Strain-Stabilized Highly Concentrated Pseudomorphic $\mathrm{Si}_{1-x}\mathrm{C}_x$ Layers in Si

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We present evidence that $\mathrm{Si}_{1-x}\mathrm{C}_x$ layers with $x \approx 0.20$ can be grown pseudomorphically on a Si(001) substrate despite the large difference of the C and Si lattice constants. Calculations based on density-functional theory and a Keating model predict that embedded layers of certain structures with stoichiometry $\mathrm{Si}_{n-1}\mathrm{C}$ where $n = 5, 6, \ldots$ are considerably more stable than isolated C impurities. The common feature of these structures is that the carbon atoms tend to arrange as third-nearest neighbors. Multilayer structures grown by molecular beam epitaxy strongly suggest that defect-free heterostructures with such high C concentrations can be fabricated.

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Carbon impurities prefer the substitutional site in a silicon lattice [1–3] with a solubility limit [4] of only 3.5×10^{17} atoms/cm^3. The most striking feature of the Si-C system is the extreme difference between the native bond lengths of the constituents, which are 2.35 Å for Si, 1.55 Å for diamond, and 1.89 Å for the zinc-blende β-SiC phase. Disordered alloys would exhibit large local strain and according to the Si-C phase diagram, stoichiometric SiC is the only stable compound. The preparation of $\mathrm{Si}_{1-x}\mathrm{C}_x$ layers with $x \neq 0.5$ is only possible by growth at conditions far from thermodynamic equilibrium in a molecular beam epitaxy (MBE) system [5]. It is generally accepted that Si-C alloys cannot be grown pseudomorphically on a Si substrate if the C content exceeds a few percent; for larger C concentrations, as a rule, one encounters defects, nonplanar growth, or the formation of SiC microcrystallites.

Contrary to this, we show here for the first time that layers of a Si-C phase with a considerably higher C content can be embedded pseudomorphically in a Si lattice. Using *ab initio* density-functional calculations [6] and a carefully tuned Keating model [7], total energies were determined for a large variety of ordered $\mathrm{Si}_{1-x}\mathrm{C}_x$ structures constrained to match the Si lattice constant parallel to the (001) plane. We find a number of cases which are stable in comparison to isolated substitutional C impurities by ≈0.4 eV per C atom with a carbon concentration up to 20%. As the common geometric element of these structures, the C atoms are arranged preferably as third-nearest neighbors relative to each other. The various low-energy structures have similar total energies so that growth conditions determine which one will result in practice. Using molecular beam epitaxy (MBE), samples were made whereby the growth of Si on a Si(001) substrate was interrupted several times by the deposition of approximately 1.5 monolayers of carbon. High-resolution transmission electron microscopy (TEM) showed a defect-free lattice containing well-defined narrow layers. These extend over approximately 7–8 layers, indicating a C concentration of ≈ 20% in agreement with the calculations.

Because of the difference in the Si-Si, Si-C, and C-C bond lengths, the microscopic strain plays a dominant role in the energetics of substitutional carbon in Si. The advantage of *ab initio* calculations based on density-functional theory (DFT) is that all relevant effects are included. However, the computational effort is large and an exhaustive *ab initio* investigation of $\mathrm{Si}/\mathrm{Si}_{1-x}\mathrm{C}_x/\mathrm{Si}$ layer structures is impractical. We have therefore fitted a Keating (valence-force-field) model to DFT total energies obtained using the full-potential linear muffin-tin orbital (FP-LMTO) method [8]. The total energies were taken from various geometries for embedded half and full C monolayers and for the structure obtained by distributing one C monolayer over two neighboring planes without creating nearest-neighbor C-C pairs. For the Si-C system, results depend to some extent on the chosen atomic sphere radii. To obtain a close sphere packing, the radii of the Si spheres were set to 2.15 bohrs, the C spheres were maximized, and the size and position of the interstitial spheres were optimized for each geometry. Other details were as in Ref. [8]. Our purpose was to use the Keating model to search for low-energy pseudomorphic $\mathrm{Si}/\mathrm{Si}_{1-x}\mathrm{C}_x/\mathrm{Si}$ structures, for which final *ab inito* calculations are performed. Preliminary investigations showed that all geometries involving carbon nearest-neighbor pairs are unfavorable due to the short C-C bond. Consequently the following discussion does not consider these cases. In the structures of interest, the Si-C bonds are stretched by ≈ 7% relative to β-SiC and the model was adjusted to be accurate in this range. The Keating model [9] reproduces the *ab initio* total energies to which it was fitted to within 0.05 eV.

It has been observed previously [10,11] that semiconductor structures which are not found in the bulk phase diagram can be stabilized by the substrate-imposed strain in pseudomorphic epitaxial growth. The energy of an epitaxially confined structure can be decomposed as $E_{\mathrm{ep}} = E_{\mathrm{equib}} + E_{\mathrm{strain}}$ where E_{equib} is the energy at the unconstrained equilibrium lattice constant and E_{strain} is the work needed to strain the material to match the Si substrate. An epitaxially stabilized structure X oc-

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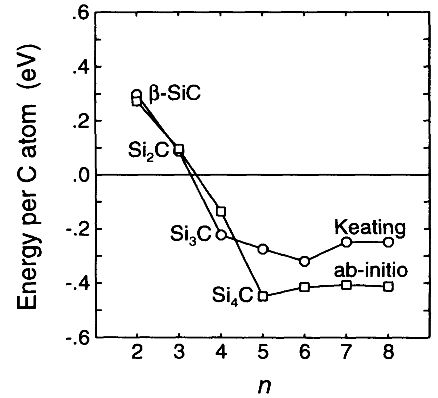

FIG. 1. Energy per carbon atom relative to the isolated substitutional C impurity for optimal $Si_{n-1}C$ structures strained to match the Si substrate. *Ab initio* results are for the relaxed positions obtained from the Keating calculation.

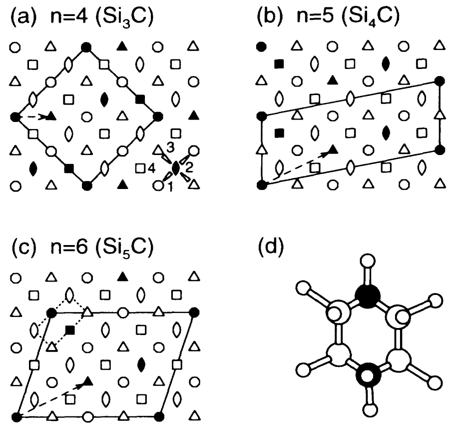

FIG. 2. Optimal epitaxially confined structures with stoichiometries Si_3C, Si_4C, and Si_5C (a)–(c). Four successive layers are indicated by circles, lenses, triangles, and squares. Carbon sites are black. The unit cell is defined by the solid lines in the lowest layer and by the dashed vector into the third layer. The coordination of a typical atom is sketched in (a). The characteristic structural element, a sixfold ring containing two C atoms, is shown in (d) and indicated in (c).

curs when $E_{\rm ep}(X)$ lies below that of the most stable bulk phase [in this case, $E_{\rm ep}(\beta\text{-SiC})$]. Using the Keating model, we have systematically searched the structures with stoichiometry $Si_{n-1}C$ (where n ranges from 2 to 8) for low values of $E_{\rm ep}$. Note that n is the reciprocal carbon concentration; it can be interpreted as the number of (001) planes over which one carbon monolayer is spread. The search included all periodic arrangements in which the unit cell contains one or two $Si_{n-1}C$ formula units without nearest neighbor C-C pairs. The energy was minimized with respect to the atomic positions and the height of the unit cell. Figure 1 displays the lowest obtained energy per C atom, relative to the energy of the isolated C impurity [12] for each n. For $n = 2$ the only possible case is the β-SiC phase. For $n \geq 4$, the energy of the optimized structure lies below the impurity energy, showing that it is favorable for the impurities to condense into a narrow, relatively highly concentrated layer. For $n \geq 5$, the energy gain is almost constant in the final *ab initio* result.

Next, we trace the stability of the optimized structures to a common feature in the arrangement of the C atoms. The almost constant energy $E_{\rm ep}$ for $n \geq 5$ results from the increasing equilibrium energy $E_{\rm equib}$ and the decreasing strain energy $E_{\rm strain}$ with increasing n. These trends are to be expected: as the carbon atoms are progressively diluted, the system moves farther from the strongly bound β-SiC case, while the mismatch to the Si lattice is reduced. But it is only for specific arrangements of the C atoms that the sum of $E_{\rm equib}$ and $E_{\rm strain}$ lies under the impurity energy. These structures, of which our optimized geometries are the most favorable, are characterized by a low value of $E_{\rm equib}$ and are all constructed in a similar way. Figures 2(a)–2(c) show that the C atoms in successive (001) planes are arranged in a third-nearest-neighbor "knight's-move" position relative to each other. The preference for the third-nearest-neighbor arrangement is consistent with the interaction energy between two substitutional C impurities (Fig. 3), which shows a minimum at this distance. This suggests that the carbon impurities gain energy when positioned to maximize the number of third-nearest-neighbor C-C pairs while avoiding first- and second-nearest C-C pairs. A structure of this type has many six-member rings in which two opposite Si atoms are replaced by carbon [Fig. 2(d)]. For an isolated ring of this type, the bond lengths can relax while maintaining the ideal tetrahedral bond angles. Among the optimized structures, Si_4C has the highest C concentration possible without making first- or second-

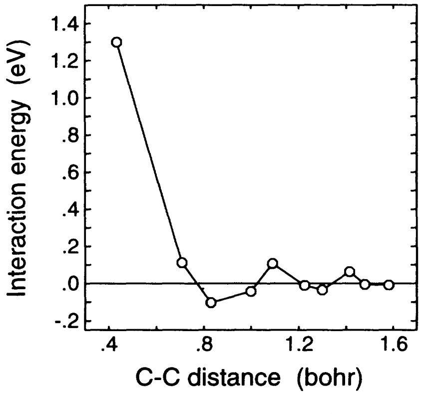

FIG. 3. Interaction energy for two substitutional carbon impurities as obtained from the Keating model applied to a unit cell of 2000 atoms. The first-nearest-neighbor interaction was taken from Ref. [3] since the Keating model was not tuned to describe the C-C bond. The interaction is strongly repulsive for first- and second-nearest neighbors but shows an energy gain at the third-nearest-neighbor distance.

nearest neighbor C-C pairs [13].

The main conclusions from the calculations are as follows: (1) the energy of C impurities in Si is lowered substantially when these concentrate in a pseudomorphic layer in a certain type of structure; (2) the low-energy structures are characterized by the abundance of third-nearest-neighbor C-C pairs; (3) the upper limit for the carbon concentration in the plausible structures is 20%. However, the energy gain is almost equal for $n = 5, 6, \ldots$ and therefore the specific structure which would result in practice depends on the growth process.

The crucial question is now whether such highly concentrated embedded $\mathrm{Si}_{1-x}\mathrm{C}_x$ layers can be fabricated. The major uncertainty is whether growth is possible without the formation of SiC microcrystallites; even in the optimized structures, the separation into the pure Si and SiC phases would still gain ≈1.5 eV per carbon atom. Also, a pseudomorphic structure such as $\mathrm{Si}_4\mathrm{C}$ is stretched by 8% in the x, y plane. For thicker layers, strain relief by defects or nonplanar growth must eventually occur. Layer growth using the deposition of both constituents simultaneously (coevaporation) does not seem promising. Instead the deposition of carbon atoms followed by Si under high supersaturation at moderate temperatures might be more successful. To test this approach, samples were prepared using MBE and inspected with TEM as described below. At this stage, we seek trustworthy evidence for the feasibility of pseudomorphic $\mathrm{Si}/\mathrm{Si}_{1-x}\mathrm{C}_x/\mathrm{Si}$ structures with $x \approx 0.2$ whereby the C atoms occupy substitutional sites, as suggested by the theory. Should this be the case, a number of questions arise which are beyond the scope of this investigation but are relevant for possible applications. Such questions are (a) the exact microscopic structure in the $\mathrm{Si}_{1-x}\mathrm{C}_x$ layer (this could be complicated because theory predicts several low-energy structures); (b) the growth process by which the structure is formed; (c) the density of carbon-related defects in the crystal which could significantly affect optical and electrical properties.

The layers were grown in a three-chamber MBE system with a base pressure below 10^{-10} mbar. Silicon was evaporated from an *e*-beam evaporator and a pyrolitic graphite-filament sublimation source was used as a solid carbon source. The typical silicon growth rate was 0.05 nm/s. *p*-type Si(001) substrates were prepared by an appropriate *ex situ* and an *in situ* cleaning procedure [14], resulting in an atomically clean and (2×1) reconstructed silicon surface. First a 60 nm thick Si buffer layer was deposited at a growth temperature of 600 °C (kept constant throughout the whole deposition process). Next, 1.0–1.5 monolayers of carbon were deposited followed by the next silicon deposition. The growth interruption between individual materials was 30 s. The carbon deposition step was repeated several times, alternating with deposition of pure Si spacers with thickness ranging from 20 to 5 nm.

For our purpose, it is important to obtain a reasonably accurate estimate of the amount of deposited carbon. The total carbon source flux density was calibrated earlier using secondary ion mass spectroscopy (SIMS) on amorphous Si-C mixtures to be 6.8×10^{12} atoms/cm^2 s. Alternatively, the amount of C in substitutional lattice positions was estimated from homogeneous Si-C and Si-Ge-C samples grown with the same apparatus under the assumption of Vegard's law, giving a flux about 30% smaller. The reason for the discrepancy is not clear at present but does not affect our overall conclusions. By opening the carbon source shutter for 150 s we thus deposited 1.0 ± 0.2 carbon monolayers (or 1.5 ± 0.3 according to the SIMS calibration) in each carbon deposition step. Additional SIMS measurements on the grown samples confirm the value of 1.5 monolayers.

Observing the deposition process with reflection high-energy electron diffraction (RHEED) using an incidence angle of 0.5° gives some intriguing but presently incomplete information about the growth process. A (2×1) reconstruction is clearly visible after the carbon deposition. The streak distance [(01) to $(0\bar{1})$] equals that of the reconstructed Si surface. No evidence of islanding is observed. Possibly the C atoms terminate the Si dangling bonds and form the usual dimerized reconstruction, as is known for other monolayers (e.g., Sb) deposited on Si(001) [15]. Alternatively, the C atoms could quickly move to subsurface sites, initiating the generation of the low-energy ordered structures. In any case, we do not suggest that diamond can be grown epitaxially on Si to any relevant thickness. Immediately after opening the silicon source shutter following the carbon deposition, the streaky (2×1) RHEED pattern disappears and another complicated pattern occurs, possibly due to discontinuities in the growth-direction lattice periodicity as the structure is optimized. The RHEED pattern then quickly recovers to the perfect (2×1) pattern with the same streak distance as before.

TEM investigations were done on cross-sectional samples. Seven-beam lattice imaging in the $\langle 110\rangle$ direction indicates the existence of well-defined epitaxial layers. The inset of Fig. 4 shows the four carbon-containing layers separated by 20, 10, and 5 nm of silicon. A high-resolution micrograph of a typical part of a single layer takes up the main part of the figure. From this and similar images we estimate the carbon-rich layer to be about 7 to 8 monolayers thick. In contrast to the often observed [14] formation of crystallographic defects originating from silicon carbide contaminations on an imperfectly cleaned Si surface, no defects were seen in all the TEM images studied. The results contrast with previous experiments [16] in which $\mathrm{Si}_{1-x}\mathrm{C}_x$ alloys were grown on a Si(001) substrate. In these, the carbon concentration could not be raised above a few percent before SiC crystallites occurred. We believe the most important feature of the present procedure is that carbon is deposited without simultaneous Si deposition. This avoids having

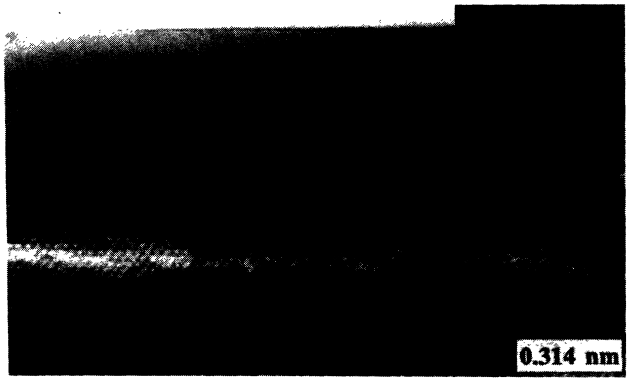

FIG. 4. Cross-sectional transmission electron micrograph of a MBE-grown Si(001) sample with three carbon-containing layers separated by 5, 10, and 20 nm of Si (inset) and a high-resolution close-up of one layer (main picture). Each carbon-rich layer extends over no more than 7–8 planes and contains 1.0–1.5 monolayers of C, indicating a carbon concentration of (15–20)%.

highly mobile Si and C atoms available at the same time, thereby trapping the system in a thermodynamically forbidden state.

In conclusion, total-energy calculations predict that the energy of carbon impurities in Si is lowered when these concentrate in a narrow epitaxial layer with a carbon concentration of up to 20%. The characteristic feature of the stable structures is that the carbon atoms are arranged as third-nearest neighbors, thereby accommodating the short Si-C bond with minimal strain. $Si/Si_{1-x}C_x/Si$ layer structures were grown by MBE using a procedure in which carbon was deposited on a Si(001) surface without simultaneous coevaporation of silicon. Inspection of the samples by TEM strongly suggests perfect pseudomorphy and the predicted carbon concentration of about 20% within the embedded layer.

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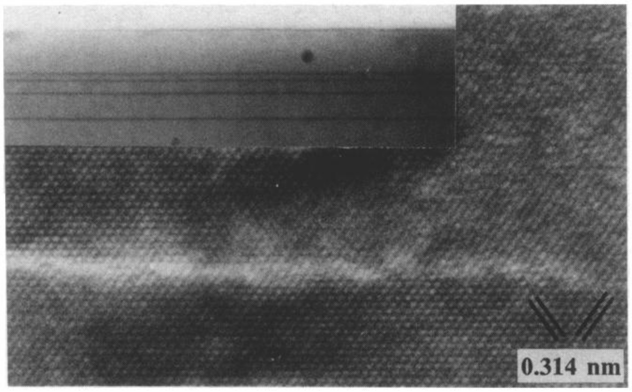

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