Ion implantation enhanced formation of 3C-SiC grains at the SiO$_2$/Si interface after annealing in CO gas

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Abstract. SiC grains can be grown without voids at the SiO$_2$/Si interface using a simple method, i.e. annealing in CO gas. Present experiments aim to create nucleation centers for the SiC crystallite growth by carbon ion implantation. The formation of the nucleation clusters, as well as the morphology, the size and the density of the nanocrystals, were systematically studied by conventional and high resolution Transmission Electron Microscopy. The nanocrystallites were developed following two different modes of growth: The first develops facets along the $<100>$ crystallographic direction giving tetragonal grains, and the second facets along the $<110>$ direction resulting in elongated nanocrystallites. It was shown that combined low dose carbon implantation and subsequent high temperature annealing in CO leads to a substantial increase of the covering of the Si surface by high quality 3C-SiC nanocrystallites.

1. Introduction
Silicon carbide with its hexagonal and cubic polytypes is one of the wide band-gap semiconductors used for high temperature applications. Obviously the growth of cubic SiC on Si would be very advantageous, because very large, high quality substrates would then be available at relatively low cost. However, beside the problem of the large misfit, another general problem in that is the formation of voids inside Si.

Earlier experiments showed that SiC grains can be grown at the SiO$_2$/Si interface using a simple method, i.e. annealing in CO gas, and in this case no voids were formed [1]. Full SiC coverage of the silicon surface cannot be achieved due to the limits of that method. However, nanocrystals were prepared which were also separated later from the Si substrate [2].

The present experiments aim to create nucleation centers for the SiC crystallite growth by carbon ion implantation in order to increase the surface coverage of SiC. The formation of the nucleation clusters as well as the morphology, the size and the density of the nanocrystals were systematically studied by conventional and high resolution Transmission Electron Microscopy. The nanocrystallites were developed following two different modes of growth: The first develops facets along the $<100>$
crystallographic direction giving tetragonal grains, and the second facets along the \(<110>\) direction resulting in elongated nanocrystallites. It was shown that combined low dose carbon implantation and subsequent high temperature annealing in CO leads to a substantial increase of the coverage of the Si surface by high quality 3C-SiC nanocrystallites.

2. Experimental
Carbon implantation of SiO\(_2\)/Si wafers (150 nm thick oxide) was carried out at 40 keV with doses of \(8 \times 10^{14} \text{cm}^{-2}\), \(2 \times 10^{15} \text{cm}^{-2}\) and \(4 \times 10^{15} \text{cm}^{-2}\) both at RT and at 550°C. The implanted wafers were annealed in CO atmosphere at 1080°C (and some of them, as reference samples, in nitrogen atmosphere) for 130 minutes. The specimens were characterized by conventional and high resolution transmission electron microscopy (TEM) in cross-section and in plan view as well.

Transparent TEM specimens were prepared by Ar\(^+\) ion milling at 10 keV and finished at 3 keV. In the case of plan view samples the SiO\(_2\) layer was removed from the top surface by HF etching prior to ion milling from the backside. Conventional TEM images were taken on a Philips CM20 transmission electron microscope working at 200 kV as well as on a JEM 120 working at 100 kV, while high resolution images were taken on a JEOL 3010 operating at 300 kV.

3. Results
Despite careful analysis carried out on samples implanted to the lowest dose (\(8 \times 10^{14} \text{cm}^{-2}\)) and annealed in nitrogen, SiC precipitates were not found in the sample. However, a few grains of cubic SiC were detected in a sample implanted by carbon ions to the highest dose (\(4 \times 10^{15} \text{cm}^{-2}\)) and subsequently annealed in nitrogen (Fig. 1). Another important observation was the high number of bright features appearing on a dark field image taken using the silicon (220) reflection (Fig. 2). They appeared as black and white contrast in the high resolution images [3] on the scale of about 5 nm and that contrast was attributed to Si-C complexes [3], which were considered as possible nucleation sites for 3C-SiC formation during subsequent annealing in CO.

Figure 1. Dark field image taken with the (220) reflection of SiC. Dose: \(4 \times 10^{15} \text{cm}^{-2}\), annealed in nitrogen

Figure 2. Dark field image taken with the (220) reflection of silicon.

Another reference sample was annealed in CO, but not implanted. That specimen showed well developed 3C-SiC grains formed exactly at the SiO\(_2\)/Si interface with a mean size of 18 nm and a characteristic thickness of about 10 nm. All of those crystallites are epitaxial to the silicon and are tetragonal with sides along the [100] and [010] directions. About 24% of the silicon surface is covered by the 3C-SiC crystallites.

In all of the samples implanted by carbon and subsequently annealed in CO, a high number of 3C-SiC grains were formed, all of them epitaxially aligned to the single crystalline silicon matrix. Moiré patterns show those grains clearly. The relatively large SiC grains (shown in bright field in Fig.3) are situated down to the depth of 50 nm. This is a remarkable difference from the former results, in which
Implantation was not carried out. Carbon implantation enhanced the nucleation of SiC successfully, as it was planned.

Figure 3. Cross section of a sample implanted to the dose of $2 \times 10^{15}/\text{cm}^2$, at room temperature, subsequently annealed in CO.

Figure 4. High resolution image taken in plan view on a sample implanted to a dose of $4 \times 10^{15}/\text{cm}^2$ at 550°C and annealed in CO at 1080°C for 130 min. Tetragonal grains are marked by letter T, while an elongated rectangular one is marked by E.

However, two types of the cubic SiC grains were formed (in all cases, when carbon implantation was done prior to annealing in CO), the first is tetragonal with sidewalls parallel to the $<100>$ type directions (exactly like in the case of the former results achieved without ion implantation), the second is elongated, rectangular grains with sides along the $<110>$ type directions (Fig. 4). The longer sidewall of the latter grains is 3-4 times longer than the shorter one.

When the sample was implanted to the lowest dose and annealed subsequently (see Fig. 5) the number of 3C grains formed was exactly the same as in the case of the annealed, non-implanted sample. It seems, that there is a threshold for this process below which new nucleation sites for the later growing SiC are not formed.
Despite the implantation processing and the high density of the nanocrystallites which were formed during annealing in CO, no extended defects were observed in the Si matrix. The formation of the 3C-SiC nanocrystallites is not a conventional epitaxy where the growth starts on the Si surface and the grains grow into the free space above the surface. In the present case the 3C-SiC nanocrystals start growing from the surface towards the Si substrate. It is easy to show that the excess volume in the Si lattice due to formation of 3C-SiC crystallites is only 3.25%. Due to this very small increase in the volume the stress imposed in the Si matrix by the nanocrystallites with the observed size can not reach the critical value to create extended defects [4]. It is worth noticing that the critical size of the SiC precipitates required to generate defects in the Si matrix is above 150 nm [5], almost one order of magnitude larger than in the present case.

4. Conclusions
Thanks to the creation of nucleation sites the density of SiC epitaxial grains formed during annealing in CO gas was increased. Parallel to that the surface coverage by 3C-SiC was also increased to the range of 30-32%. The mean size of the cubic SiC crystallites was decreased down to 10-11 nm. Further experiments are planned in which that crystallite size will be decreased further in order to use their quantum dot properties.

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References
[1] Krafcisik OH, Josepovits KV, Toth L, Pecz B and Deak P 2002 J. Electrochem. Soc. 149, G297
[2] Makkai Z, Pécz B and Bársomy I 2005 Appl. Phys. Lett. 86, 253109
[3] Pécz B, Stoemenos J, Voelskow M, Skorupa W, Dobos L, Pongrácz A and Battistig G 2009 J. Appl. Phys., in press
[4] Ashby MF and Johnson L 1969 Phil. Mag. 20, 1009
[5] Nejim A, Hemment PL and Stoemenos J 1995 Appl. Phys. Lett. 66, 2646