Nanostructuring in Ni/SiC reaction layers, investigated by imaging of atomic columns and DFT calculations

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Abstract

Formation and structuring of the product phases of solid state reactions between nickel and silicon carbide were evidenced by high resolution electron microscopy (HREM), as well as by high angle annular dark field scanning transmission technique (HAADF-STEM) allowing the element-sensitive Z-contrast. The observed preferential orientation relationships between precipitated graphite and $\delta$-Ni$_2$Si as well as between the silicide and the 6H-silicon carbide substrate could be explained by epitaxial relations between the corresponding phases. The diffusion-related mechanisms of the carbon precipitation were investigated in the framework of density functional theory (DFT), yielding information on the diffusion barriers and preferential diffusion directions of carbon atoms in $\delta$-Ni$_2$Si. The calculated driving forces for solution and precipitation of carbon within the silicide phase are discussed.

Keywords

Thin films, textured growth, nickel silicide, graphitic carbon, silicon carbide, high resolution and analytical electron microscopy (HAADF-STEM, Z-contrast), diffusion, density functional theory.

Introduction

Nanostructured interlayers with carbon and silicide have electronic and micromechanical relevance for SiC- and Si-O-C-based high-tech materials. Thus, the improvement of the mechanical properties of composites demands the tailoring of their interlayers [1-4], which is possible by graphitic phases in the layer with basal plane alignment parallel to the SiC/matrix interface. An oriented growth of graphitic
regions can be achieved via the catalytic graphitisation by transition metals [5, 6]. The involved chemical reactions between metals and silicon carbide are also of interest in the context of both, the joining of metallic and ceramic structure materials and the formation of metallic contacts in electronic SiC-devices [7-10]. Recently, the evolution of reaction layers on 7.5° off oriented (0001) 4H-SiC has been studied in dependence on both, the thickness of the Ni-deposit and the annealing temperature [10]. A two stage model of layer formation has been proposed with the first stage of the initial growth being reaction rate controlled and the second stage of the subsequent growth being controlled by diffusion processes. In summary, the model emphasises the strong effect of the diffusion of the various species on the formation of the reaction products. That is in agreement with a previous work [11], in which we reported on related investigations on two different series of 6H-SiC based sandwich structures: (i) microsystems as reaction couples made by heat-treatment of SiC wafers and nickel discs, and (ii) nanosystems of SiC crystal slides coated with 5 nm nickel and subsequently heat-treated. In the continuous reaction layers of the microsystems we observed an orientation relationship between a polycrystalline silicide phase (δ-Ni$_2$Si) and the silicon carbide substrate, which can be denoted as fibre texture. Besides, graphite base planes precipitate nearly perpendicular oriented to the {0006} planes of the 6H-SiC within the silicide matrix. However, in the discontinuous reaction layers of the nanosystems, such graphitic base planes cover the grown silicide particles and the silicide-free SiC surface, yielding a roughly parallel growth with respect to the {0006} planes of the 6H-SiC. These observed texturisation mechanisms of graphite were suggested to be governed by both, the principle of surface energy minimisation, and the specifics of the diffusion flows of the atomic species in the chemical systems. Especially for the thicker reaction product layers in the microsystem, the reaction between Ni and SiC tends to be controlled by the diffusion of nickel through the δ-Ni$_2$Si [7-13]. At first, a supersaturated Ni$_x$Si$_y$:C solid solution is formed from which the excessive carbon is precipitated. In the nanosystems, where the reaction products are formed in nanosized dimensions, the diffusion paths for carbon are short enough to enable its precipitation outside the silicide phase, i.e. on the particle surface.

The concept of the diffusion-controlled Ni-SiC reaction is in agreement with experiments on the growth of δ-Ni$_2$Si on silicon-substrates, in which nickel has been identified to be the dominant diffusion species in both, the grain boundaries and the lattice of δ-Ni$_2$Si [14,15]. Moreover, in marker experiments on the reaction system Ni/SiC, nickel was indeed verified to be virtually the only mobile species, from which a low diffusivity and solubility of carbon within the silicide is concluded [8]. Carbon SIMS profiles for NiSi:C films annealed at 450°C showed that about ~0.8-1.0 at.% carbon can be solved in Ni$_x$Si$_y$:C phases [16]. However, there is no clear experimental information on the diffusion and the solution of carbon in δ-Ni$_2$Si. Nevertheless, as described in [11], we could clearly observe the precipitation of excessive carbon from the supersaturated Ni$_x$Si$_y$:C solid solution within the product layer, indicating a relatively low diffusion rate of carbon in nickel silicide.

The present paper is focused on details of the epitaxial relations between the phases involved and diffusion-based growth features of the graphitic carbon. We now have combined a new experimental insight in the Ni$_x$Si$_y$:C system, provided by direct imaging of the atomic columns constituting the related interfaces, with theoretical modellings of the involved atomic arrangements and their formation kinetics via density functional theory (DFT) approximation, to understand the interplay of the two important factors, which may control the observed orientation relationships of the
product phases: (i) the relaxation of strains due to the correlation of crystal lattices via epitaxial behaviour, and (ii) the specifics of the carbon diffusion in the Ni$_2$Si product layers at the interface between the reacting Ni and the 6H-SiC. In addition, the theoretical study of this system is also challenging with respect to the possible concurrent phase transition kinetics between the two Ni$_2$Si modifications (orthorhombic $\delta$ and hexagonal $\theta$ phase) under the solid state reaction conditions.

**Experimental**

**Reaction couples:** The 6H-SiC$^{11}$ based heat-treated sandwich structures with nickel were prepared as follows. The reaction couples were made by heat-treating pieces of N-doped (0001) 6H-SiC wafers (4 x 3 x 0.25 mm$^3$) and discs of pure Ni (Ni: 99.99 percent, diameter: 4 mm, thickness: 125 µm). For that, the pieces of SiC and Ni were placed on a silicon support in an alumina crucible, pressed together by a cover of quartz glass, and finally positioned in a horizontal mullite tube furnace, which was equipped with a continuous gas-supplying system and a ZrO$_2$ oxygen sensor including a Pt/PtRh thermocouple. Using this sensor near the sample both, the partial pressure of oxygen and the temperature could be monitored. All experiments were performed under argon flow. By positioning tantalum foils inside the tube, the partial pressure of oxygen could be reduced to about 10$^{-11}$ Pa while heating-up the furnace to the maximum temperature of 1245K, which was kept for 3 h before cooling-down again. Specimens appropriate for high resolution transmission electron microscopy (HRTEM) have been made using a refined cross-section technique.

**Electron microscopy technique:** For the atomically resolved characterisation we used an aberration-corrected (Cs probe corrector) FEI TITAN 80-300 analytical scanning transmission electron microscope, allowing a spatial resolution of better than 1 Å in the STEM mode. Applying a high angle annular dark field detector (HAADF), elastic, thermal diffuse scattering (TDS) events can be recorded. If the inner detector angle is high enough (70 mrad in our case), the intensity of these localized, incoherent scatter processes is proportional to $Z^2$, and thus, the position of atom columns or individual atoms is imaged with a brightness related to their atomic number Z. This is usually referred to as Z-contrast technique and can be regarded as a powerful tool in materials science and nanoanalysis.

For further TEM investigations we additionally used selected-area electron diffraction (SATED) and high resolution (HRTEM) techniques, carried out in a Philips CM 20 FEG (field emission gun) microscope, operating at 200 keV with a point to point resolution of 0.24 nm and equipped with both, a Gatan Imaging Filter (GIF 200) and an EDX-detector enabling the detection of light elements (IDFix-system, SAMx-Germany).

**DFT calculations:** The self-consistent density functional theory (DFT) calculations on the 3D periodic structures were performed within the generalized gradient approximation (GGA) using the Perdew-Burke-Erzenhof exchange-correlation (PBE) functional and Vanderbilt ultrasoft pseudopotentials [17, 18]. The plane wave basis set and the density representation were limited by a kinetic energy cutoff of 25 and 180 Ry, respectively. Total energy calculations have been performed taking into account spin-polarization effects. In the DFT studies the crystal structure of $\delta$-Ni$_2$Si has been represented by a 1x2x2 supercell. The integrals in the Brillouin zone were

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$^1$ SiCRYSTAL AG, Erlangen, Germany
sampled on a 3×2×3 k-point mesh. The ionic positions have been optimized until the atomic forces were less than 0.025 eV/Å, and the cell parameters were optimized by using damped dynamics of the Parrinello-Rahman extended Lagrangian as implemented in PWSCF code [19].

**Electron microscopy results**

*Oriented growth of graphitic carbon within the reaction layer*

The reaction layer near the interface to 6H-SiC consists of a polycrystalline matrix of mainly µm-sized δ-Ni$_2$Si grains, in which particles of graphitic carbon are precipitated. The overview of Fig. 1 shows in the lower part the interface-parallel (0001) lattice planes of the silicon carbide substrate, and in the upper part, left and right, two neighboured silicide grains differing in diffraction contrast and in the directions of moiré lines. The carbon precipitates can clearly be distinguished from the nickel silicide matrix by their bright contrast.

![Fig. 1](image_url)

*Fig. 1:* Microstructure of the reaction layer (above) near the interface to the SiC substrate (below, note the interface-parallel (0001) lattice planes). Two neighboured silicide grains (above, left and right) differing in contrast and in the directions of moiré lines are shown. The carbon precipitates can clearly be distinguished by their bright contrast.

The orientation relationship between the precipitated graphitic carbon and the surrounding silicide matrix is represented in the typical diffraction pattern of Fig. 2:
Fig. 2: Diffraction pattern of a δ-Ni$_2$Si grain in $<010>$ orientation with the arcs of the $\{0002\}$ graphitic base planes aligned to the reflexes of the $\{101\}$ planes of the δ-Ni$_2$Si matrix.

The bright arcs of the $\{0002\}$ graphitic basal planes are aligned to the reflexes of the $\{10\bar{1}\}$ planes of the silicide matrix, which has been indeed observed by HRTEM as demonstrated in Fig. 3. The lattice fringes of both, the $\{10\bar{1}\}$ planes of the silicide with a distance of 3.29 Å, and the $\{0002\}$ planes of the graphitic carbon with a distance of about 3.4 Å, can be seen in an interfacial region between the silicide-matrix and a graphitic particle. The $\{0002\}$ graphitic base planes are arranged parallel to the $\{10\bar{1}\}$ planes of the surrounding δ-Ni$_2$Si, as shown in Fig. 3. A further interesting detail is worth to be mentioned: The graphite planes seem to emerge directly from these $\{10\bar{1}\}$ silicide planes, which is clearly indicated in the lower part of the magnified interface region in Fig. 3.

Fig. 3: HREM-images of the interfacial region between the silicide-matrix and a graphitic precipitate, showing their relative orientations by the alignment of the lattice fringes of $\{10\bar{1}\}$ δ-Ni$_2$Si and of $\{0002\}$ carbon.
Additional information on the participation of the different atomic species in this formation process can be provided by HAADF imaging in the Z-sensitive contrast on the subnanometer level as presented in Fig. 4.

Fig. 4: Left: HAADF-STEM image (Z-contrast) showing the positions of the atomic columns of Ni (green) and Ni+Si (blue) with respect to the graphite base planes (red). Note that the latter are in line with the purely Ni-occupied type of \{10\_\} planes; Middle: Scheme of the relative orientation of (0002) graphite and (10\_\) \(\delta\)-Ni\(_2\)Si; Right: STEM image processed by FFT, for clearer evidence of the observations.

As can be seen on the lower part of the HAADF-image on the left of Fig. 4, the imaging of the atomic columns of the \(\delta\)-Ni\(_2\)Si in \(<010>\) orientation allows to distinguish between columns of nickel atoms and those, which consist of both, nickel and silicon atoms. The brightest dots correspond to the nickel columns, which occupy the \{10\_\} planes of the silicide. From these Ni-occupied planes the graphitic base planes indeed emerge, as can be identified on the upper part of the HAADF-image. The atomic model of the related structures, which is drawn in the middle, summarises the findings. Here, the nickel atoms are marked green, the silicon atoms light brown, and the carbon atoms red. Note that the latter are in line with those silicide planes, which only contain nickel atoms. For a clearer evidence, the HAADF-image has been processed by a fast fourier transformation (FFT), presented in the right image of Fig. 4, where the column contrasts of the mixed occupied \{10\_\} Ni/Si planes are marked blue. The processing procedure can be described as follows: (i) masking the FFT with respect to the reflexes of the differently occupied Ni\(_2\)Si-planes (\{10\_\}, and \{200\}) and of the \{0002\} planes of graphitic carbon, (ii) subsequent calculating of the three inverse FFT-images, and, (iii) addition of the respectively coloured inverse FFT-images. The sum image of the described procedure clearly demonstrates that the \{0002\} planes of the graphitic carbon continue that type of silicide planes which is purely consisting of nickel atoms. This result is a strong indicator to the kind of acting diffusion mechanism which will be considered in the theoretical part below.
**Orientation relationship of nickel silicide growth on silicon carbide**

The oriented growth of δ-Ni$_2$Si on {0001} 6H-SiC was previously described by us in detail [11]. As outlined, the δ-Ni$_2$Si grains of the reaction layer are crystallographically characterised by a <506> fibre texture with the <0001> direction being parallel oriented to the <0001> direction of the SiC-substrate. That corresponds to the parallel growth of the {301} planes of the silicide on the {0006} planes of the silicon carbide, which is demonstrated in the FFT-filtered HAADF-STEM image of Fig. 5.

![FFT-filtered HAADF-STEM image](image)

**Fig. 5:** FFT-filtered HAADF-STEM image (Z-contrast) demonstrating a typical relationship of a δ-Ni$_2$Si-grain (above) and the 6H-SiC substrate in [1120] orientation (below) with the (301) of the silicide being parallel to the (0006) of the silicon carbide (distances of the respective planes: $d_{(0006)} = 2.52$ Å, $d_{(301)} = 1.99$ Å, $d_{(111)} = 2.75$ Å). Note: the (301) is crystallographically equivalent to the (301) of the {301} family.

The bright spots in the SiC-region (lower part) correspond to the columns of Si- and C- atoms forming the (0006) atomic planes. The sixfold stacking sequence of the (0006) atomic planes in the 6H-polytype can be recognised, ending at the interface to the δ-Ni$_2$Si. Here, in the silicide-region, the bright lines can be attributed (in the frame of the precision of the method) to the (301) and the (111) planes of the δ-Ni$_2$Si, which are occupied by Ni- and Si-atoms. The typical parallel arrangement of the (301) planes with respect to the (0006) planes of the carbide can be recognised, and it is evidenced that the (111) silicide planes with a distance of 2.75 Å match to the inclined (1102) planes of the 6H-SiC with a distance of 2.52 Å, which yields a semicoherent interface between the silicide and the carbide.

**Theoretical aspects and results of DFT calculations**

To elucidate the processes, which yield the oriented structuring of graphitic carbon within the silicide-matrix, theoretical analyses have been performed on:
(i) the orientation relationships between the involved phases: silicon carbide, nickel silicide, carbon,
(ii) the diffusion of carbon and the driving forces for its solution and precipitation within the silicide.
In a separate paper [20], we will discuss the theoretical results concerning the accompanying processes in the product layers and the substrate in detail. Here, in the present paper, we will restrict only to such results directly related to the above described experimental observations.

Epitaxial effects between $\delta$-Ni$_2$Si, 6H-SiC and 2H-C from crystallographic aspects

The nickel silicide Ni$_2$Si is known to exist in a hexagonal high-temperature modification ($\theta$-Ni$_2$Si) and in a low-temperature modification ($\delta$-Ni$_2$Si) which may be considered as an orthorhombically distorted version of the $\theta$-phase. The question, which modification is formed under the conditions of solid-state reactions, is essential for any theoretical study of the oriented growth of the Ni$_2$Si product phase, but the experimental data on the $\delta$-$\theta$ transformation are rather controversial. Our DFT calculations [20] concerning this phase transition have evidenced that even at the temperature of the solid state reaction the orthorhombically distorted $\delta$-Ni$_2$Si crystal lattice is energetically more favoured than the high-symmetry $\theta$-Ni$_2$Si. Thus, we concentrate in the following part on the discussion of the theoretical models based on the $\delta$-Ni$_2$Si crystal lattice only.

The most important factor, which may lead to the mutual orientation of phases, is a certain degree of coherence between the crystal lattices, resulting in a fibre texture, epitaxy or axiotaxy, thus we have checked the coherence of 6H-SiC, $\delta$-Ni$_2$Si and 2H-C crystal lattices in different orientations using general crystallographic considerations.

Due to the low symmetry of $\delta$-Ni$_2$Si and its considerable misfit to the $\{0001\}$ surface of the 6H-SiC in any translation direction, only relatively large supercells can be fitted at the interface to each other. The best fit between the lattices is observed if the $\delta$-Ni$_2$Si is oriented with the $\{301\}$ parallel to the $\{0001\}$ of 6H-SiC (cf. Table 1) as illustrated in Fig. 6. The new 2D lattice parameters $a \times b$ correspond to $3c_{\text{ortho}}/\sin(120^\circ+\phi) \times b_{\text{ortho}}$ and $4a_{\text{hex}} \times \sqrt{3}a_{\text{hex}}$ for $\delta$-Ni$_2$Si and 6H-SiC, respectively, with $\angle(a,b) = 90^\circ$. The angle $\phi$ represents the deviation of $2.32^\circ$ caused by the orthorhombic distortion of the hexagonal crystal lattice, where $\phi = 0$. In the case described, the 2D-lattice of $\delta$-Ni$_2$Si shows a similar negative and positive mismatch to the 2D-lattice of the 6H-SiC in the perpendicular translation directions (-7.0% and +7.2%, respectively). The frequent occurrence of this specific orientation of the $\delta$-Ni$_2$Si to the 6H-SiC, i.e. the $<506>$ fibre texture of $\delta$-Ni$_2$Si grains in parallel orientation to the $<0001>$ direction of the 6H-SiC, is indeed observed and shown in Fig. 5, including the $<506>$ fibre texture, which we investigated in [11]. The alternative orientations of $\delta$-Ni$_2$Si grains seem to be related to each other by the $60^\circ$ rotation, reflecting the underlying hexagonal symmetry of the 6H-SiC substrate. This might also be an indication to the phenomenon of axiotaxy, where the texture is characterized by the alignment of planes of two phases which share the same d-spacing. The experimental and theoretical investigation of the supposed effect is under work. However, the preliminary results of the calculations on the matching of Ni$_2$Si and SiC are in certain agreement with recently published findings to the
axiotaxial growth as a general feature of several silicide films formed by solid state reactions on silicon-substrates [21].

**Fig. 6.** Correlation of crystal lattices at the interface between {0006} 6H-SiC and {301} δ-Ni$_2$Si surfaces. The 2D unit cells corresponding to the translation unit (see Table 2) are depicted by red boxes. Both crystal lattices are represented in the same mutual orientation as experimentally observed by HAADF-STEM (Fig 5).

An even better fit can be predicted theoretically concerning the epitaxial growth of graphite (2H-C) on the {301} planes of δ-Ni$_2$Si. In that case, the lattice parameters of the $2c_{\text{hex}} \times 2a_{\text{hex}}$ 2D-supercell of 2H-C have a very good fit with respect to the $3c_{\text{ortho}}/\sin(120^\circ + \varphi) \times b_{\text{ortho}}$ 2D-supercell of δ-Ni$_2$Si (-1.6% and +1.2% in the perpendicular translation directions; cf. Tab. 2). That orientation of graphitic carbon relative to the {301} planes and nearly parallel to the {101} planes of δ-Ni$_2$Si has been indeed observed preferentially, as already demonstrated in Figs. 2, 3 and 4.

**Table 1.** Epitaxial relations between different crystallographic planes of 6H-SiC and δ-Ni$_2$Si.

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<th>6H-SiC</th>
<th>δ-Ni$_2$Si</th>
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<tbody>
<tr>
<td>Relation of supercell to the original unit cell</td>
<td>$4a_{\text{hex}} \times \sqrt{3}a_{\text{hex}}$</td>
<td>$3c_{\text{ortho}}/\sin(120^\circ + \varphi) \times b_{\text{ortho}}$</td>
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<tr>
<td>Supercell parameters and the corresponding misfit to 6H-SiC at the interface plane</td>
<td>$a = 12.32 \text{ Å} (0.0%)$ $b = 5.34 \text{ Å} (0.0%)$ $\angle(ab) = 90^\circ$</td>
<td>$a = 13.21 \text{ Å} (+7.2%)$ $b = 4.99 \text{ Å} (-7.0%)$ $\angle(ab) = 90^\circ$</td>
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<tr>
<td></td>
<td>$2a_{\text{ortho}} \times b_{\text{ortho}}$</td>
<td>$2a_{\text{ortho}} \times c_{\text{ortho}}$</td>
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<tr>
<td></td>
<td>$a = 14.12 \text{ Å} (+14.6%)$ $b = 4.99 \text{ Å} (+1.2%)$ $\angle(ab) = 90^\circ$</td>
<td>$a = 14.12 \text{ Å} (+14.6%)$ $b = 3.72 \text{ Å} (-24.5%)$ $\angle(ab) = 90^\circ$</td>
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</table>

**Table 2.** Epitaxial relations between different crystallographic planes of 2H-C (graphite) and δ-Ni$_2$Si.

<table>
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<tr>
<th></th>
<th>2H-C</th>
<th>δ-Ni$_2$Si</th>
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</thead>
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<tr>
<td>Relation of supercell to original unit cell</td>
<td>$2c_{\text{hex}} \times 2a_{\text{hex}}$</td>
<td>$3c_{\text{ortho}}/\sin(120^\circ + \varphi) \times b_{\text{ortho}}$</td>
</tr>
<tr>
<td>Supercell parameters and the corresponding misfit to 2H-C at the interface plane</td>
<td>$a = 13.42 \text{ Å} (0.0%)$ $b = 4.93 \text{ Å} (0.0%)$ $\angle(ab) = 90^\circ$</td>
<td>$a = 13.21 \text{ Å} (-1.6%)$ $b = 4.99 \text{ Å} (+1.2%)$ $\angle(ab) = 90^\circ$</td>
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<td></td>
<td>$2a_{\text{ortho}} \times b_{\text{ortho}}$</td>
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Carbon atoms in nickel silicide, diffusion processes, and atomic interface arrangement

The DFT calculations revealed a relatively large difference of 8.2 eV in the solvation enthalpies of carbon in 6H-SiC and $\delta$-Ni$_2$Si. This result suggests that carbon atoms released in the course of the solid state reaction between silicon carbide and nickel do not penetrate in the interstitial cavities of the 6H-SiC crystal lattice, but are preferentially solved in the appearing silicide phase as illustrated by the energy diagram of Fig. 7.

Fig. 7: The differences between relative energies, corresponding to the change of the solvation enthalpy by the transition of carbon atom from interstitials positions in the 6H-SiC to those in the $\delta$-Ni$_2$Si crystal lattice (8.2 eV) and to the formation enthalpy of the graphite phase from the carbon atoms, dissolved in the $\delta$-Ni$_2$Si (2.9 eV). The relative energies are presented for the geometric configurations corresponding to the lowest local minimum at the potential energy surface. Additionally, the relative height of the calculated diffusion barriers for carbon atom in the $\delta$-Ni$_2$Si (a, red) and the change of the relative energy due to the presence of vacancies in the Ni sublattice of $\delta$-Ni$_2$Si near interstitial carbon (b, blue) are shown for comparison (see text).

Furthermore, the separation of the graphite phase from the $C_i/\delta$-Ni$_2$Si solid solution ($C_i$ interstitial carbon atoms) is favoured by a further decrease of the relative energy by 2.9 eV. As visible in Figs. 1 and 3, and already discussed in [11], the separation of the graphite phase occurs not directly at the interface with 6H-SiC, but inside the $\delta$-Ni$_2$Si layer. This implies that the solid solution of carbon in $\delta$-Ni$_2$Si remains initially in the metastable state. The observed clear correlation between the 6H-SiC and $\delta$-Ni$_2$Si crystal lattices suggests a topotactical mechanism of the conversion of 6H-SiC to $\delta$-Ni$_2$Si, minimising the interface energy and the number of extended interface defects. Thus, the carbon atoms remain firstly solved within the silicide, and subsequently, with increasing concentration of extended defects within the silicide volume, nucleation processes of the graphite occur, resulting in the separation of the graphite phase. To further support this mechanism we additionally studied a possible influence of any stabilisation of the $C_i/\delta$-Ni$_2$Si solid solution due to the interaction of carbon interstitials with vacancies within the nickel sublattice. Such kind of interaction is, e.g., responsible for the notable increase of the solubility of oxygen in iron [22]. Our calculations for different combinations of carbon interstitials in $\delta$-Ni$_2$Si with one and two nickel vacancies ($V_{Ni}$) in its nearest (octahedral) coordination sphere have shown that the binding energies between $C_i$ and $V_{Ni}$ vary in the range between -
0.28 and -0.32 eV. Thus, the effect of the interaction between carbon interstitials and nickel vacancies on the formation enthalpy of graphite from the $\text{C}_i/\delta$-$\text{Ni}_2\text{Si}$ solid solution should be negligible, as it amounts only to ca. 11% of the value for the separation of the graphite phase, which is illustrated by the level of the blue line in Fig. 7. However, such an interaction may influence the diffusion barriers for carbon in the $\delta$-$\text{Ni}_2\text{Si}$ phase.

A further DFT-result concerns the observed arrangement of the silicon, carbon and nickel atoms in the silicide/carbon interfacial region via imaging of atomic columns and is related to the diffusion mechanisms: As demonstrated experimentally in Fig. 4, the growing graphene sheets turn to be in plane with the distorted octahedral cavities within the $\delta$-$\text{Ni}_2\text{Si}$, which corresponds to the suggested theoretical model in Fig. 8.

[Fig. 8: Scheme showing the centres of the octahedral cavities in the $\delta$-$\text{Ni}_2\text{Si}$ crystal structure (white circles). In agreement with the HAADF-STEM result (cf. Fig. 4), the epitaxial growth of graphene sheets parallel or nearly parallel to the (101) plane and the [101] direction is demonstrated (blue: silicon; grey: nickel; brown: carbon).]

The DFT calculations revealed that the octahedral cavities are the most probable locations of the interstitial carbon in the $\delta$-$\text{Ni}_2\text{Si}$, corresponding to the local energy minima on the potential energy surface. This specific atomic arrangement allows the growth of the graphite planes by the addition of the carbon atoms to the edges of the graphene sheets, which can be considered as analogy to the growth of the basal graphite lattice planes in the metal dusting on Ni-base and Fe-base alloys, where the edges of these atomic planes act as active sites in the disintegration process [23].

The growth of graphite occurs on steps of the {301} surfaces of the $\delta$-$\text{Ni}_2\text{Si}$, which are locally equivalent to the {101} surfaces. The estimated energy barriers for the diffusion of the carbon atoms in different crystalographic directions within the $\delta$-$\text{Ni}_2\text{Si}$ lattice amount to 1.3 eV, 1.6 eV and 1.8 eV for the <001>, <101>, and <010> directions, resp., in the $1\times2\times2$ supercell of $\delta$-$\text{Ni}_2\text{Si}$ (see [20] for details), which is comparable to the calculated diffusion energy barriers for a carbon atom in the bulk nickel (1.6-1.7 eV [24], 1.8 eV [25]), and slightly less than the experimentally determined total activation energy for the reaction between Ni and SiC (1.9 eV [12], 2.2 eV [13]). According to the observed processes, the diffusion of carbon is more favoured in the directions <001> and <101> within the $\delta$-$\text{Ni}_2\text{Si}$ crystal lattice (1.3 eV and 1.6 eV, resp.), which are in the same plane perpendicular to the reaction front. In
the case of Fig. 8 these directions are within the image plane, and in the middle of the figure, the (101) plane containing the [101]-direction is correlated with a graphene sheet, which corresponds to the HAADF-STEM result demonstrated in Fig. 4. The above mentioned interaction of nickel vacancies with the diffusing carbon atoms may include the subsequent formation and decay of vacancy/interstitial complexes with the varying number of species and may strongly depend on the concentration of vacancies and carbon atoms in the silicide crystal lattice. Further study is intended to elucidate the role of these effects in the diffusion processes of carbon in nickel silicide.

Conclusions

Atomically resolved characterisation of the reaction layer in silicon carbide/nickel-couples combined with crystallographic considerations and theoretical modelling of the involved atomic structuring via DFT calculations, provided a new insight in the interplay of the processes, which control the observed orientation relationships of the product phases. Electron diffraction and HREM reveal a parallel alignment of the {0002} graphitic base planes and the {101} planes of the silicide. More details on the participation of the different atomic species in the reaction processes could be gained by HAADF-STEM imaging via Z-contrast, which evidences that the {0002} planes of the graphitic carbon continue that type of silicide planes which is purely consisting of nickel atoms. Together with theoretical analyses, these observations elucidate the formation of the product phases and the nanostructuring of the graphitic regions:

The conversion of 6H-SiC to $\delta$-Ni$_2$Si appears to follow a topotactical mechanism, minimising the interface energy and the number of extended interface defects. The carbon atoms remain firstly solved within the silicide. With increasing concentration of extended defects within the silicide volume, nucleation processes of the graphite occur, resulting in the separation of the graphite phase. Carbon atoms released in the course of the solid state reaction between Ni and 6H-SiC are preferentially solved in the $\delta$-Ni$_2$Si product phase, rather then in 6H-SiC, as implied by the large difference of 8.2 eV between the solvation enthalpies of carbon in these two phases.

Concerning the growth of graphite on the {301} planes of $\delta$-Ni$_2$Si an epitaxial behaviour could be predicted theoretically: The lattice parameters of the $2c_{hex} \times 2d_{hex}$ 2D-supercell of 2H-C have a very good fit with respect to the $3_{ortho}/\sin(120^\circ+\phi) \times b_{ortho}$ 2D-supercell of $\delta$-Ni$_2$Si, amounting to -1.6% and +1.2% in the perpendicular translation directions. That orientation of graphitic carbon relative to the {301} of $\delta$-Ni$_2$Si has been indeed observed preferably in our experiments.

The estimated energy barriers for the diffusion of the carbon atoms in different crystallographic directions within the $\delta$-Ni$_2$Si lattice amount to 1.3 eV, 1.6 eV and 1.8 eV for the <001>, <101>, and <010> directions, resp. Thus, according to the observations, the diffusion of carbon is more favoured in the directions <001> and <101> within the $\delta$-Ni$_2$Si crystal lattice, which are in the plane perpendicular to the reaction front. Altogether, the reaction between silicon carbide and nickel is maintained by oppositely directed diffusion flows of nickel and carbon, which are probably coupled via vacancies in the Ni-sublattice of the $\delta$-Ni$_2$Si, while the silicon atoms remain essentially less mobile and might assure a certain degree of coherence with the original lattice of the SiC-substrate. At the reaction front, nickel vacancies and carbon
atoms are continuously injected in the $\delta$-Ni$_2$Si lattice. The specific atomic arrangement at the reaction front allows the growth of the graphite planes by the addition of the carbon atoms to the edges of the graphene sheets, which can be considered as analogy to the growth of the basal graphite lattice planes in the metal dusting on Ni-base and Fe-base alloys, where the edges of these atomic planes act as active sites in the disintegration process.

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**References**