Available online at www.sciencedirect.com

ScienceDirect

Scripta Materialia 60 (2009) 858–861

Scripta MATERIALIA

www.elsevier.com/locate/scriptamat

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

A. Hähnel,* E. Pippel and J. Woltersdorf

*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*

Received 25 November 2008; revised 19 January 2009; accepted 22 January 2009
Available online 5 February 2009

Atomic-scale processes between Ni and 6H–SiC, mediated by a Ge interlayer, are reported; these processes are relevant for microelectronics and composite design. In particular, the structure and the phase composition in these Ni/Ge/6H–SiC specimens were studied by high-resolution transmission electron microscopy, high-angle annular dark field imaging, and energy dispersive X-ray spectroscopy. On the 6H–SiC surface $\varepsilon$-$Ni_{5-\delta}Ge_3$ 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 involves SiC-based composites, in which reactions between SiC and metals boost the graphitization and texturization of C 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 Ni and C through the $\delta$-$Ni_2Si$ product phase, formed on the SiC in the case of Ni nanolayers. We were able to explain the observed orientation relationships between the silicide and the 6H–SiC in terms of epitaxial relations [10]. The growth features of the graphitic C, which were dependent on the thickness of the silicide, were suggested to be governed by both the principle of surface energy minimization, and the specifics of the diffusion flows of the atomic species in the chemical systems. A supersaturated $Ni_xSi_y$:C solid solution is first formed, from which the excess C is precipitated. In systems with nanosized reaction products the diffusion paths for C are short enough to enable its precipitation outside the silicide phase. Thus, the graphitic baseplanes 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 SiC is the pronounced 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, 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 phase formation in the Ni/Ge/SiC system is of interest for SiC heterojunction device applications [11].

The present paper describes results of a study on the effect of Ge, which is known to form a number of binary and ternary phases with Ni and Si [12–17].

To investigate the related reaction kinetics, 6H–SiC-based sandwich structures were prepared: cleaned, N-doped $\{000\bar{1}\}$ 6H–SiC crystal slides were coated with ~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 (SAED) techniques, carried out in a Philips CM 20 field emission gun microscope operating at 200 kV. Atomically resolved characterization and energy dispersive X-ray

---

* Corresponding author. E-mail: ah@mpi-halle.de

1359-6462/$ - see front matter © 2009 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.scriptamat.2009.01.038

spectroscopy (EDXS) were performed by use of an aberration-corrected ($C_s$ probe corrector) FEI TITAN 80–300 analytical scanning transmission electron microscope, allowing a spatial resolution of better than 1 Å in scanning transmission mode. Applying a high-angle annular dark field (HAADF) detector, elastic, thermal diffuse scattering events could be recorded. As the inner detector angle is high enough (70 mrad in our case), the intensity of these localized, incoherent scattering 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.

The heat treatment of the bilayer-coated 6H–SiC resulted in the formation of germanide by the reaction between the deposited Ni and Ge. The experimental findings of the SAED, EDXS and HAADF investigations can be best described by the monoclinic $\varepsilon'$-Ni$_5$Ge$_3$ phase (see Ref. [13] for structural details). This is demonstrated on the subnanometer level by HAADF imaging in Figure 1: the $Z$-contrast imaging of the atom columns of $\varepsilon'$-Ni$_5$Ge$_3$ in the <1 0 0> orientation makes it possible to distinguish between columns of Ni atoms, columns of Ge atoms, and also between Ni columns with different Ni occupancies. As can be seen in the right image of Figure 1, the model of the <1 0 0>-oriented $\varepsilon'$-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 $\{0\bar{2}0\}$ planes (marked yellow) at a distance of 3.37 Å, clearly correspond to the Ge columns ($Z_{\mathrm{Ge}} = 32$). Hence, the slightly grey tails of these dots can be attributed to the Ni columns ($Z_{\mathrm{Ni}} = 28$) with an occupancy 33% lower in comparison to those Ni columns that form the nearly vertical $\{0\,0\,2\}$ planes (marked yellow) at a distance of 2.47 Å. The $\{0\bar{2}0\}$ planes of $\varepsilon'$-Ni$_5$Ge$_3$ are oriented nearly parallel (at an angle of 3.5°) to the $(0\,0\,0\,\bar{6})$ planes of the 6H–SiC substrate, as can be seen in the HAADF image on the left of Figure 1 at slightly lower magnification. In the 6H–SiC substrate, the bright spots correspond to the columns of Si and C atoms forming the $(0\,0\,0\,\bar{6})$ atomic planes. The 6-fold stacking sequence of the $(000\bar{6})$ atomic planes in the 6H polytype can be recognized, ending at the interface to the $\varepsilon'$-Ni$_5$Ge$_3$. On the nanometer level, the germanide has been observed to agglomerate in particles on the $(0\,0\,0\,\bar{6})$ surface of the 6H–SiC. That can be seen on Figure 2, showing the $\varepsilon'$-Ni$_5$Ge$_3$ particle, which has been grown with the $\{0\,\bar{2}\,0\}$ planes declined 3.5° to the $(0\,0\,0\,\bar{6})$ planes of the SiC. The identification of $\varepsilon'$-Ni$_5$Ge$_3$ is not straightforward, as a number of Ni–Ge phases are crystallographically similar, which is common for B8-type 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$_2$Ge$_3$, Ni$_7$Ge$_4$ and Ni$_{19}$Ge$_{12}$ all with their own types of structure [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 $\varepsilon'$-Ni$_5$Ge$_3$, and thus the reflexes in the electron diffraction pattern were attributed to the $\{0\,0\,1\}$, $\{0\,\bar{2}\,0\}$ and $\{0\,\bar{2}\,\bar{1}\}$ reflexes of $\varepsilon$-Ni$_5$Ge$_3$ and to those of 6H–SiC in $\langle 1\,\bar{1}\,2\,0\rangle$ orientation.

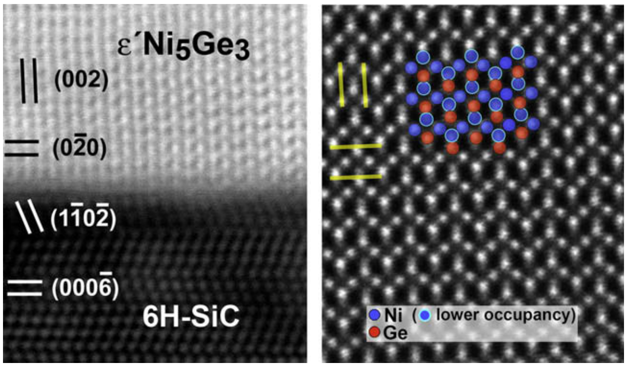

**Figure 1.** (Left) HAADF-STEM image (Z-contrast) showing the interfacial region between $\varepsilon'$-Ni$_5$Ge$_3$ and 6H–SiC (distances of the respective planes: $d_{(000\bar{6})} = 2.52$ Å, $d_{(1\bar{1}0\bar{2})} = 2.52$ Å, $d_{(0\bar{2}0)} = 3.37$ Å, $d_{(002)} = 2.47$ Å). (Right) Z-contrast image clearly demonstrating the arrangement of atomic columns of $\varepsilon'$-Ni$_5$Ge$_3$ in <1 0 0> orientation.

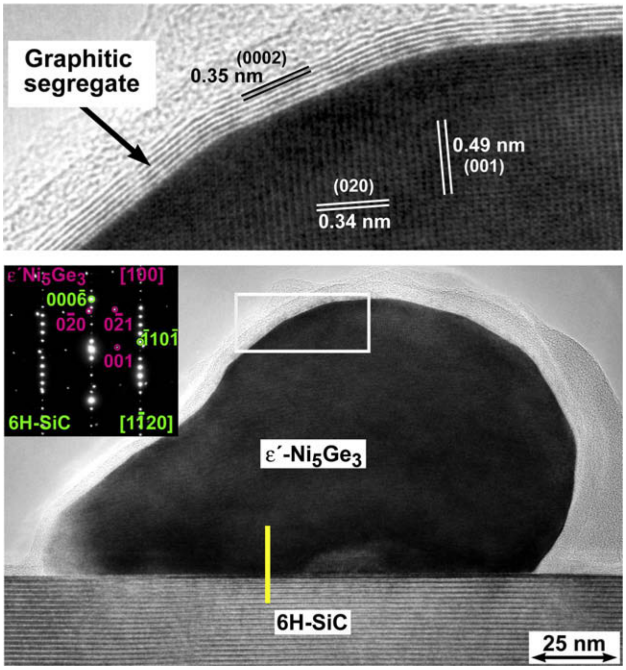

**Figure 2.** Typical germanide particle on the 6H–SiC substrate with the SAED pattern showing reflexes of the $\langle 1\,\bar{1}\,2\,0\rangle$-oriented SiC and the $\varepsilon'$-Ni$_5$Ge$_3$ in the <1 0 0> orientation (the yellow line marks the measuring line of the EDXS profile—see text). The detail marked in the upper part of the particle is magnified above and images the segregation of graphitic base planes on the germanide surface.

As demonstrated by HREM in the upper part of Figure 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 Ge [4,9]. In that case the graphitic enveloping was formed by the precipitation of C as the second product phase of the Ni/SiC reaction in addition to the silicide phase. The observed graphitic C