Control of Ni/SiC reactions by germanium, studied on atomic scale

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Atomic scale processes between Ni and 6H-SiC, mediated by a germanium interlayer, are reported, relevant for microelectronics and composite design. In particular, the structure and the phase composition in such Ni / Ge / 6H-SiC specimens were studied by HR-TEM, HAADF-imaging, and EDXS. On the 6H-SiC surface $\varepsilon$-Ni$_{5-x}$Ge$_x$ was formed, which interacted with the 6H-SiC, resulting in a solid solution between nickel silicide and nickel germanide with dissolved carbon. Subsequently, the carbon segregated graphitically.

Keywords: Thin films, nickel germanide, graphitic carbon, silicon carbide, high resolution and analytical electron microscopy (HAADF-STEM, Z-contrast)

Interfacial processes between metal layers and silicon carbide are 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 [1-4]. A further field of application implies the SiC-based composites, where reactions between SiC and metals boost the graphitisation and texturisation of carbon in the mechanically relevant interlayers [5-8]. In previous studies [4, 9] the reaction between Ni and SiC was shown to be maintained by the diffusion of nickel and carbon through the $\delta$-Ni$_2$Si product phase, formed on the SiC in the case of Ni-nanolayers. We could explain the observed orientation relationships between the silicide and the 6H-SiC by epitaxial relations [10]. The growth features of the graphitic carbon being dependent on the thickness of the silicide, 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. At first, a supersaturated Ni$_x$Si$_y$:C solid solution is formed, from which the excessive carbon is precipitated. In systems with nanosized reaction products the diffusion paths for carbon are short enough to enable its precipitation outside the silicide phase. Thus, the graphitic base planes cover the silicide particles and the silicide-free SiC surface, yielding a roughly parallel growth with respect to the {0006} planes of the 6H-SiC. However, a drawback of the chemical reactions between metals and silicon carbide is the strong roughening of the interface between the product phases and the SiC [8, 9]. To reduce this roughening, a tuning of the reactions is necessary, possibly provided by silicides or germanides instead of the metal. Germanides as compounds with germanium as the next group 14 element are expected to be the better candidates, because silicides are also product phases of the metal/SiC reactions and would further complicate the analysis. In addition, the investigation of the phase formation in the Ni/Ge/SiC system is of interest for SiC heterojunction device applications [11].
The present paper describes recent results of a corresponding study on the effect of germanium, which is known to form a number of binary and ternary phases with nickel and silicon [12-17].

To investigate the related reaction kinetics, 6H-SiC based sandwich structures were prepared: Cleaned N-doped (0001) 6H-SiC crystal slides were coated with ca. 11 nm Ge and 5 nm Ni and heat-treated at 1245 K for 30 min under flowing argon, from which the oxygen was gettered in situ. Specimens appropriate for high resolution transmission electron microscopy (HRTEM) were prepared using a refined cross-section technique [9]. For the microstructure investigations we used HRTEM and selected-area electron diffraction techniques (SATED), carried out in a Philips CM 20 FEG operating at 200 kV. The atomically resolved characterisation and the energy dispersive X-ray spectroscopy (EDXS) we performed by use of 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 could be recorded. As 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 was imaged with a brightness related to their atomic number Z. This is usually referred to as Z-contrast technique, a powerful tool in materials science and nanoanalysis.

![Image](image_url)

Fig. 1: **Left**: HAADF-STEM image (Z-contrast) showing the interfacial region between $\varepsilon^\prime$-Ni$_5$Ge$_3$ and 6H-SiC (distances of the respective planes: $d_{(00\bar{5})} = 2.52$ Å, $d_{(110\bar{2})} = 2.52$ Å, $d_{(02\bar{0})} = 3.37$ Å, $d_{(002)} = 2.47$ Å); **Right**: Z-contrast image clearly demonstrating the arrangement of atomic columns of $\varepsilon^\prime$-Ni$_5$Ge$_3$ in <100> orientation.

The heat-treating of the bilayer-coated 6H-SiC resulted in the formation of germanide by the reaction between nickel and germanium of the deposit. The experimental findings of the SATED-, EDXS-, and HAADF-investigations can be best described by
the monoclinic $\varepsilon^\prime$-Ni$_5$Ge$_3$ phase (see [13] for the structural details). That is demonstrated on the subnanometer level by HAADF-imaging on Fig. 1:
The Z-contrast imaging of the atom columns of $\varepsilon^\prime$-Ni$_5$Ge$_3$ in <100> orientation allows to distinguish between columns of nickel atoms, columns of germanium atoms, and also between those nickel columns, having a different occupancy of nickel. As can be seen in the right image of Fig. 1, the model of the <100>-oriented $\varepsilon^\prime$-Ni$_5$Ge$_3$ structure fits very well with the arrangement of the different bright dots related to different atomic species (and/or occupancies). The brightest dots, which form zig-zag lines around the nearly horizontal (020) planes (marked yellow) with a distance of 3.37 Å, correspond obviously to the Ge-columns ($Z_{Ge} = 32$). So, the slightly gray tails of these dots can be attributed to the Ni-columns ($Z_{Ni} = 28$), which show an occupancy being lower by 33% in comparison to those Ni-columns, forming the nearly vertical (002) planes (marked yellow) with a distance of 2.47 Å. The (020) planes of $\varepsilon^\prime$-Ni$_5$Ge$_3$ are nearly parallel oriented (with an angle of 3.5°) to the (0006) planes of the 6H-SiC substrate, as can be seen on the HAADF-image on the left of Fig. 1 at slightly lower magnification. In the 6H-SiC substrate, the bright spots 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 $\varepsilon^\prime$-Ni$_5$Ge$_3$. On the nanometer level the germanide has been observed to agglomerate in particles on the (0006) surface of the 6H-SiC. That can be seen on Fig. 2, showing the $\varepsilon^\prime$-Ni$_5$Ge$_3$-particle, which has been grown with the {020} planes 3.5° declined to the (0006) planes of the SiC. The identification of $\varepsilon^\prime$-Ni$_5$Ge$_3$ is not straightforward, as a number of nickel germanide phases are crystallographically similar, which is common for the B8-type of phases, formed in the complex Ni-Ge system. A very large number of phases are described in the literature: Ni$_2$Ge with the Co$_2$Si-type structure, Ni$_2$Ge with the Ni$_2$In-type structure, $\varepsilon$-Ni$_5$Ge$_3$ with the NiAs-type structure and Ni$_3$Ge$_3$, Ni$_7$Ge$_4$ and Ni$_{19}$Ge$_{12}$ all with their own type structures [14, 16]. However, both, the measured distances of the lattice planes and their included angles (compare the diffraction pattern of Fig. 2), fit very well with the monoclinic $\varepsilon^\prime$-Ni$_5$Ge$_3$, and thus, the reflexes in the electron diffraction pattern were attributed to the {001}, {020} and {021} reflexes of $\varepsilon^\prime$-Ni$_5$Ge$_3$ and to those of 6H-SiC in <1120> orientation.

As demonstrated by HREM in the upper part of Fig. 2, graphitic base planes segregated parallel on the surface of the particle, which is similar to the graphitic segregates on the surfaces of $\delta$-Ni$_2$Si -particles, observed in the Ni/SiC - systems without germanium ([4, 9]). In that case the graphitic enveloping was formed by the precipitation of carbon as the second product phase of the Ni/SiC -reaction besides the silicide phase. The observed graphitic carbon on the germanide also appears to result from SiC-consuming reactions, which have taken place at the interface between the germanide and the SiC, because troughs (being several 100 nm in diameter and only several nm in height) have been found around the germanide particles on the flat SiC-surface.
Fig. 2: Typical germanide particle on the 6H-SiC substrate with the SATED-pattern showing reflexes of the $<\bar{1}120>$-oriented SiC and the $\epsilon^\prime$-$Ni_5Ge_3$ in $<100>$ orientation (the yellow line marks the measuring line of the EDXS-profile, see text). The detail marked in the upper part of the particle is magnified above and images the segregation of graphitic base planes on the germanide surface.
Actually, such a reaction course becomes evident by the results of the EDXS-measurements: **Fig. 3** shows the concentration profiles of silicon, nickel and germanium, acquired at points along the yellow line, extending from the silicon carbide to the germanide in **Fig. 2** (from left to right of the abscissa in **Fig. 3**). Within the germanide, the ratios of the respective mean concentrations are calculated to $c_{\text{Ni}} / c_{\text{Ge}} = 1.88$ and $c_{\text{Ni}} / (c_{\text{Ge}} + c_{\text{Si}}) = 1.65$. Together with the SATED-findings, this strongly indicates the formation of a ε′-$\text{Ni}_5\text{Ge}_3$-based phase, which contains silicon being probably located at germanium sites. That corresponds to the composition $\varepsilon′-\text{Ni}_5\text{Ge}_{2.66}\text{Si}_{0.38}$.

According to the phase diagrams for the systems Ni-Ge and Ni-Si (for details, see [14, 16, 17]) there are a number of phases, which can be related to the B8 intermetallic compounds of a wide homogeneity range between the limiting nominal type structures $\text{B8}_1$ (NiAs) and $\text{B8}_2$ (Ni$_2$In). In all those structures the germanium or silicon atoms form a hexagonal close-packed array, into the octahedral and trigonal bipyramidal interstices of which the nickel atoms are placed, yielding the limiting phases NiGe or NiSi (NiAs-type), and Ni$_2$Ge or Ni$_2$Si (Co$_2$Si-type for the low-temperature modifications and Ni$_2$In-type for the high-temperature modifications). At high temperature in the system Ni-Ge the formation of $\varepsilon$-$\text{Ni}_{1.5}\text{Ge}_3$ (with the homogeneity field of 33.8 at% $< c_{\text{Ge}} < 38$ at% being described by $\delta$) has been actually indicated by theoretical and experimental studies of the kinetics [16]. Thus, $\varepsilon$-$\text{Ni}_{1.5}\text{Ge}_3$ is assumed to be formed by the reaction of nickel with the germanium interlayer on the 6H-SiC-substrate. Then, interfacial reactions between the germanide and the SiC-substrate result in a substitution of germanium for silicon within the Ge sublattice of the $\varepsilon$-$\text{Ni}_{1.5}\text{Ge}_3$. Without any germanium interlayer, mainly $\delta$-Ni$_2$Si forms at the interface between Ni and SiC in Ni / SiC reaction couples [4, 10]. Taking into account the crystallographic similarity between $\varepsilon$-$\text{Ni}_{1.5}\text{Ge}_3$ and $\delta$-Ni$_2$Si based on the h.c.p. arrays of germanium or silicon atoms, solid solutions of the type $\text{Ni}_{1.5}\text{Ge}_3-x\text{Si}_x$ between nickel germanides and silicides can be formed. The main difference between the structure types of $\varepsilon$-$\text{Ni}_{1.5}\text{Ge}_3$ and Ni$_2$Si is the amount of Ni-vacancies: In Ni$_2$Si the Ni-sublattice is completely filled, whereas in $\varepsilon$-$\text{Ni}_{1.5}\text{Ge}_3$ there are one sixth of the Ni-sublattice places vacant. In the excess of germanium the formation of $\varepsilon$-$\text{Ni}_{1.5}\text{Ge}_3$ is preferred, but the presence of silicon in the Ge sublattice should result in the decrease of the amount of vacancies in the Ni sublattice. This is confirmed by the experimental
observation of the enrichment of nickel in a 1 nm region at the interface (compare the profiles in the yellow filled rectangle in Fig. 3). The change of the chemical potential by the introduction of silicon in the germanides is the case of future theoretical studies.

Altogether, the findings suggest the following processes:

During the heat-treatment, the Ni/Ge bilayer on the 6H-SiC reacts, forming ε-Ni$_{5-\delta}$Ge$_3$, which agglomerates in particles on the SiC-substrate:

$$\text{Ni} + \text{Ge} \rightarrow \varepsilon - \text{Ni}_{5-\delta}\text{Ge}_3$$

Interface reactions take place between the ε-Ni$_{5-\delta}$Ge$_3$ and the SiC-substrate, which are maintained by diffusion of nickel in the germanide to the interface with the SiC. As indicated by the Ni excess near the interface (compare Fig. 3), at the interface nickel reacts with the silicon carbide, possibly forming silicide. That silicide is assumed to be immediately solved in the ε-Ni$_{5-\delta}$Ge$_3$ by the diffusion of silicon into the germanide, as this is found to contain silicon. If the solved silicon atoms are located at germanium-sites in the Ge-sublattice of the ε-Ni$_{5-\delta}$Ge$_3$, the germanide can be described as ε-Ni$_{5-\delta}$Ge$_3$-Si$_x$ (whereas x corresponds approximately to 0.38). In addition, carbon is formed as a second reaction product being solved in the germanide as well. Thus, the interfacial reaction between SiC and ε-Ni$_{5-\delta}$Ge$_3$ can be summarized as follows:

$$\varepsilon - \text{Ni}_{5-\delta}\text{Ge}_3 + \text{SiC} \rightarrow \varepsilon - \text{Ni}_{5-\delta}\text{Ge}_3-x\text{Si}_x + [C]^\text{germanide}$$

(2)

The carbon (which is solved in the germanide) diffuses to the surface of the particle, where it graphitically precipitates.

$$[C]^\text{germanide} \rightarrow C_{\text{graphite}}$$

(3)

Obviously, there is no clear difference in the precipitation of the graphitic carbon on the ε-Ni$_{5-\delta}$Ge$_3$-Si$_x$ and that on δ-Ni$_2$Si, which implies similar texturisation mechanisms [9]. On cooling from 1245K to room temperature the hexagonal ε-Ni$_{5-\delta}$Ge$_3$-Si$_x$ phase transforms into the monoclinic phase ε'-Ni$_{5}$Ge$_{3-x}$Si$_x$.

Summarizing, a ternary phase Ni$_{3}$Ge$_{2.66}$Si$_{0.38}$ has been formed by the reaction of a Ni / Ge bilayer coating on (0001) 6H-SiC. As demonstrated by the SATED-, EDXS-, and HAADF-results the Ni$_{3}$Ge$_{2.66}$Si$_{0.38}$ could be best described by the monoclinic structure of the ε'-Ni$_{5}$Ge$_3$ phase. However, according to the phase diagram Ni-Ge, a high-temperature B8-type phase (e.g. ε-Ni$_{5-\delta}$Ge$_3$) might have formed first. That high-temperature germanide, being clustered in particles, is suggested to react with the SiC-substrate, which yielded flat troughs in the SiC around the particles. This can be described by a solid solution of nickel silicide and nickel germanide. The carbon, which is also dissolved within the germanide, precipitates graphitically on the surface of the ε-Ni$_{5-\delta}$Ge$_3$-Si$_x$-particle. In comparison to the violent processes on 6H-SiC with a single layer of nickel, the ε-Ni$_{5-\delta}$Ge$_3$-Si$_x$ formation on 6H-SiC reduces the reaction between nickel and silicon carbide without inhibiting the graphite segregation, which should allow a tuning of the Ni/SiC reaction.

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