Nanocrystalline SiC layers produced by ion-beam-induced crystallization—morphology and resistivity

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Abstract

Ion-beam-induced crystallization was used to transform amorphized, heavily Al doped SiC layers to nanocrystalline material. The morphology of the as-implanted and the annealed layers was studied by XTEM. The electrical properties were analyzed by sheet resistance and Hall measurements and compared with crystalline reference samples. A high-temperature annealing step is necessary to activate the implanted Al acceptor atoms. During annealing the mean grain size of the nanocrystals grow from 3 to 35 nm. The Al doped, nanocrystalline SiC has a much lower sheet resistance than the crystalline reference samples. It was found that this is due to the enhanced hole concentration which could be explained by a higher solid solubility of Al in the nanocrystalline SiC.

Keywords: Silicon carbide; Ion bombardment; Morphology, p-Type doping

1. Introduction

Nanocrystalline (nc) materials have attracted considerable interest during the last decade, because the reduced size of the crystallites and grain boundary effects cause changes in their optical and electrical properties with respect to single crystalline materials [1]. The special properties of nc materials can be exploited in sensors, electronic and optoelectronic devices. Ion beam induced crystallization (IBIC) has been proven as a useful tool to produce layers of nc-SiC with reproducible structure and composition inside a single-crystalline SiC matrix [2,3]. The scheme of the IBIC process is shown in Fig. 1. In a first step the surface layer is amorphized by ion implantation [4]. Then a second implantation at elevated temperature above the critical temperature of dynamic defect annealing [5] stimulates random nucleation of 3C-SiC grains in the amorphous matrix which continue to grow under irradiation. The kinetics of IBIC is very complex and depend on the nuclear energy deposition, ion fluence \( \Phi \), flux \( j \) and temperature \( T \) [6]. For the typical implantation conditions used in our experiments with the nuclear deposited energy density per ion in the range between 50 and 500 eV/nm the mean diameter \( d \) of the 3C-grains can be described by the following empirical formula [7]:

\[
d = 1.3 \times 10^{-20} \text{cm}^3 \text{s} \times j \times \exp(45 \text{ meV/kT}) + 3.6 \times 10^{-10} \text{cm}^{-1} \times (\Phi/j) \times \exp(-82 \text{ meV/kT})
\]

(1)

The first term is related to the nucleation rate whereas the second one describes the grain growth under irradiation after the complete amorphous-to-crystalline transformation (Ostwald ripening).

For electronic applications the nc-layers must be doped. Dopant activation in SiC requires high annealing temperatures [8] which could change the structure of the nc layer. One goal of this study is to investigate the morphology of the nc-SiC layers after high temperature annealing. The most challenging task in the field of SiC doping is the production of low resistivity, p-type layers [8]. We produced heavily Al doped nc-SiC by the combination of high dose Al ion implantation, IBIC and high temperature annealing. The sheet resistance (SR) of the as-implanted and annealed layers was determined as function of temperature.

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2. Experimental

6H–SiC single-crystalline wafers from Cree Inc. [(0001)-oriented, Si-face, n-type, \( N_D = 2.7 \times 10^{18} \) N cm\(^{-3}\), \( \rho = 0.052 \) Ω cm] were used as substrates. A multi-energy implantation of Al (50–450 keV), which is equivalent to the doping scheme described in Wirth et al. [9], was carried out in order to form a box-like acceptor profile with a width of approximately 500 nm. The total Al fluence was \( 3.3 \times 10^{16} \) cm\(^{-2}\) which yields a mean Al concentration of \( 5 \times 10^{20} \) cm\(^{-3}\). During implantation the target was either heated to 400 °C in order to maintain the crystallinity (standard doping process) or cooled by liquid nitrogen in order to form an amorphous layer. A second implantation was performed with 500 keV, \( 5 \times 10^{15} \) Si\(^{+}\) cm\(^{-2}\) at a flux of \( 3 \times 10^{12} \) cm\(^{-2}\) s\(^{-1}\) and a temperature of 500 °C, which stimulates random nucleation of nanocrystals in the preamorphized layer (IBIC process). Additionally, reference samples were prepared with Si implantation at 500 °C in the crystalline, Al doped layer (standard Si). The sample list is given in Table 1. After implantation the samples were cut into pieces of approximately 4.5 mm and annealed in a rf-heated furnace under Ar atmosphere at 1500 °C for 10 min. The Al profiles were measured by SIMS. The desired, box-like Al profiles could be confirmed. The structure of the implanted layers was investigated by XTEM. The layer resistivities were determined by SR measurements in van der Pauw configuration. For this purpose Al contacts (0.5 mm diameter, 500 nm thick) were sputter-deposited on the corners of the samples and then annealed at 600 °C for 10 min under Ar flow.

3. Results and discussion

The cross-sectional micrograph of the as-implanted SiC specimen is shown in Fig. 2. The implanted layer has a homogeneous, fine-granular structure and consists of randomly distributed nanocrystals. As revealed by the selected area diffraction (SAD) pattern in the inset of Fig. 2, the predominating structure is cubic (3C–SiC) and the grain orientations are isotropically distributed. The mean grain size as determined from the micrograph is approximately 3 nm which is in good agreement with the 2.5 nm predicted by Eq. (1). The nc-layer is separated from the 6H–SiC substrate by a columnar transition zone of approximately 30 nm width which is caused by disturbed epitaxial regrowth [2,10]. The effect of high-temperature annealing on the structure of the nc-layer can be seen in Fig. 3. A broad size distribution of irregularly shaped grains can be recognized. The mean grain size increases to approximately 35 nm. Stacking faults inside the grains were observed. Nevertheless, the grains retain their 3C-structure and have an isotropic orientation distribution as indicated by

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fluence Al impl. (50–450 keV)</th>
<th>Temp. Al impl. (°C)</th>
<th>Fluence Si impl. (500 keV, 500 °C)</th>
<th>Layer structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>( 3.3 \times 10^{16} ) cm(^{-2})</td>
<td>400</td>
<td>No</td>
<td>Crystalline</td>
</tr>
<tr>
<td>Stand. + Si</td>
<td>( 3.3 \times 10^{16} ) cm(^{-2})</td>
<td>400</td>
<td>( 5 \times 10^{15} ) cm(^{-2})</td>
<td>Crystalline</td>
</tr>
<tr>
<td>IBIC</td>
<td>( 3.3 \times 10^{16} ) cm(^{-2})</td>
<td>−130</td>
<td>( 5 \times 10^{15} ) cm(^{-2})</td>
<td>Nanocrystalline</td>
</tr>
</tbody>
</table>
Fig. 3. XTEM micrograph of the implanted layer after annealing. The SAD pattern is shown in the inset. The diffraction rings of 3C–SiC are indicated.

driven by the reduction of the grain boundary energy \( w_{12} \). There is also a broadening of the interface region due to columnar growth on expense of the nc-zone. The very rough surface of the specimen is likely an artifact of the XTEM-sample preparation.

The results of the SR measurements are summarized in Fig. 4. A linear temperature scale is used in the logarithmic plot of the SR because the data do not fit straight lines neither as function of \( 1/T \) (Arrhenius plot) which would indicate thermal activation of dopants nor as a function of \( 1/T^{1/4} \) which would reveal hopping conduction [13].

The room temperature SR of the implanted, unannealed samples is much higher than that of the n-type substrate. This implies that the implanted layer must be electrically insulated from the low resistivity, n-type substrate. The formation of a pn-junction with an insulating space charge region can be excluded since the acceptor activation requires high-temperature annealing [8]. Very likely a high-resistivity zone is produced by end-of-range defects which confines the current within the layer [14]. Then the high SR can be explained by implantation damage that deactivates dopants and diminishes the carrier mobility within the layer. A very strong temperature dependence of the SR was found in the unannealed samples. It decreases by more than four orders of magnitude when the temperature is increased by 100 K. It can be supposed that this dramatic behavior is due to growing leakage currents flowing through the substrate. Consequently, the SR should finally reach the substrate value. In comparison to the standard doping process the additional implantation of Si leads to a substantial reduction of the sheet resistance. Obviously, the defect-based barrier between layer and substrate is lowered by the Si enrichment in the end-of-range zone. Therefore, the structure of the layer, nanocrystalline or crystalline, has no influence of the conduction behavior in the unannealed samples. Unfortunately, a detailed analysis of the conduction mechanism in the unannealed samples by Hall measurements was not possible because the offset voltages were much higher than the Hall voltages.

A quite different conduction behavior was observed for the annealed samples. As revealed by Hall measurement the implanted layers show p-type conductivity and are insulated from the substrate by a pn-junction [15]. Therefore, the SR is only determined by the implanted layer. Generally, the SR of the annealed samples decreases with increasing temperature but the temperature dependence is relatively weak in the investigated temperature range. The simple model of thermal ionization of non-interacting Al acceptors fails to describe the temperature dependence [15]. It can be assumed that the extremely high Al concentration leads to the formation of an impurity band with almost metallic conduction [16]. Compared to the specimen prepared by standard doping the nc layer shows a SR which is around one order of magnitude lower, whereas the additional Si implantation into the crystalline layer increases the SR. The latter effect is known from doping
experiments [17], where it was found that Si co-
implantation reduces the number of Al on electrically
active Si sites in the SiC lattice due to site competition
between Si and Al impurities. The mechanism of the
reduction of the SR in the nc layer is not quite clear.
Since the Hall effect measurement reveals that a sub-
stantial enhancement of the hole concentration is
achieved in the nc-layer and considering that in crystal-
line SiC the concentration of active Al acceptors is
limited by Al precipitation above $2 \times 10^{11} \text{ cm}^{-3}$ [11],
it can be assumed that the nc structure enhances the solid
solubility of Al in SiC. Finally, it should be mentioned
that the resistivity of the doped nc-layer at room tem-
perature ($0.034 \ \Omega \text{ cm}$) is the lowest ever obtained at
that Al concentration [15]. This low resistivity in com-
bination with the low temperature dependence make the
crystalline SiC. Such low-resistivity, nc, p-type SiC
layers could be useful in contact layer systems to
moderately p-type doped SiC.

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