Ordered Structures in Unstrained, Epitaxial Ge−Si−C Films

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An ordered $GeSi_2$ structure has been observed in layers of approximate composition $GeSi_2C_x$ grown epitaxially on Si. Except for regions very close to the interface, the ordered phase forms throughout the layer and is readily identified by high-resolution electron microscopy and electron diffraction. The structure is formed by Ge−Si−Si ordering along the diamond [111] direction to yield a new structure with $P\bar{3}m1$ symmetry. Analogous (but not as extensive) ordering in the Ge_2SiC_x ($x = 6\%$) system is also observed. The role of carbon, which is incorporated into the material as Si_4C tetrahedra, is used to explain the formation of these novel structures.

Introduction

Alloys of $Si_{1-x}Ge_x$ have a continuously variable lattice parameter and band gap[1] and have attracted much recent attention because they offer the potential for numerous practical applications.[2] For example, they have been successfully used to create heterojunction bipolar transistors with cutoff frequencies in excess of 100 GHz, which are substantially higher than those of the traditional Si counterparts.[3] For this reason, the Si−Ge system has been considered as the natural complement to silicon in high-frequency applications.

Bulk Si and Ge form a continuous solid solution with diamond cubic type structure which has generally been accepted as an almost ideal solution. A recent extended X-ray absorption fine structure (EXAFS) study of polycrystalline Si−Ge films annealed at 700 °C provided strong evidence for an essentially random alloy at all compositions,[4] but ordered phases in bulk Si−Ge have not yet been reported.[5,6] Short- and long-range order, believed to be induced by strain, have been observed or suggested in thin Ge−Si strained-layer superlattices grown under metastable conditions on Si substrates. Early reports indicate that annealing of strained layers grown on (100) Si by molecular beam epitaxy yields an order−disorder transition in the SiGe sublayer.[7,8] The proposed model is based on a GeGeSiSi... sequence of atomic layers along the (111) direction. Further investigations by Raman spectroscopy and electron diffraction of the same $Si_{0.5}Ge_{0.5}$ composition revealed a short-period ordering in unstrained layers.[9,10] More recently, another two coexisting ordered models have been suggested in a strained $Si_{0.6}Ge_{0.4}$ layer.[11] On the basis of extremely weak superlattice reflections in the X-ray diffraction pattern, the atoms in the structure are purported to align in the sequences Ge−Si−Ge−Si and Ge−Si−Si−Si along the (111) axis. However, no microstructural data was provided to support the claim. A similar Ge−Si−Si−Si ordering is proposed for isolated grains in a material with bulk composition $Si_{0.70}Ge_{0.30}$.[12] In nearly all of these cases, the ordered phase is a minority component of the bulk material.

A problem facing Si−Ge technology is the inherent 4% lattice mismatch between Si and Ge which causes compressive strain in $Si_{1-x}Ge_x$ grown heteroepitaxially on Si. A possible solution is the incorporation of C which, in the diamond form, has a lattice constant of 3.57 Å and is significantly smaller than those of Si (5.43 Å) and Ge (5.65 Å). A Ge to C ratio of about 9:1 would provide an alloy that is lattice-matched with Si. The incorporation of a third component also adds additional flexibility in band gap engineering. Indeed, it has been suggested that the advent of a high-quality $Si_{1-x-y}Ge_xC_y$

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material could push the performance into even higher frequency ranges, posing a new threat to GaAs technologies that have dominated the high-frequency market.[13]

Work on the incorporation of C into SiGe has been ongoing since the early 1990s using techniques such as molecular beam epitaxy and solid phase epitaxy, as well as conventional chemical vapor deposition (CVD). These attempts have typically resulted in maximum carbon incorporation levels of about 1−2 at. % which allow a limited range of Si−Ge compositions under lattice-matched conditions. However, we have recently used the precursors $C(SiH_3)_4$ and $C(GeH_3)_4$ with mixtures of SiH_4 and GeH_4 in an ultrahigh vacuum (UHV) CVD system to grow Si−Ge−C films with C content substantially higher than that obtained previously.[14] The absence of strong C−H bonds in the precursors allows relatively low deposition temperatures and thus promotes substitution of higher carbon concentrations in the material. In particular, we discovered that $C(SiH_3)_4$ decomposes at 650 °C with loss of H_2 to yield homogeneous Si−C films with composition $Si_{80}C_{20}$ (i.e. Si_4C).[15] At 450 °C, the precursor reacts readily with GeH_4 to yield monocrystalline materials that have Si to C compositions in the same ratio (4:1) as the precursor. By growing the material at 470 °C, we were able to produce Si−Ge−C films with carbon contents as high as 4−6 at. % as determined by Rutherford backscattering. With a growth rate of 0.6 nm/min, $Si_{1-x-y}Ge_xC_y$ films, where $x = 0.31−0.34$ and $y = 0.06−0.04$, produced layers that were nominally lattice-matched with the substrate. In the work to be described here, the films had a composition close to $(GeSi_2)C_x$ where $x \sim 6$ at. %.

Results and Discussion

The depositions were carried out in a custom built UHV CVD load-locked system that has been described elsewhere.[16] The single-crystal (100) Si substrates were first RCA-prepared in a clean room and then treated with 10% HF to passivate their surface. The passivating layer was removed at 450 °C in the reactor, and shortly thereafter the reactants were introduced into the reactor intermixed with a large excess of ultrahigh purity H_2. The interaction of SiH_4, GeH_4, and $C(SiH_3)_4$ at 450−475 °C on the Si surface resulted in the formation of films that were indistinguishable from the underlying substrate.

The Si−Ge elemental concentrations were obtained by Rutherford backscattering (RBS) utilizing 2 MeV He^{2+} ions, and the C content was measured with a carbon resonance $^{12}C(\alpha,\alpha)^{12}C$ reaction at 4.265 MeV. Figure 1 shows a 2 MeV spectrum and a 4.265 MeV carbon resonance RBS spectrum for the $(GeSi_2)C_x$ ($x = $ 6 at. %) sample. Cross-sectional transmission electron microscopy (TEM) of the as-deposited samples showed that the material had the diamond cubic structure and was essentially heteroepitaxial and single crystalline.
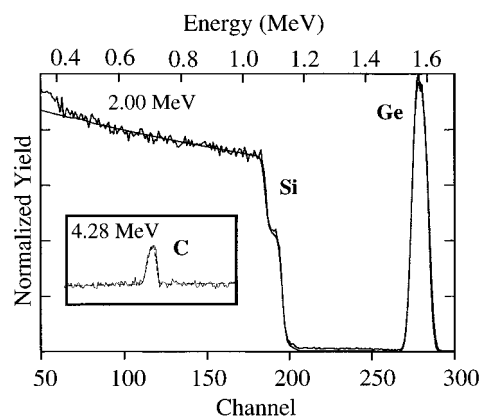
Figure 1. Rutherford backscattering spectrum of $(Si_2Ge)C_x$ on Si with composition $Si_{63}Ge_{31}C_6$ and film thickness of 110 nm, with corresponding carbon resonance spectrum inset.

However, some polycrystalline domains as well as large concentrations of defects such as twins and stacking faults were also observed.

The crystallinity of the material was improved by annealing. The samples were heated in situ at 700 °C for several hours followed by slow cooling in a flow of H_2 at 10^{-4} Torr of pressure. Cross-sectional TEM revealed a dramatic change in the microstructure. The layer near the interface was heteroepitaxial, and the lattice planes of the material were completely commensurate with the corresponding Si (111) planes, as expected for disordered, nearly lattice-matched $Si_{1-x-y}Ge_xC_y$. The region of the layer above the interface was dominated by a periodic superlattice pattern that had a periodicity along the (111) direction that was three times larger than that of the underlying Si lattice. Typical regions are shown in Figures 2 and 3. The selected area electron diffraction pattern (inset) consists of the primary diamond cubic spots as well as two additional weak spots between each primary spot that corresponded to the tripling of the (111) periodicity. These electron microscopy observations are consistent with the formation of an ordered superstructure.

To show that the carbon is completely substitutional and has four silicons as nearest neighbors, transmission Fourier transform infrared analysis (FTIR) was routinely performed after each deposition. The FTIR spectra revealed a weak absorption centered at 615 cm^{-1}. The typical absorption of the localized mode for substitutional C in Si is at 615 cm^{-1} and for substitutional C in Ge is at 515 cm^{-1}, whereas the strong phonon mode for the stoichiometric SiC is at 800 cm^{-1} (stoichiometric GeC is an unknown phase).[17] No absorptions were observed that would correspond to SiC phonons or to Ge−C local vibrational modes in either the as-deposited or annealed samples. We therefore conclude that C primarily occupies substitutional tetrahedral Si sites consistent with the incorporation of the entire Si_4C tetrahedron into the Si−Ge−C lattice. Using diffractogram analysis of the high-resolution electron micrographs, the average lattice parameter of the diamond cubic cell was determined to be 5.47 Å, very close to the lattice parameter of Si ($a_{Si} = 5.43$ Å). The close matching of the lattice constants provides further
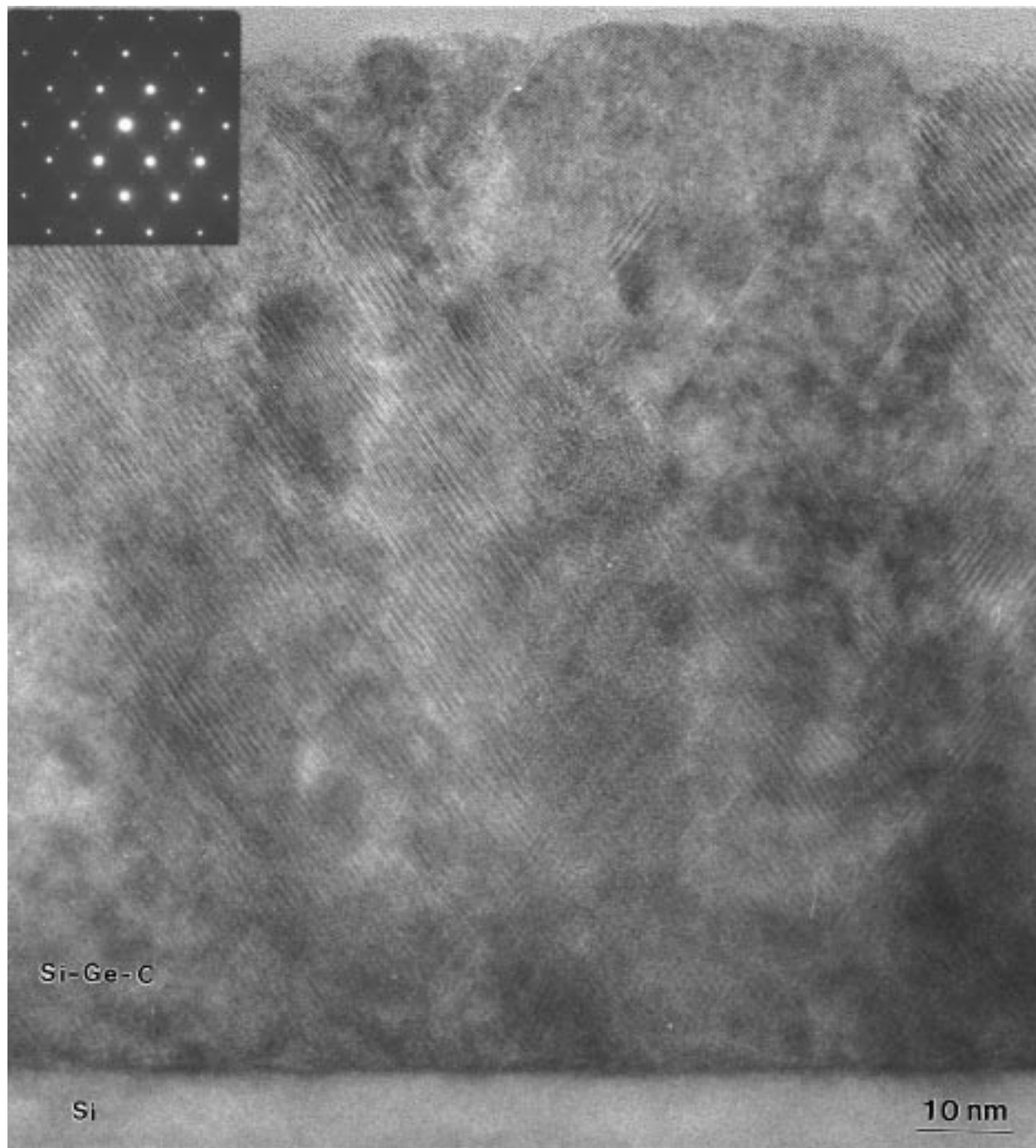
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Figure 2. Cross-sectional transmission electron micrograph of a $(Si_2Ge)C_x$ sample demonstrating that the ordered phase forms throughout the layer. Diffraction pattern (inset) of the entire layer and part of the Si substrate shows extra superlattice spots corresponding to the ordering along the (111) direction. No splitting of high-order spots was observed, indicating a good match between substrate and layer.

evidence for substantial incorporation of substitutional carbon in the Si–Ge lattice. Secondary ion mass spectrometry (SIMS) verified that the elemental content was constant throughout the sample before and after annealing, indicating that the Si_4C building block was randomly distributed in the material.

On the basis of the observations of a superlattice structure, we carried out ab initio quantum mechanical modeling that led to a proposed Si_2Ge structure with symmetry *Pm*1 as shown in Figure 4. In this structure, a plane of atoms presumably dominated by Ge is followed by two planes of Si atoms doped with carbon (although some Ge incorporation in these two planes

and some Si incorporation in the Ge plane cannot be ruled out). Another way to describe the structure is that a plane of Ge atoms is followed by two planes that consist of randomly distributed Si_4C tetrahedra linked together by Si atoms. We use coordinates determined with the empirical many-body potential of Tersoff[18] which accurately reproduces the structure of pure Si and Ge and, in this case, gives a hexagonal unit cell with parameters $a = 3.891$ Å and $c = 9.530$ Å. There are two kinds of Si atoms: Si(1) atoms are located at $\pm(0, 0, 0.1237)$ and bonded to four Si atoms (some of these

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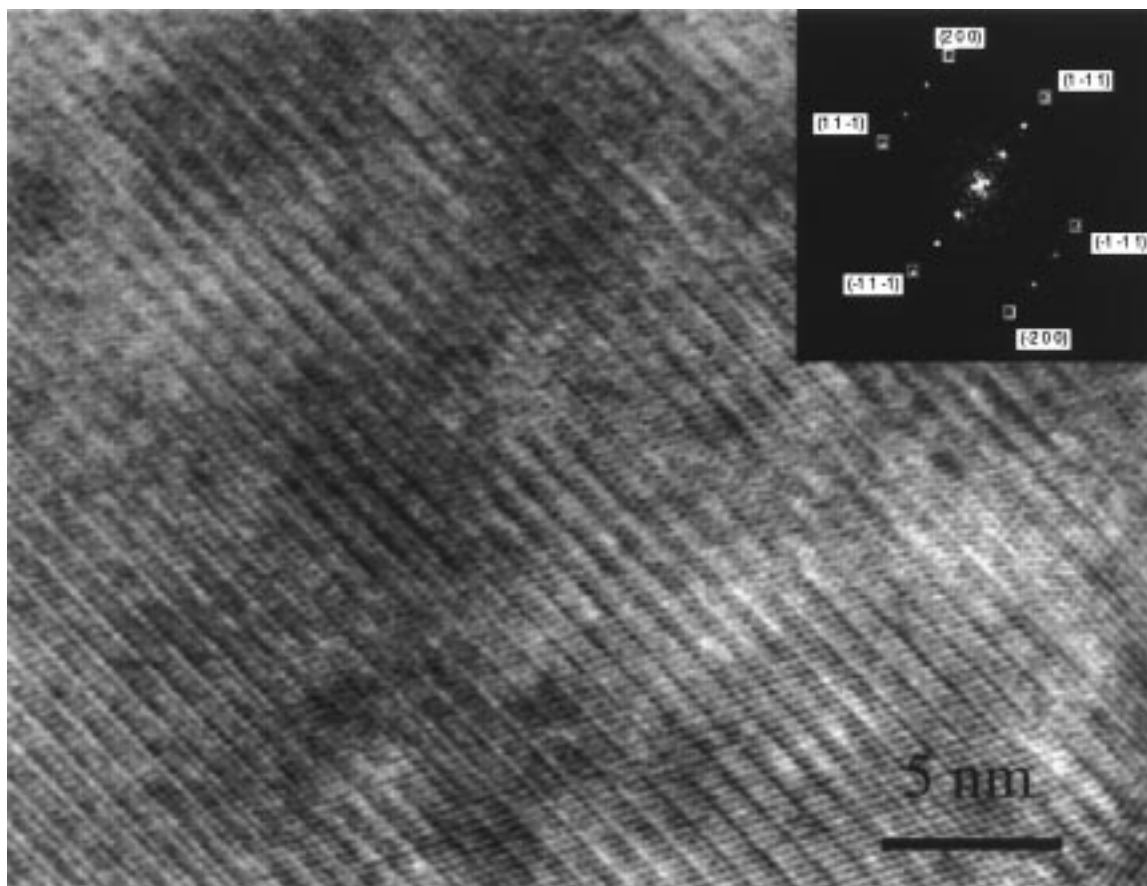
Figure 3. High-resolution electron micrograph of the $(Si_2Ge)C_x$ ordered structure on (100) Si. Digital diffraction pattern (inset) corresponds to the entire layer. Note diamond cubic host reflections marked by frames and labeled with Miller indices. Superlattice spots indicating tripling along (111) are located between spots marked.

Si atoms are replaced by C to give the true $(Si_{2-x}Ge)C_x$ material); and Si(2) atoms at $\pm(^1/_3, \, ^2/_3, \, 0.7972)$ are bonded to three Si and one Ge. Finally, Ge atoms at $\pm(^1/_3, \, ^2/_3, \, 0.5454)$ are bonded to one Si and three Ge. Of interest is the fact that the rhombohedral subcell of Si_2-Ge, corresponding to the cubic cell in the disordered phase, has $a = 5.503$ Å and $\alpha = 90.01°$. Incorporation of C will reduce the lattice parameter in accord with the lattice spacing of 5.47 Å. Essentially, the same structure is found from an ab initio quantum mechanical calculation.[19]

In contrast to our observation of extensive ordering, the absence of this ordering in earlier reports immediately suggests C must play a role in this ordering. There is strong evidence[17] that use of the $C(SiH_3)_4$ precursor results in C being incorporated into the structure as Si_4C units, immediately imposing substantial short-range order on the structure. Notice that in the proposed ordered structure, Si(1) atoms are surrounded by four Si atoms, so it is natural to assume that this is the preferred site for incorporation of C. The incorporation of Si_4C tetrahedra clearly requires formation of at least two adjacent lattice planes that consist of Si atoms connecting the randomly distributed Si_4C units.

The proposed structure of Si_2Ge was also examined by comparing computer-simulated images with the experimental micrographs. The structure parameters

(lattice constants, space group, atomic coordinates) and the microscope parameters were used as input to obtain theoretical images utilizing the molecular simulation package CERIUS. Calculations were made for a wide range of crystal thickness (10–30 unit cells) and microscope defocus values (200–600 Å underfocus): matching between calculated and experimental images is shown in Figure 5. Digital diffractograms of the experimental images (i.e. based on the Fourier transform of the experimental images) clearly confirmed the expected superstructure. A typical diffractogram is shown as an inset in Figure 3. Note the primary diffraction spots (labeled) of the cubic host lattice and the weak spots of the proposed GeSiSi superlattice which are located in between. The experimental diffraction pattern of the entire layer and substrate (Figure 2) reveals the diamond cubic nature of the lattice and also shows the superlattice reflections for Si_2Ge. We conclude that the calculated diffraction data for the Si_2-Ge structure shown in Figures 3 and 5 are in excellent agreement with the experiment and support the proposed ordered layering in this composition.

An investigation was made into the possibility of similar ordering in the corresponding $(Ge_2Si)C_x$ system. The desired composition was readily obtained from the reaction of $C(SiH_3)_4$ with GeH_4 at 500 °C in our UHV CVD system. Materials with the general formula $(Si_4C)_xGe_y$ had Si and C concentrations in the same 4:1 ratio as in the precursor. A range of $(Si_4C)_xGe_y$ samples containing 3–7 at. % C were prepared using conditions

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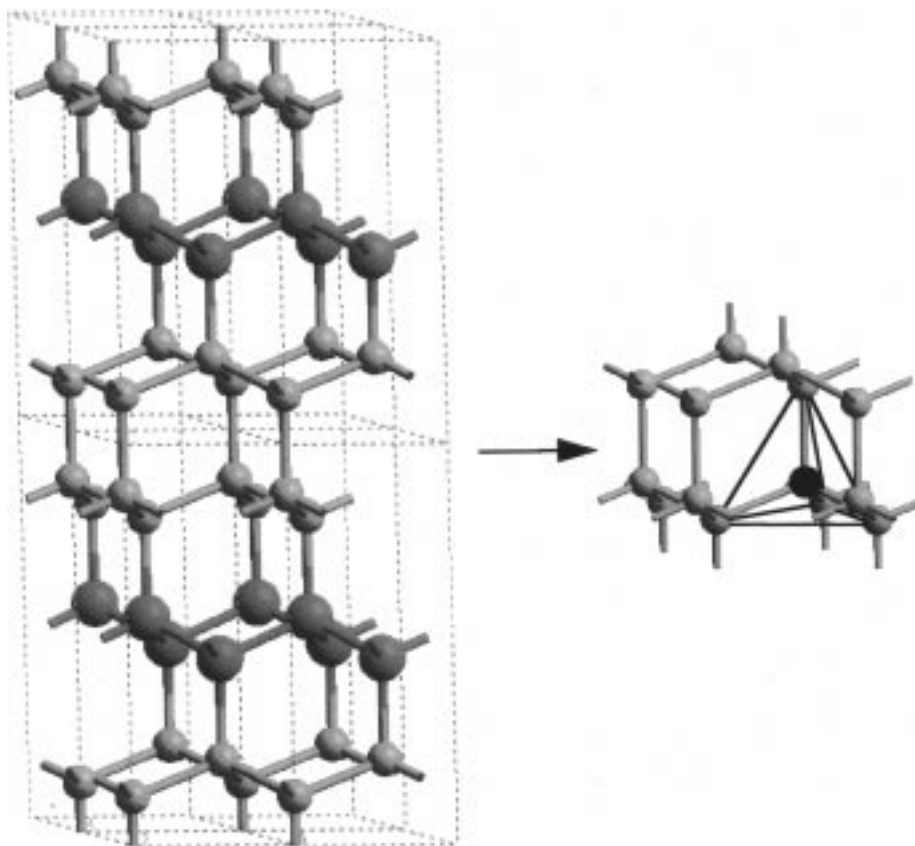
Figure 4. Illustration of proposed ordered diamond structure. Only Ge and Si atomic planes are shown. These are depicted by one layer of large blue spheres and two layers of small orange spheres, respectively, stacked along the vertical direction. A possible carbon site (small dark sphere) and corresponding Si_4C tetrahedron (marked) are also shown inset in the Si bilayer.

and deposition procedures similar to those described above. High-resolution electron microscopy revealed that a typical sample having 3% C, 12% Si, and 85% Ge was monocrystalline and epitaxial whereas the crystallinity of a sample having higher C content (5% C, 20% Si, and Ge 75%) was much inferior and indicative of a disordered $Si_{1-x-y}Ge_xC_y$ alloy. Surprisingly, the crystallinity of a sample with approximate composition 7% C, 30% Si, and 62% Ge, corresponding to the desired $(Ge_2Si)C_x$, was nearly monocrystalline and epitaxial. The microstructure observed in cross section was dominated by [111] lattice fringes of the disordered phase. However, regions were observed that displayed a 3-fold periodicity along the (111) direction similar to that observed in $(Si_2Ge)C_x$. Since the compositional and IR data indicate that C is incorporated as Si_4C units, we infer that the tripling of the lattice is again due to a Ge atomic layer followed by two layers consisting of Si_4C tetrahedra linked by Ge atoms rather than Si atoms as proposed for the $(Si_2Ge)C_x$ system. Computer-simulated images of a model based on a $Ge-(Si_{0.5}Ge_{0.5})-(Si_{0.5}Ge_{0.5})$ sequence appear consistent with the experimental images for $(Ge_2Si)C_x$. Furthermore, the lattice constant of the "ordered" areas is slightly smaller than that of the disordered regions, implying that a larger concentration of Si_4C building blocks is incorporated into the ordered areas, thereby imposing short-range order. To further characterize ordering in the $(Ge_2Si)C_x$ system, we are currently directing our efforts to obtain material in which the ordered structure is the dominant phase.

Summary

In summary, we have observed long-range ordering in thick unstrained Si−Ge−C layers with composition $(Si_2Ge)C_x$. The ordering occurs along the (111) direction and corresponds to an alternating double layer of Si−Si(doped with C) and a single layer of Ge. The carbon incorporation is clearly an important factor in the formation of this new phase since similar ordering has not been reported in pure Si−Ge alloys. It is known from previous studies that the Si_4C composition and the structure of the precursor are maintained in the solid state, and it is likely that it facilitates the nucleation of the ordered structure in the present study. The annealing temperature may also play a considerable role in this ordering. Indeed, no ordering (or very little) was observed in $(Si_2Ge)C_x$ samples grown at 450 °C, and the ordering that occurred in as-deposited $(SiGe_2)C_x$ samples at 450 °C was very limited. The systematic effect of temperature is now under investigation in both systems.

Experimental Section

The precursor $C(SiH_3)_4$ was prepared using a procedure described by Schmidbaur,[20,21] and it was purified by a series of distillations to separate the byproducts and the reaction medium. Its purity was checked by nuclear magnetic resonance (NMR) and IR spectroscopy. $C(SiH_3)_4$ was diluted with

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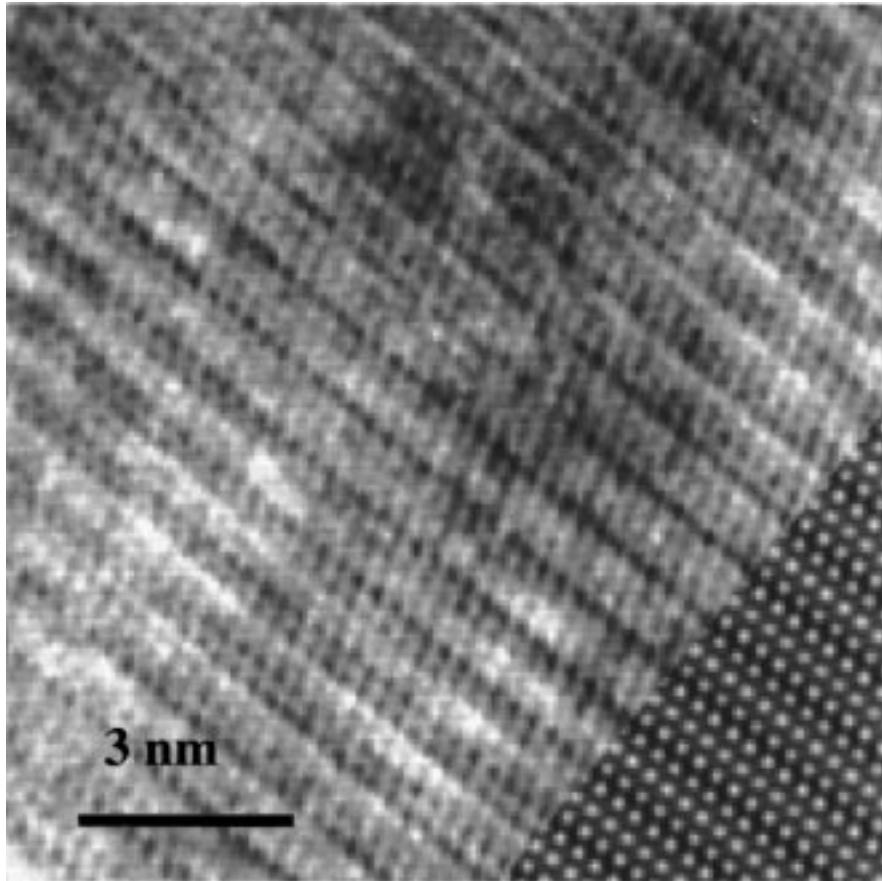
Figure 5. Image simulation of ordered structure shown in inset (right corner) is compared with a magnified section of the experimental electron micrograph.

a large excess of ultrahigh purity H_2, and it was introduced into the reactor through calibrated mass-flow controllers. Semiconductor grade SiH_4 (Matheson) and GeH_4 (Voltaix) were used neat. Films were deposited using an ultrahigh vacuum chemical vapor deposition with typical base and deposition pressures $(8-9) \times 10^{-9}$ and 2×10^{-4} Torr, respectively. RBS spectra were collected on a General Ionics Model 4117 instrument using 2 and 4.28 MeV ions. The SIMS experiments were performed using a CAMECA IMS 3F spectrometer, and the FTIR spectra were recorded on a Nicolet Magna 550 spectrometer. Cross-sectional samples for the microscopy studies were prepared using standard methods, and the observations were performed in a JEOL 4000 EX high-resolution transmission electron microscope.

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