Evaluation of nitrogen incorporation into bulk 4H-SiC grown on seeds of different orientation from optical absorption spectra

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Abstract. The effectiveness of *n*-type nitrogen doping of bulk 4H-SiC grown on seeds of different orientation is studied by optical absorption measurements. The 4H-SiC ingots have been grown by physical vapour transport (PVT), with nitrogen doping from the SiC source. The nitrogen concentration was determined at room temperature from the absorption peak intensity at 464 nm, with account for the degree of donor ionization. It has been shown that 4H-SiC ingots grown on Si (11-22) faces are significantly less doped by nitrogen than the ones grown on C (11-2-2).

1. Introduction

Silicon carbide is a very significant material for high-power and high-temperature electronics because of its wide energy gap, high breakdown field and thermal conductivity [1]. SiC ingots of large diameter can be grown by physical vapour transport (PVT) on their own seeds. The most prominent *n*-type dopant for silicon carbide is nitrogen, and doping is carried out from the gas phase by adding nitrogen (N_2) into the inert atmosphere (Ar). However, the raw material (SiC powder) appears to be an additional source of nitrogen, leading to unintentional variations in the doping level.

Despite the fact that seeds of basal (0001) orientation are the most popular for PVT growth of SiC, one can also use other orientations, which may be interesting from several points of view. Firstly, some groups have demonstrated the possibility of an increase of charge carrier mobility in the channel of the field effect transistor implemented on a (11-20)-face, compared to that on the basal plane [2]. Secondly, the usage of the substrates of prismatic orientation (11-20) for light-emitting structures can reduce the effect of high piezoelectric and spontaneous polarization along the [0001] axis, and so to increase radiative recombination efficiency [3,4]. Thirdly, because of the strong dependence of the defect structure `on the growth direction, i.e. seed orientation, the ingots grown on the prismatic seed can be described as defect-free, concerning the defects propagating along the [0001] direction, namely threading dislocations and micropipes.

It should be noted that SiC doping levels, even under identical growth parameters, should be different for various seed orientations due to the different incorporation kinetics of nitrogen. The aim of this work is to study the effectiveness of n-type nitrogen doping of bulk 4H-SiC during growth on seeds of various orientations by means of optical absorption measurements.

2. Experimental setup

4H-SiC ingots were grown using the modified Lely (PVT) method in a reactor with resistive heating of the crucible [5]. The growth temperature measured in the bottom of the crucible was $2150^{o}C$, and $2060^{o}C$ at the cap of it. The pressure during growth was 3.5 Torr. The gas atmosphere was argon of high purity, or Ar and N_2 (5% vol.) mixture for intentional nitrogen doping (sample N-2). The nitrogen incorporated in the rest of the grown ingots was from the SiC source. The temperature gradients were in the range of 10-20 K/cm. The duration of the growth was 40 hours. The average growth rate was about 0.5 mm/hour for all the experiments. The seeds fixed at the top of the crucible were 4H-SiC substrates. As a source we used the silicon carbide powder of 100 microns, manufactured by Saint-Gobain (Norway).

Wafers of (0001) and (11-20) orientations were cut from ingots grown on standard off-cut (000-1) C seeds with an inclination of 4 degrees to [11-20]. The (11-22)- and (11-2-2)-oriented wafers were cut from ingots grown on seeds of the same orientations, correspondingly. Initially, (11-22)-oriented 4H-SiC seeds were cut from an (000-1)C ingot at the angle of 73° with respect to the basal plane.

The wafers were faceted by two crystallographically non-equivalent faces, i.e., quasi-polar silicon Si(11-22) and carbon C(11-2-2). The studied samples were approximately rectangular with linear sizes of 51×15 mm. The 4H-SiC single crystals were grown simultaneously on seed faces of both polarities in one experiment.

Prior to the optical measurements, all wafers under consideration were subsequently subjected to mechanical grinding, polishing, and chemical etching in the KOH melt (600°C, 15 min). The parameters of the studied wafers are presented in table 1.

Table 1. Parameters of the studied 4H-SiC samples.

Sample number	Seed orientation	Surface	Thickness, μm	Comments
N-1	(000-1)	C	590	
N-2	(000-1)	C	680	N_2 doping
P-0	(11-20)	no	965	
Si-1	(11-22)	Si	920	
Si-2	(11-22)	Si	920	
Si-3	(11-22)	Si	920	
Si-4	(11-22)	Si	925	
C-1	(11-2-2)	C	705	
C-2	(11-2-2)	C	725	
C-3	(11-2-2)	C	670	
C-4	(11-2-2)	C	630	

The optical setup was based upon a VERTEX 80 Fourier-transform infrared (FTIR) spectrometer equipped for spectra measurements in the $0.4 - 1.1$ μm range. This setup enables rapid registration of the spectra with a high signal-to-noise ratio. The samples were placed into a specialized accessory to perform transmission and reflection measurements in the same spot of the sample. The light incidence angle was 11°, corresponding to a ~4° angle inside the SiC crystal – which is rather close to normal. The probe beam was polarized by a linear polarizer, and the studied samples were rotated in order to change the angle between the optical axis of the crystal c and the electric field vector of the incident electromagnetic wave E. All the measurements were carried out at room temperature.

3. Results and discussion

It has been described in several works [6-8] that nitrogen-doped n-type 4H-SiC exhibits specific optical absorption in the visible range, which is dependent on the polarization of the incident light. In order to evaluate this effect in our case, we have measured the transmission $T(\lambda)$ and reflection $R(\lambda)$

spectra of an (11-20) oriented sample in the extreme cases of the electric field vector **E** parallel and perpendicular to **c** axis (figure 1).
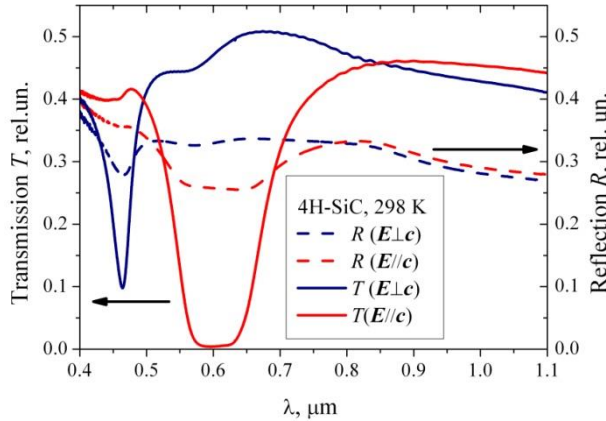

Figure 1. Transmission and reflection spectra of a typical nitrogen-doped 4H-SiC sample of (11-20) orientation for different light polarization.
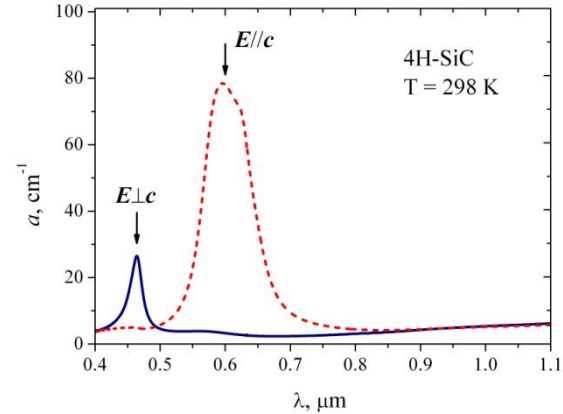

Figure 2. Absorption spectra of the nitrogen-doped 4H-SiC sample (figure 1) in the case of different light polarization.

As can be seen from figure 1, the transmission coefficient T of 4H-SiC decreases significantly at $\lambda \sim 0.46\ \mu m$ – or at $\lambda \sim 0.6\ \mu m$, depending on the polarization – which implies the presence of absorption bands. The absorption coefficient of the wafer material a (cm^{-1}) can be determined from the measured transmission T and reflection R coefficients. The transmission coefficient of the plate-parallel sample in the case of normal light incidence is defined by the following expression:

$$T = \frac{(1-R_0)^2 e^{-ad}}{1 - R_0^2 e^{-2ad}} \ , \tag{1}$$

where d is the sample thickness (cm), and R_0 is the reflection from a single sample-air interface.

The reflection coefficient of the same sample is described as follows:

$$R = R_0 - \frac{(1-R_0)^2}{R_0} + \frac{(1-R_0)^2}{R_0 - R_0^3 e^{-2ad}} \ . \tag{2}$$

In the equations (1) and (2), it is taken into account that multiple reflection of light occurs from the front and rear edges of the samples. The solution of these equations for a at each wavelength allows one to determine the absorption spectra $a(\lambda)$ of the sample material without the exact knowledge of $R_0(\lambda)$. The absorption spectra corresponding to the $R(\lambda)$ and $T(\lambda)$ of the n-type 4H-SiC sample from figure 1 are shown on figure 2.

It can be seen that 4H-SiC exhibits strong absorption at $\lambda = 464$ nm, or at $\lambda = 600$ nm, depending on the relative orientation of the **c** axis and the electric field vector **E** of the polarized light. The origin of these absorption peaks is conventionally attributed to nitrogen-related optical transitions into the upper sub-bands of the conduction band [6].

In the work [9], an empirical relation between the absorption intensity at 464 nm (**E** $\perp$ **c**) and the free electron concentration n (cm^{-3}) in nitrogen-doped 4H-SiC has been proposed:

$$a = a_0 + kn \ , \tag{3}$$

where $a_0 = 2.4\pm1.3$ cm^{-1}, $k = (3.6\pm0.1)\cdot10^{17}$ cm^2.

In order to use the approximation (3) for determining carrier concentration in 4H-SiC, the condition of (**E** $\perp$ **c**) must be fulfilled during the $R(\lambda)$ and $T(\lambda)$ optical measurements.

The corresponding absorption spectra ($E \perp c$) obtained by eq. (1) and (2) for two 4H-SiC (0001) wafers are shown on figure 3. It can be seen that the sample N-2, which was grown with additional doping by N_2 from the gas phase, exhibits considerably stronger absorption. The according electron concentration value n obtained with (3) is by an order of magnitude higher than in the sample N-1, as can be seen from the inset of figure 3.
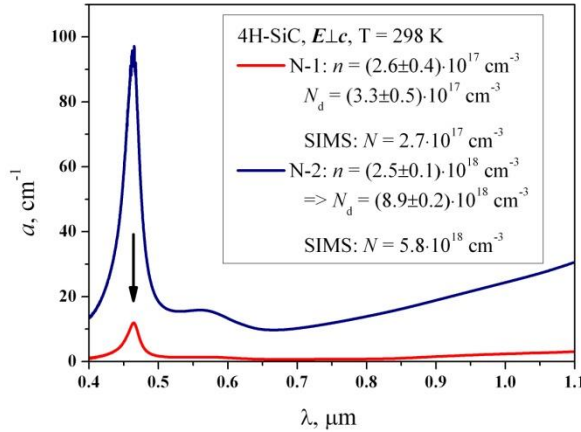

Figure 3. Absorption spectra of 4H-SiC wafers grown on (0001) seeds with (sample N-2) and without (sample N-1) additional nitrogen doping.
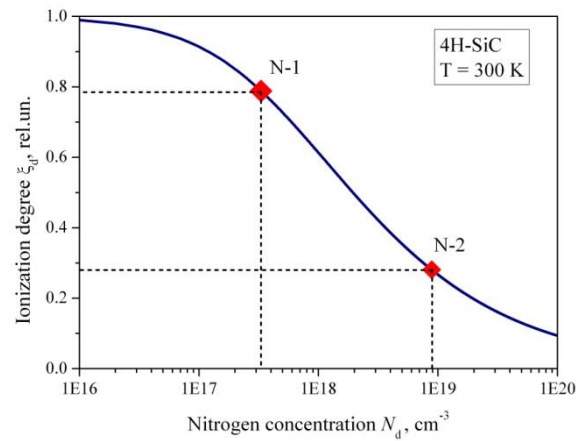
Figure 4. Ionization degree of nitrogen donors in 4H-SiC as a function of nitrogen concentration at room temperature [10]. Dots mark the nitrogen concentration values for the samples from figure 3.

To determine the concentration of nitrogen donors N_d from the free electron concentration values obtained with (3), we have accounted for the degree of donor ionization ξ_d given by the relation [10]:

$$\xi_d = N_d^+ / N_d = \left\{ 1 + \left[1 + 4g_d \frac{N_d}{N_c} \exp\left(\frac{\Delta E_d}{k_B T}\right) \right]^{1/2} \right\} \left[2g_d \frac{N_d}{N_c} \exp\left(\frac{\Delta E_d}{k_B T}\right) \right]^{-1}, \quad (4)$$

where T is the lattice temperature (K), $g_d = 2$ is the degeneracy factor, k_B is the Boltzmann constant, $N_c = 3.25 \cdot 10^{15} \, T^{3/2}$ cm^{-3} [11] is the effective density of states in the conduction band, and $\Delta E_d = 0.059$ eV [12] is the ionization energy of nitrogen in 4H-SiC. The ionization degree ξ_d decreases with the increase of nitrogen concentration, as plotted in figure 4.

The concentration of the ionized donors can be described by a steady-state Gibbs distribution [10]:

$$N_d^+ = N_d \left[\frac{n g_d}{N_c} \exp\left(\frac{\Delta E_d}{k_B T}\right) + 1 \right]^{-1}. \quad (5)$$

Assuming that the equilibrium electron concentration in an extrinsic ($N_d \gg N_a$) SiC at room temperature is given by the amount of ionized nitrogen donors ($N_d^+ = n$), we come to the following:

$$N_d = n \left[\frac{n g_d}{N_c} \exp\left(\frac{\Delta E_d}{k_B T}\right) + 1 \right]. \quad (6)$$

The nitrogen concentration values N_d obtained with (6) for 4H-SiC samples N-1 and N-2 are shown in an inset of figure 3. The results are in good agreement with the independent data of secondary ion mass spectrometry (SIMS) measurements.

The described method of determining nitrogen concentration in 4H-SiC has been applied to study the crystals grown simultaneously on seeds of various orientations. The absorption spectra $a(\lambda)$ of the sample series grown on Si (11-22) and C (11-2-2) faces are shown on figure 5. The studied samples C-1 and Si-1 were cut from the part of each ingot which was in 4 mm from the seed, C-2 and Si-2 – in

5 mm from the seed and so on. The corresponding values of n in the studied wafers are listed on an inset of figure 5.
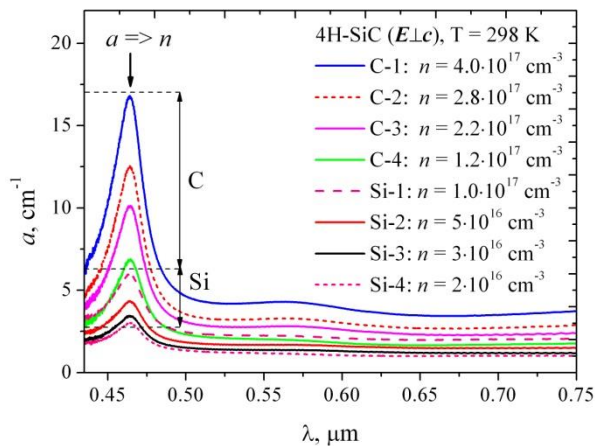

Figure 5. Absorption spectra of 4H-SiC bulk samples grown on Si- and C- faces. The arrow marks the absorption peak used to determine the electron concentration n.
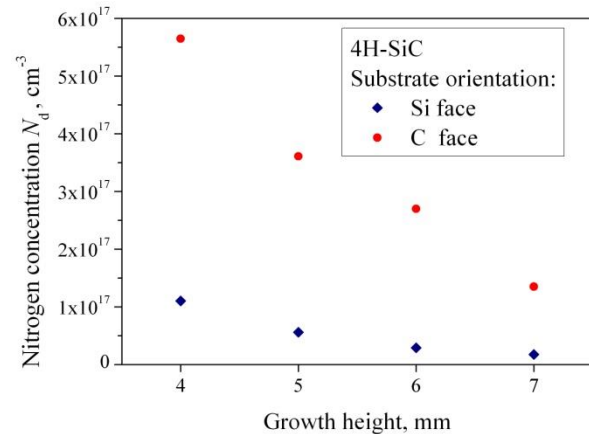
Figure 6. Variation of nitrogen concentration in the (11-22) and (11-2-2) 4H-SiC samples plotted in the ingot growth direction.

The nitrogen concentration values in the studied structures obtained with (6) are plotted in the figure 6. It can be seen that initiating the growth of 4H-SiC on the Si (11-22) faces significantly decreases the injection of nitrogen into the bulk 4H-SiC compared to the C (11-2-2) ones. In addition, a decrease of nitrogen concentration along the growth direction is observed, which is presumably caused by depletion of nitrogen in the SiC source. The obtained results allow us to conclude that growth of 4H-SiC on a Si (11-22) face can be used to obtain lightly doped bulk material.

Acknowledgements

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