

Full-length paper

Matrix-dependent structure of GeSi nanocrystals in SiC

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Abstract It is shown experimentally that GeSi nanocrystals in SiC created after high-dose Ge ion implantation and high-temperature annealing are hexagonal in a hexagonal 4H-SiC matrix and are of cubic structure in a cubic 3C-SiC matrix. This interesting fact could be explained by molecular dynamics as the force of the system nanocrystal-matrix to minimize its interface energy.

Keywords HRTEM, Molecular Dynamics, Nanocrystals, Silicon Carbide

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Introduction

Ge and Si nanocrystals embedded in SiC are of interest for applications in micro-optoelectronics because quantum confinement [1] and direct optical transitions [2] are expected. They can be formed by high-temperature implantation of Ge or Si, respectively, into SiC and subsequent annealing. However, in the case of Ge implantation, GeSi nanocrystals are formed containing ~20% Si instead of pure Ge nanocrystals [3]. Bulk Ge and Si crystallize in the diamond-like structure but small free-standing Ge and Si nanocrystals can also be multi-twinned [4,5]. As has been shown, the properties and especially the structure of the nanocrystals embedded in SiC depend on the structure of the SiC and on the implantation parameters [6]. The Molecular Dynamics (MD) computer calculations have been proved to be a useful tool to investigate and to understand the properties of the GeSi and Si nanocrystals. Previous investigations using MD calculations concentrated on the shape and orientation of GeSi nanocrystals in 4H-SiC [7] and on the size of Ge, GeSi and Si nanocrystals in 4H-SiC [3,6].

In this paper the structure of the GeSi nanocrystals embedded in 3C-SiC is investigated for the first time and compared with the structure in 4H-SiC. Using the relaxed structures obtained by the MD calculation, the high-resolution (HR)-TEM images and diffractograms are simulated and compared with the measured ones.

Methods

Experimental setup

The nanocrystals were formed by high-temperature (700°C) ion implantation of Ge (10^{20} cm^{-3} , 250 keV ion energy) into

SiC (4H-SiC and 3C-SiC epilayer samples) and subsequent annealing at 1600°C for 120 s (for more details see Schubert *et al.* [8]).

Cross-sectional TEM sample has been prepared using standard sample preparation techniques, including mechanical polishing, dimpling and low-angle Ar-ion milling. HRTEM and high-angle centred dark-field (HACDF)-TEM [9] observations were carried out using a JEM 3010 equipped with a LaB₆ cathode operating at 300 kV.

Molecular dynamics calculation

MD calculations have been performed with a standard MD code [10] using the Tersoff potential [11].

Nanocrystal (NC) models with stacking along the *c*-axis of 2H, 4H, 3C and irregular stacking sequences of 'abcabababaca' (called irreg1-NC in the following) and 'abcbabcabcb' (called irreg2-NC in the following) according to the Ramsdell notation [12] were prepared. The different stacking sequences are graphically shown in Fig. 1.

All models contain an approximately equal number of atoms between 2892 and 2896 (about $4 \times 4 \times 4 \text{ nm}^3$ in size). The facets of the nanocrystals are chosen to be {111}, {110} and {112} planes, respectively, in hexagonal Miller-Bravais notation {0001}, {1 $\bar{1}$ 00} and {11 $\bar{2}$ 0} planes according to the HRTEM experiments (see Kaiser *et al.* [7]). Because the experimental investigations showed that the nanocrystals created after Ge ion implantations into 4H-SiC do not only consist of Ge but GeSi (EDX-measurements showed a Si content of ~20% [3]), the constructed nanocrystal models were built of mixed composition. This was taken into account by replacing randomly chosen Ge atoms by Si atoms and changing the lattice parameter according to the

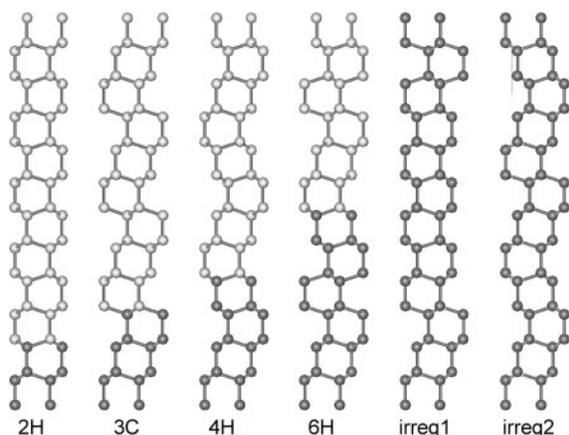


Fig. 1 Stacking sequences of the nanocrystal models used for MD calculations. Regular 2H, 3C, 4H, 6H, and the irregular stacking irreg1 and irreg2. The repeated unit is drawn in bold.

Vegard's law. For all calculations the ratio between Ge and Si was set to be 80:20 according to the experimental results [3].

As the next step, the nanocrystal model was embedded into a cube of 4H-SiC, respectively, 3C-SiC. The systems have sizes of up to $9 \times 9 \times 9 \text{ nm}^3$ ($\sim 70\,000$ atoms) and zero temperature. The embedding of the GeSi nanocrystals was performed by removing Si and C atoms of the SiC matrix with a distance to any of the nanocrystal atoms smaller than a critical one. These critical distances were chosen according to the bond lengths given by the Tersoff potential: GeSi 2.4 Å, GeC 2.0 Å and SiC 1.9 Å [11]. The nanocrystal models were embedded with the following orientation relationships to the matrix taken from the experimental data: $(0001)_{\text{hexNC}} // (0001)_{\text{hexSiC}}$ and $(1\bar{1}00)_{\text{hexNC}} // (1\bar{1}00)_{\text{hexSiC}}$ for the hexagonal nanocrystal within hexagonal SiC, $(11\bar{2})_{\text{cubNC}} // (11\bar{2})_{\text{cubSiC}}$ and $(111)_{\text{cubNC}} // (111)_{\text{cubSiC}}$ for the cubic nanocrystal within cubic SiC, $(0001)_{\text{hexNC}} // (111)_{\text{cubSiC}}$ and $(1\bar{1}00)_{\text{NC}} // (11\bar{2})_{\text{cubSiC}}$ for the hexagonal nanocrystals within cubic SiC and $(111)_{\text{cubNC}} // (0001)_{\text{hexSiC}}$ and $(11\bar{2})_{\text{cubNC}} // (1\bar{1}00)_{\text{hexSiC}}$ for the cubic nanocrystal within hexagonal SiC. The position of the nanocrystal with respect to the centre of the matrix has been chosen to be flexible in all three directions and was varied in steps of 0.1 Å in a range of -1 to 1 Å. For each position of the nanocrystal ($\sim 20\,000$ different positions) the potential energy of the whole system was calculated using periodic boundary conditions. The position with the lowest potential energy was determined and then for this configuration a fast static zero temperature relaxation was performed until the minimum of the total potential energy $E_{\text{pot, total}}$ was reached with an accuracy of 0.1 eV. The interface energy E_{int} between nanocrystals and matrix can be determined as follows:

$$E_{\text{int}} = E_{\text{pot, total}} - E_{\text{void}} - E_{\text{NC}}, \quad (1)$$

where $E_{\text{pot, total}}$ is the total potential energy of the matrix-nanocrystal-system after the relaxation mentioned above. E_{void} is the potential energy of the SiC without the nanocrystal (the atoms of the nanocrystals have been

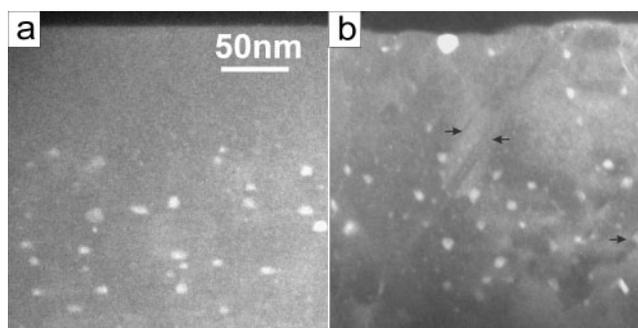


Fig. 2 HACDF images [9] showing GeSi nanocrystals inside 4H-SiC (a) and inside cubic SiC (b), revealed by Z-contrast. The black arrows in (b) are pointing to the stacking faults in inclined $\{111\}$ planes.

removed) calculated with periodic boundary conditions and E_{NC} is the potential of the free nanocrystal in vacuum, calculated with non-periodic boundary conditions (to include the effect of free bonds at the nanocrystal surface). E_{int} can be understood as the part of the total potential energy that is used to bond the nanocrystal with the matrix.

For example, a few full dynamic relaxations at an annealing temperature of 1400 K have been performed. The main result is that the absolute values of the interface energies for the different matrix-nanocrystal-systems are systematically lower than that obtained by the static zero temperature relaxation, however, the relations between the different matrix-nanocrystal-systems are not changed. This means that the stable structures obtained with the static zero temperature relaxation and that obtained with the full dynamic relaxation are the same. This justifies the application of the much faster static zero temperature relaxation for the investigation of the structures considered here.

Results and discussion

Figure 2 shows HACDF images of GeSi nanocrystals in 3C-SiC (a), and in 4H-SiC (b) revealed by their Z-contrast. Independent of the SiC matrix structure, the main part of the nanocrystals is located $\sim 150 \text{ nm}$ away from the surface. However, in the cubic matrix case, nanocrystals are found near the surface as well. This can be explained in the following way by the fact that the Ge atoms are able to glide along the SiC stacking faults [6]. In the hexagonal SiC matrix, stacking faults are in principal present in surface-parallel planes ($\{0001\}_{\text{SiC}}$) only which gives the Ge atoms no chance to diffuse towards the surface. However, in the cubic SiC matrix, stacking faults may also be present in inclined $\{111\}_{\text{SiC}}$ planes (inclined stacking faults can be seen in Fig. 2, they are marked by arrows), which enables the Ge atoms to diffuse along these planes towards the surface and form GeSi nanocrystals near the surface.

HRTEM image analysis of a number of nanocrystals within cubic SiC revealed that they are always of cubic structure (Figs 3a and 3c). They show the regular 3C stacking, which is also revealed in the diffraction pattern. In contrast, the

nanocrystals within hexagonal matrix contain stacking faults and are therefore of hexagonal structure (high percentage of hexagonality) as already shown previously [6,7] (see Figs. 3b and 3d). Surprisingly, although the nanocrystals are formed via an identical growth process (including high-temperature (700°C) implantation and annealing (at 1600°C, 120 s), see Kaiser and co-workers [3,8]) the resulting crystallographic structure differs.

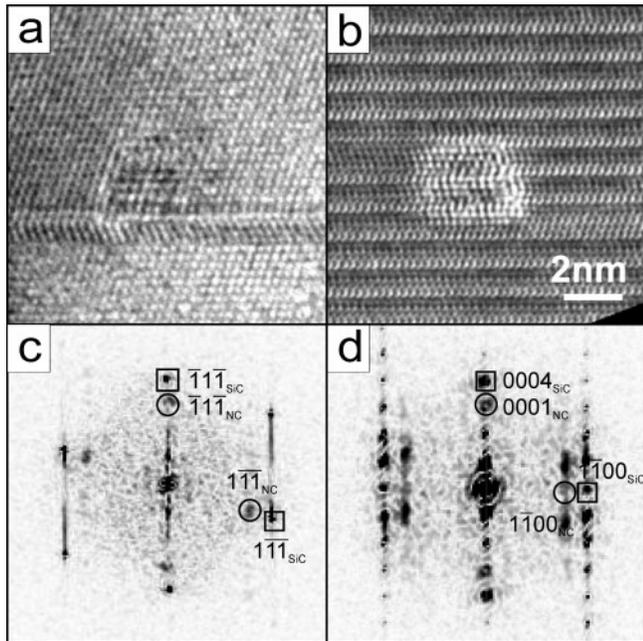


Fig. 3 Experimental HRTEM images of GeSi nanocrystals inside cubic SiC (a) and inside hexagonal 4H-SiC (b). Underneath, the diffractograms (c and d) with the main reflection shown for nanocrystals (open circles) and matrix (open squares).

In order to find out what determines the GeSi nanocrystal structure in SiC, MD computer calculations of GeSi nanocrystals of different structures embedded in 4H-SiC and 3C-SiC are performed. The quantity of interest is the interface energy of the relaxed system as defined in eq. (1), which provides information about the stability of the nanocrystals considered. The results for a cubic GeSi nanocrystal and for four hexagonal GeSi nanocrystals with periodic stacking (2H, 4H) and with irregular stacking (irreg1-NC, irreg2-NC) are shown in Fig. 4.

As can be seen, there is a clear dependency of the nanocrystal structure on the matrix structure. In cubic SiC, only cubic nanocrystals can be formed because the absolute value of the corresponding interface energy is about a factor of 2 larger than that of all the hexagonal nanocrystals considered. In the hexagonal 4H-SiC matrix, hexagonal nanocrystals are clearly energetically preferred over cubic ones. However, it is not clear which kind of the hexagonal nanocrystals is most stable. From the nanocrystals considered, obviously both, the 2H-NC and the irreg2-NC give the energetically preferred structure of nanocrystals embedded in 4H-SiC.

In the following text we compare the results of the MD computer calculations with the experimental data. Figure 5 shows HRTEM image calculations of cubic GeSi nanocrystals embedded in 3C-SiC and hexagonal GeSi nanocrystals embedded in 4H-SiC after MD relaxation of the system. For the image calculations, the program Musli [14] has been used applying the atomic coordinates obtained from the MD results. The experimental imaging conditions are voltage = 300 kV, Cs = 1.4, defocus = -64 nm, aperture = 0.6 \AA^{-1} and vibrations = 1 Å.

The calculated HRTEM images after MD relaxation as well as diffraction pattern show mainly the same features as the

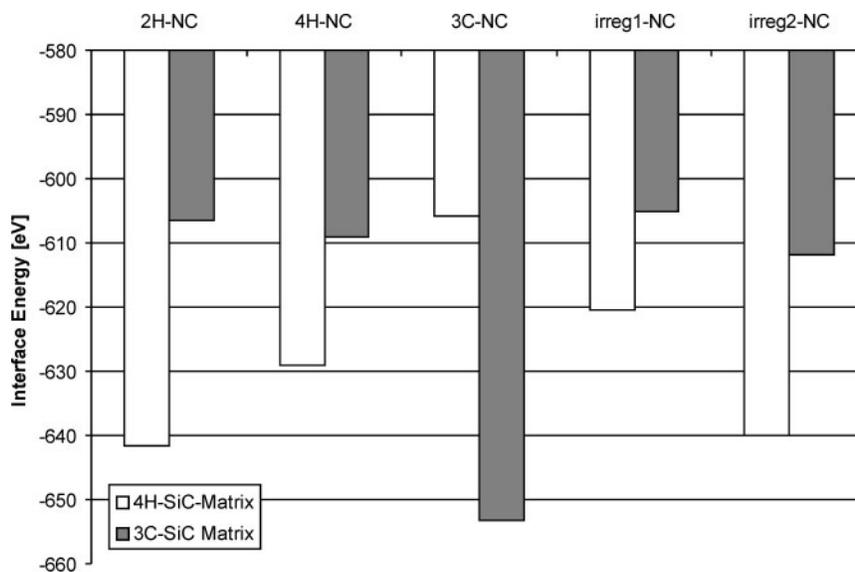


Fig. 4 Interface energy E_{int} of differently stacked GeSi nanocrystals (NC) in cubic 3C-SiC and hexagonal 4H-SiC. Periodically stacked 2H and 4H as well as the irregularly stacked hexagonal GeSi nanocrystals (irreg1-NC and irreg2-NC) are preferred within hexagonal SiC. The cubic nanocrystal (3C-NC) is preferred in cubic SiC only.

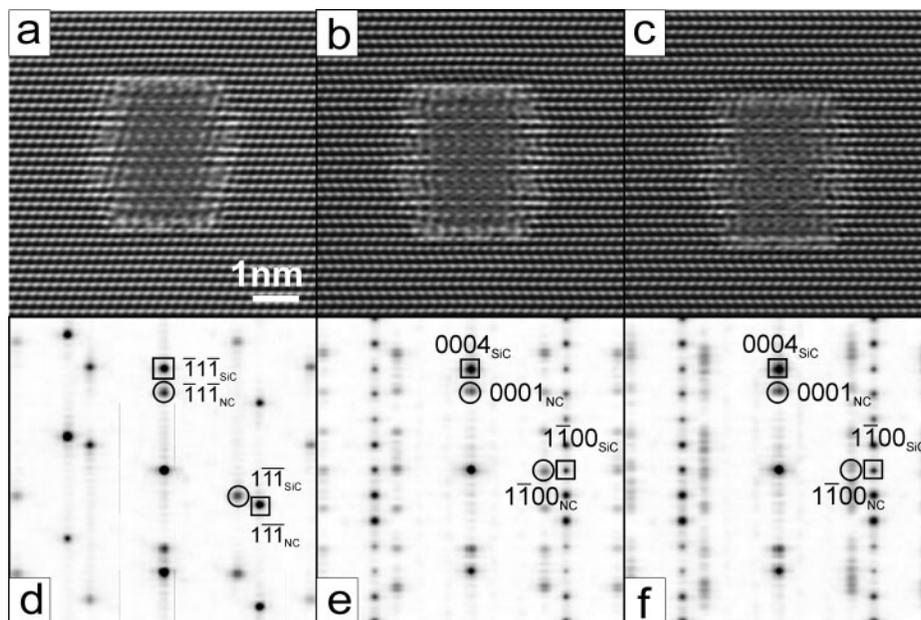


Fig. 5 Calculated HRTEM images and diffraction patterns of GeSi nanocrystals in SiC. 3C-GeSi nanocrystal in [110] 3C-SiC (a and d), GeSi nanocrystal with 2H stacking (b and e) and irregular stacking (irreg2-NC) (c and f) in [11 $\bar{2}$ 0] 4H-SiC. Major nanocrystal (open circles) and matrix (open squares) reflections are shown in the diffraction patterns.

experimental HRTEM images and the diffractograms (Fig. 2). In the case of 4H-SiC, the results of the computer calculations for the 2H-NC and the irreg2-NC are similar. Obviously, the main difference is that the $1\bar{1}00_{\text{NC}}$ reflex is less sharp for the irreg2-NC, which is in better agreement with the experimental diffraction pattern (Fig. 2d). This may indicate that the irregular stacking of the nanocrystal is preferred.

Conclusion

In summary, it can be stated that in cubic SiC only cubic GeSi nanocrystals can be formed and that in 4H-SiC only hexagonal GeSi nanocrystals can be formed, obviously preferentially with irregular stacking sequence.

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