset to Fig. 1) and $T=750$ °C. The peak near 625 cm^{-1} is due to the presence of 3-nn carbon pairs, in agreement with the calculation of Rücker *et al.*[13] Only qualitative comparisons between theory and experiment can be made at this point, since the calculations ignore clusters of 3 or more carbon atoms and the overall line shape is very sensitive to the Raman frequency of each configuration. However, it is interesting to point out that our *ab initio* results are in basic agreement with the calculations of Rücker *et al.* using an empirical potential.[13] We observe that the peak near 625 cm^{-1} is more prominent in the ''weighted'' calculation. This occurs because the 3-nn configuration (at a C-C distance of $0.83a_0$, where a_0 is the Si-lattice constant) has one of the lowest energies. Hence we conclude that the carbon-implanted samples—where the 3-nn peak is not seen at all—are closer to a random distribution of carbon atoms, whereas the MBE-grown samples must be closer to equilibrium, since they show clear evidence for the low-energy 3-nn carbon configuration.

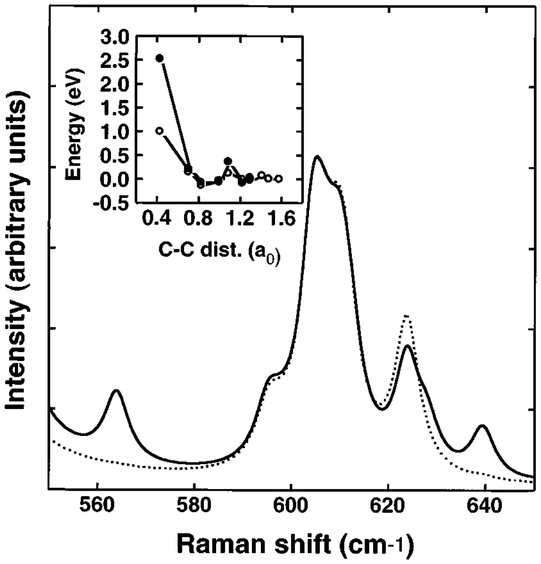

FIG. 2. Theoretical Raman spectra for a $\mathrm{Si}_{0.968}\mathrm{C}_{0.32}$ alloy, obtained as averages of spectra computed for a $\mathrm{Si}_{63}\mathrm{C}_1$ supercell and several possible $\mathrm{Si}_{62}\mathrm{C}_2$ supercells. For the dotted-line spectrum, each configuration was weighted according to its energy, as described in the text. The solid-line spectrum corresponds to a random distribution of carbon atoms. In both cases, the spectra were shifted so that the main peak coincides with the experimental main peak at 605 cm^{-1}. The inset shows the excess energy of two substitutional carbon atoms in a silicon lattice relative to the energy of two infinitely separated substitutional carbon impurities. This excess energy is shown as a function of the C-C separation, expressed in units of the Si lattice constant a_0. Filled black circles correspond to our *ab initio* calculations. The empty circles were computed using the extended Keating model of Rücker *et al.* (Ref. 13).

The SPE regrowth temperatures in implanted samples are higher than typical MBE growth temperatures. Hence we would expect—contrary to experiment—a higher fraction of low-energy carbon configurations in carbon-implanted samples. Figure 1(b) shows the Raman spectrum of the same samples as in Fig. 1(a) after a 4-h annealing at 857 °C under flowing Ar gas. The peak intensity has been reduced by approximately 50% due to SiC precipitation, but we still see no evidence of the high-energy shoulder assigned to 3-nn carbon pairs. These results can only be understood if the kinetic barrier for the formation of low-energy carbon structures is much lower near the growing surface, so that the formation of these structures is enhanced in layer-by-layer growth processes. We thus conclude that surface effects, as predicted by Tersoff,[11] play a key role in the formation of ordered Si-C structures in $\mathrm{Si}_{1-y}\mathrm{C}_y$ alloys.

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[*] On leave from Departamento de Fı́sica, CINVESTAV-IPN, Apdo. Postal 14-740, D.F. 07000, Mexico.

[†] Electronic address: jose.menendez@asu.edu

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