Epitaxial aluminum carbide formation in 6H–SiC by high-dose Al\(^+\) implantation

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Aluminum carbide precipitates are formed after Al ion implantation with dose \(3 \times 10^{17} \text{ cm}^{-2}\) at 500 °C into single crystalline 6H–SiC. The aluminum carbide (Al\(_4\)C\(_3\)) precipitates are in epitaxial relation with 6H–SiC matrix, having the following orientation relation, \([0001]_{6\text{H–SiC}}//[0011]_{\text{Al}_4\text{C}_3}\), and \([11\overline{2}0]_{6\text{H–SiC}}//[1\overline{1}20]_{\text{Al}_4\text{C}_3}\) as transmission electron microscopy reveals. The aluminum carbide appears around the maximum of the Al depth distribution. Silicon precipitates were also detected in the same zone. © 1999 American Institute of Physics.

Silicon carbide (SiC) has outstanding properties for electronic and mechanical applications under extreme conditions.\(^1,2\) Very often the material properties of SiC are modified by impurity atoms. In order to understand and control these modifications basic information about the chemical and structural changes induced by the impurities in the SiC lattice is necessary. Particular effects like precipitation and compound formation can be expected if the impurity concentration exceeds the solubility limit.

One of the most important impurity elements in SiC is Al. It is a very attractive \(p\)-type dopant because of its lower ionization energy compared to other acceptors.\(^3\) Relatively high Al concentrations up to 0.1% are required in order to achieve low resistivity \(p\)-type SiC. Still higher Al concentrations are necessary for metallic-like conduction\(^4\) or ohmic contact formation.\(^5\) Al metallization of SiC including Al compound formation is a further problem under investigation.\(^6\) Composite materials frequently contain Al or an Al compound and SiC components which can react during thermal treatment.\(^7,8\) Therefore the study of the behavior of high concentrations of Al atoms in SiC is of particular interest. One way to perform such studies under definite conditions is to use ion implantation of Al impurities into single crystalline SiC (Refs. 3, 4, and references therein). However, most of them are devoted to \(p\)-type doping of SiC. Only a few experiments were performed using ion doses high enough to produce Al peak concentrations exceeding 1%. In order to reduce radiation defects in SiC, implantations are often performed at elevated temperature.\(^9\)

In this letter we report on compound formation in 6H–SiC after high dose Al implantation performed at elevated temperature. The results have been obtained during an experiment initially designed for the investigation of ion beam induced crystallization and surface erosion of SiC.\(^10\) Doses of \(1 \times 10^{17} \text{ Al}^+ \text{ cm}^{-2}\) and \(3 \times 10^{17} \text{ Al}^+ \text{ cm}^{-2}\) with an energy of 350 keV have been implanted into (0001) oriented 6H–SiC single crystalline substrates, partly through amorphized surface regions, at a temperature of 500 °C. According to TRIM calculations maximum Al concentrations of about 5% and 15%, respectively, can be expected in a depth of 380 nm.

An extended, highly defected zone was formed by the Al\(^+\) implantation. In Fig. 1(a), a cross section micrograph of the layer implanted with \(3 \times 10^{17} \text{ cm}^{-2}\) Al\(^+\) ions is shown in...
the depth region between 300 and 600 nm. Within this damaged zone a narrow band of large crystalline precipitates, denoted by the letter $P$, were formed, around the mean projected ion range of 380 nm. Selected area diffraction pattern (SADP) taken from the precipitated area, reveals the presence of extra spots, denoted by an arrow, which can be indexed as the 111 diffraction spot of silicon shown in the inset on the right-hand side of Fig. 1(a). The 111 silicon spot reveals that the silicon precipitates have the preferential orientation of $[111]_{\text{Si}}/[0006]_{\text{SiC}}$. Extra spots in the diffraction pattern shown in the inset on the left-hand side of Fig. 1(a) were indexed as the 101$\bar{1}$ reflection of the compound Al$_4$C$_3$.

The presence of Al$_4$C$_3$ was also confirmed by the moiré pattern shown in Fig. 1(b). The moiré fringes, denoted by the letters $K$, are formed by interference of the imaging electron beams originating from the two superimposed mismatched lattices. These moiré patterns are perpendicular to the $c$ axis of the 6H–SiC matrix. The spacing $D$ of the moiré pattern is 1.19 nm. This is very close to the theoretical one; 1.18 nm, of the 6H–SiC matrix. The spacing $D$ was indexed as the 101$\bar{1}$ reflection of the compound Al$_4$C$_3$.

The permanent atomic displacements during the ion implantation in 6H–SiC with a dose of $2 \times 10^{16}$ cm$^{-2}$ and $1400^\circ$C, subsequently annealed at 1800 $^\circ$C for 5 s. 15

The precipitates were further studied by planar view TEM (PVTEM). A typical SADP from the precipitated zone when the electron beam is exactly parallel to the 6H–SiC $c$ axis is shown in Fig. 2(a). The characteristic 1120 and 101$\bar{1}$ type 6H–SiC diffraction spots of the (0001) zone are evident. In addition, similar Al$_4$C$_3$ diffraction spots, which are in perfect epitaxial orientation with the 6H–SiC matrix, are also observed. The spots are attributed to the Al$_4$C$_3$ precipitates having the orientation relation with the 6H–Si matrix, [0001]6H–SiC//[0001]Al$_4$C$_3$, and [1120]6H–SiC//[1120]Al$_4$C$_3$. No Al$_4$C$_3$ precipitates with other orientations were observed. Most of the Si precipitates are also in epitaxial relation with the 6H–SiC matrix having the orientation relationship [0001]6H–SiC//[111]Si and [1120]6H–SiC//[220]Si. However, about 30% of the Si precipitates are randomly oriented, as diffraction rings reveal in Fig. 2(a).

The dark field (DF) micrograph taken from the common 1120 reflection of 6H–SiC and Al$_4$C$_3$ is shown in Fig. 2(b). The Al$_4$C$_3$ precipitates are not distinguished directly by DF observation because the 1120 reflections of 6H–SiC and Al$_4$C$_3$ are very close, as shown in Fig. 2(a), the misfit for the common (1120) planes is 7.7%. In this case the presence of Al$_4$C$_3$ precipitates is evident from the moiré pattern produced by the common 1120 reflections, as shown in the inset in Fig. 2(b).

In contrast to the results of the implantation with the higher dose, no precipitates were found after implantation with $1 \times 10^{17}$ cm$^{-2}$ Al$^+$ ions. One can speculate that either a critical Al concentration above 5% or a critical number of displacements above 20 dpa is necessary to stimulate the precipitation. Probably, this precipitation is a thermodynamically driven phase separation like in spinodal decomposition. The permanent atomic displacements during the ion implantation facilitate this process which otherwise could not start because of the low diffusivities of the atoms in SiC. It is known that the formation of Al–C bonds is energetically favored in the ternary system Al/C/Si. 8 The energetic preference of Al–C bonds gives also the explanation why doping of SiC with Al is so successful. Almost all of the Al atoms introduced into the SiC lattice occupy Si sites where they are electrically active. 12

The formation of aluminum carbide during high dose Al$^+$ implantation in 3C–SiC at 550 $^\circ$C and in 6H–SiC at 800 $^\circ$C has been reported by other authors. 7,13,14 In these cases the precipitates exhibit some texture and are elongated along a specific orientation but no epitaxial relation with the matrix was observed. No Si precipitates were reported previously in the zone implanted with Al. According to Du et al. 13 the Si loss could be caused by outdiffusion. Implantation at very high temperature does not facilitate the formation of Al$_3$C$_4$. For example no Al$_3$C$_4$ is formed after Al$^+$ implantation in 6H–SiC with a dose of $2 \times 10^{16}$ cm$^{-2}$ at 1400 $^\circ$C, subsequently annealed at 1800 $^\circ$C for 5 s. 15

Transition metal carbides have a high electrical conduc-
tivity and thermal stability. Therefore, epitaxial layers of Al$_3$C$_4$ in SiC could be interesting for contact formation and wiring. However, for this purpose the formation of continuous layers is necessary which could be impeded by the Si precipitation. Further studies are in progress in order to investigate the phase formation after Al implantation into SiC.

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