Growth of SiC by PVT method with different sources for doping by a cerium impurity, CeO₂ or CeSi₂

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SiC crystals grown by a Physical Vapor Transport (PVT) method in the presence of varying Ce impurity contents (from 0.1 wt% up to 2.5 wt%) added to SiC source material are investigated. The presence of the cerium vapor in the growth atmosphere is confirmed by X-ray photoelectron spectroscopy measurements. Different electrical properties of SiC crystals are obtained while use was made of non-oxide (CeSi₂) or oxide (CeO₂) sources of Ce impurity. The impact of cerium on low concentrations of boron atoms in bulk SiC is reported. Presence of Ce in the vapor stabilizes the growth of the 4H-SiC polytype.

1. Introduction

Rare-earth ion doped semiconductors are usually investigated as potential candidate materials for promising applications in optoelectronic devices. The materials, such as YAG, Lu₂SiO₅, and fluoride crystals, which are doped with optically active Ce³⁺ ions, are studied as potential candidates for applications as: phosphors, scintillators or tunable lasers operating in the UV-blue region [1–4]. The Ce-doping of SiC is an interesting issue, because there is a lack of data in the literature concerned with this topic. There exists only one communication by Itoh et al. [5] concerning the PVT growth of bulk SiC crystals in the presence of a cerium impurity. For 4H-SiC crystals, which were grown using CeO₂ or CeSi₂ as sources of cerium, the authors report the non-uniform concentrations of Ce atoms at levels less than 10¹⁷ cm⁻³ (which was the detection limit in their secondary ion mass spectroscopy (SIMS) measurements) up to 10²⁰ cm⁻³.

In this work, we present the results of investigations of bulk SiC crystals grown by PVT method in the presence of CeSi₂, which was used as a source of the cerium impurity. This work is a continuation of our previous work concerning Ce incorporation into SiC, where the oxide source of the cerium impurity (CeO₂) was used.

These results have been recently published by Racka et al. [6]. The present paper is aimed: (1) to confirm that the cerium vapor is present in the growth atmosphere during the full crystal growth process, (2) to investigate consequences of the use of CeSi₂ as a non-oxide source of cerium on electrical properties of the grown SiC crystals, and (3) to compare these results with our previous results concerning SiC crystals grown in the presence of CeO₂ [6].

2. Experimental

SiC crystals were grown by the PVT method on Si- or C-faces of the on-axis 6H-SiC crystal seeds and in the presence of a different Ce impurity content (0.1 wt%, 1 wt% and 2.5 wt%) added to SiC source materials. Commercial granules of cerium silicide (CeSi₂) have been used as the source of cerium. CeSi₂ was introduced into a small graphite container, which was placed inside the SiC source. The narrow channel in the container lid allowed a gradual vaporization of CeSi₂. All SiC crystals were grown without intentional nitrogen and boron doping.

SiC crystals have been characterized by experimental techniques such as: X-ray diffraction (XRD), X-ray photoemission spectroscopy (XPS), photoluminescence measurements (PL), secondary ion mass spectroscopy (SIMS), glow discharge mass spectrometry (GDMS) and the contactless method at microwave frequencies at 300 K to characterize the electrical properties. A SiC crystal, grown.

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under equal conditions on the C-face of the crystal seed without any Ce additive has also been studied as a reference.

3. Results and discussion

The crystals, which were grown on the C-face of the crystal seed while adding 1 wt% Ce and 2.5 wt% Ce, respectively, to the source were of the 4H-SiC polytype, whereas the SiC crystal grown on the Si-face of the crystal seed using 0.1 wt% Ce was of the 6H-SiC polytype. The undoped SiC reference crystal (0 wt% Ce) grown on the C-face of the crystal seed was also of the 6H-SiC polytype. The 4H- and 6H-SiC polytypes were distinguished by X-ray diffraction (XRD spectra are not shown here).

In both cases, when CeO$_2$ [6] or CeSi$_2$ were used as the respective source of the cerium impurity, the results obtained by XPS point out the condensation of cerium vapor species on surfaces of SiC crystals, after the effective crystal growth stage, and upon cooling-crystallization process. When the CeO$_2$ source was used, the cerium oxides CeO$_2$ and Ce$_2$O$_3$ were found [6], whereas in the case of the CeSi$_2$ source, there was found a mixture of CeO$_2$ and some unidentified (at this stage) Ce-species (Fig. 1). The presence of cerium oxides and Ce-species on surfaces of the crystals (both the oxides and Ce-species were found only as surface inclusions) proves the gradual dosage of cerium from SiC source materials and also confirms the continuous presence of the cerium vapor over SiC growth surfaces during the crystal growth processes. A possible concentration of Ce atoms in bulk SiC crystals evaluated from GDMS measurements is below 10 ppb. In the near-surface regions it reaches a value of 0.1 at%, which was estimated from the XPS results.

The electrical properties of bulk SiC crystals turned out to be completely different in two cases when CeO$_2$ or CeSi$_2$ was used as the source of the Ce impurity. For both 4H- and 6H-SiC crystals grown in the presence of CeSi$_2$ on the C- as well as on the Si-face of the seed, low electrical resistivities between $\sim 0.03$ and 0.57 $\Omega$cm were found at 300 K (Fig. 2).

From SIMS measurements it was found that nitrogen was a dominating impurity in all these crystals (Figs. 3 and 4). As these crystals were grown without intentional nitrogen doping, the main sources of nitrogen were SiC source materials used in PVT growth processes. For 4H-SiC crystals, which were grown in the presence of CeSi$_2$ (1 wt% Ce and 2.5 wt% Ce) on the C-face of the crystal seed a very low concentration of boron atoms: $[\text{B}] \sim 10^{12}$–$10^{13}$ cm$^{-3}$ has been observed (Fig. 3). On the other hand, for undoped 4H-SiC crystals grown in our earlier processes without cerium addition and under equal conditions, the concentration of boron atoms was: $[\text{B}] \sim 10^{16}$ cm$^{-3}$. Thus, in this work, we report for the first time a significant reduction in the boron impurity content in a bulk SiC grown by the PVT method in the presence of cerium impurity.

The experiment was carried out in an atmosphere of argon, which was used as the source of argon. In the case of the undoped crystal, the concentration of boron was at the same level as in the 6H-SiC (Figs. 3 and 4).

For 6H-SiC crystal, which was grown in the presence of CeSi$_2$ (0.1 wt% Ce) on the Si-face of the crystal seed, the concentration of boron atoms $[\text{B}] \sim 4 \times 10^{16}$ cm$^{-3}$ was at the same level as in the case of the undoped reference 6H-SiC (Fig. 4).

Fig. 5 presents typical photoluminescence (PL) spectra measured for 4H-SiC samples cut from the crystals grown with addition of cerium to SiC source materials, and the PL spectrum of the undoped reference 6H-SiC. No presence of cerium has been detected in the UV region of the PL spectra of the 4H-SiC. For both 6H- and 4H-SiC polytypes, the PL spectra show the lines, which are attributed to nitrogen-to-aluminium donor-acceptor pair transitions (DAP, N–Al). Besides, in PL spectra of the 4H-SiC...
some features appear, which can be assigned to nitrogen-to-boron donor–acceptor pair transitions (DAP, N–B). These DAP, N–B transitions may involve both the so-called “shallow” and “deep” boron centers. It was reported in the literature that boron doping of SiC gives, in addition to a shallow boron center, a deep D-center. For 4H-SiC polytype these two types of boron centers introduce levels located in the band gap at $E_V + 0.29$ eV and $E_V + 0.54$ eV, respectively [8 and Refs. therein].

In our recently published paper [6], for 6H-SiC crystals grown in the presence of CeO$_2$ (0.4 wt% Ce or 1 wt% Ce) on the Si-face of the crystal seed, high resistivity values at 300 K are reported. For some areas of different SiC wafers cut from these crystals the resistivity values up to $\sim 1.70 \times 10^4 \Omega \text{cm}$ were observed. From SIMS measurements, the oxygen was found to be the dominating impurity in these SiC wafers. Moreover, for SiC crystals grown in the presence of CeO$_2$, a decrease in the concentration of boron atoms [B] during the crystal growth was observed, i.e. [B] was reduced from $\sim 10^{17} \text{cm}^{-3}$ up to $\sim 10^{16} \text{cm}^{-3}$ considering the beginning and the end of the growth process, respectively [6]. It should be noted that in the case of 6H-SiC crystals grown without intentional cerium doping, obtained in our earlier growth processes, as well as, presented in this work, no significant changes in the distribution of boron dopant in the crystal volume were observed. The concentration of boron atoms [B] was maintained.

Fig. 3. Exemplary SIMS depth profiles for 4H-SiC samples cut from different wafers of SiC crystals, which were grown with different cerium additive (CeSi$_2$ was used as the source of the cerium impurity) in SiC source material: 1 wt% Ce or 2.5 wt% Ce.

Fig. 4. Exemplary SIMS depth profiles for SiC samples cut from different wafers of 6H-SiC crystals: (a) undoped, and (b) the crystal, which was grown with the addition of 0.1 wt% of cerium into the SiC source material.
This cerium impurities in SiC growth by the PVT method, Ce-species on growth atmosphere during the crystal growth. Different in two cases when CeO$_2$ or CeSi$_2$ were used as Ce sources.

4. Conclusions

Czochralski-grown silicon wafers. The crystals grown in the presence of CeSi$_2$ on both Si- or C-faces of the seed caused a distinct effect on the incorporation of boron from wafer just after the SiC crystalization front.

At almost constant level in the crystals obtained and, depending on the type of the SiC source material used for crystal growth, it was at the level of: $10^{16} \text{cm}^{-3}$ (this work, Fig. 4), $10^{17} \text{cm}^{-3}$ [6] or $\sim 10^{19} \text{cm}^{-3}$ [9].

High resistivities of SiC crystals grown in the presence of CeO$_2$ may be the result of a dominant oxygen impurity and the charge-carrier compensation effects between common residual donors and acceptors (mainly, between N and Al) [6]. One can also suppose the formation of B–O complexes, which can act as deep level compensating defects. In the literature [10] it was reported the electronically active B$_2$O$_3$ defect acting as an electron–hole recombination center for compensated p- and n-type samples of Czochralski-grown silicon wafers.

4. Conclusions

In both cases, when CeO$_2$ or CeSi$_2$ were used as sources of cerium impurities in SiC growth by the PVT method, Ce-species on the SiC post-growth surfaces of bulk SiC crystals were observed. This confirms the continuous presence of the cerium vapor in the growth atmosphere during the crystal growth.

Electrical properties of SiC crystals turned out to be completely different in two cases when CeO$_2$ or CeSi$_2$ were used as Ce sources. The crystals grown in the presence of CeSi$_2$ on both Si- or C-faces of crystal seeds show low electrical resistivity values, due to dominating nitrogen donor impurity. The growth on the C-face of the seed caused a distinct effect on the incorporation of boron atoms into the SiC lattice, which was due to the presence of Ce impurity. In this work, we report for the first time a significant reduction of the boron impurity content, down to $[B] \sim 10^{12}$ at/cm$^3$, in bulk 4H-SiC. Such $[B]$ concentrations are 4 to 6 orders of magnitude lower than concentrations of boron in our standard undoped crystals, obtained in SiC growth by the PVT method and without cerium addition. SiC crystals grown in the presence of CeO$_2$ show high electrical resistivity values due to dominating oxygen impurity, charge-carrier compensation effects between common residual donors and acceptors, and possible formation of B–O complexes acting as deep level compensating defects.

In conclusion we can also say that regardless of weak Ce-incorporation effects into bulk SiC, the presence of Ce in the vapor stabilizes the growth of the 4H-SiC polytype in SiC growth by the PVT method. No foreign polytype inclusions, such as 6H- or 15R-SiC have been observed in the crystals grown on the C-face of 4H-SiC seeds.

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References