Optical Studies of Deep Centers in Semi-Insulating SiC

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Abstract. Semi-insulating SiC grown by the HTCVD technique are studied by luminescence and absorption measurements and the results are compared to PAS and SIMS results. We have found that metal impurities are present but only in very small concentrations. The semi-insulating properties are instead determined by the intrinsic defects, mostly the silicon vacancy in hydrocarbon rich grown material and the carbon vacancy in the hydrocarbon poor grown material. The hydrocarbon poor material is stable upon annealing both from a vacancy concentration point of view and from a resistivity point of view. The hydrocarbon rich grown material does not stand the annealing at 1600 °C and the resistivity is decreased; from the absorption and PAS measurements we have observed that the decrease in silicon vacancy concentration fits the growth of the vacancy clusters.

Introduction

Deep centers are important defects in semi-insulating SiC wafers mainly used for high frequency applications (MESFET and HEMT devices). Today's state-of-the-art growth techniques are able to produce epitaxial layers and wafers with such low levels of impurities that intrinsic defects become more and more important. In this paper we present our current understanding on deep centers in semi-insulating SiC from optical measurements in the infrared region combined with secondary ions mass spectrometry (SIMS), electron paramagnetic resonance (EPR) and positron annihilation spectroscopy (PAS) measurements. Annealing behavior of the silicon vacancy is discussed based on a combination of the results from optical and PAS measurements and the concentration of vacancies is also compared to concentrations of impurities (both shallow and deep) to get more insight into the defects responsible for the semi-insulating properties of SiC.

Experimental

For the absorption and luminescence measurements we have used a Bomem DA8 FTIR spectrometer equipped with a quartz beamsplitter. For the luminescence measurements we used a Ge detector and different laser excitation sources, whereas in the absorption measurements we used a quartz lamp and InSb detector. All optical measurements were made at low temperature, between 2 and 10 K. The PAS measurements are described in detail by Arpiainen et al. [1]. The samples used for the measurements are grown with the HTCVD technique [2] and the annealing is made in a standard SiC hot wall CVD reactor.

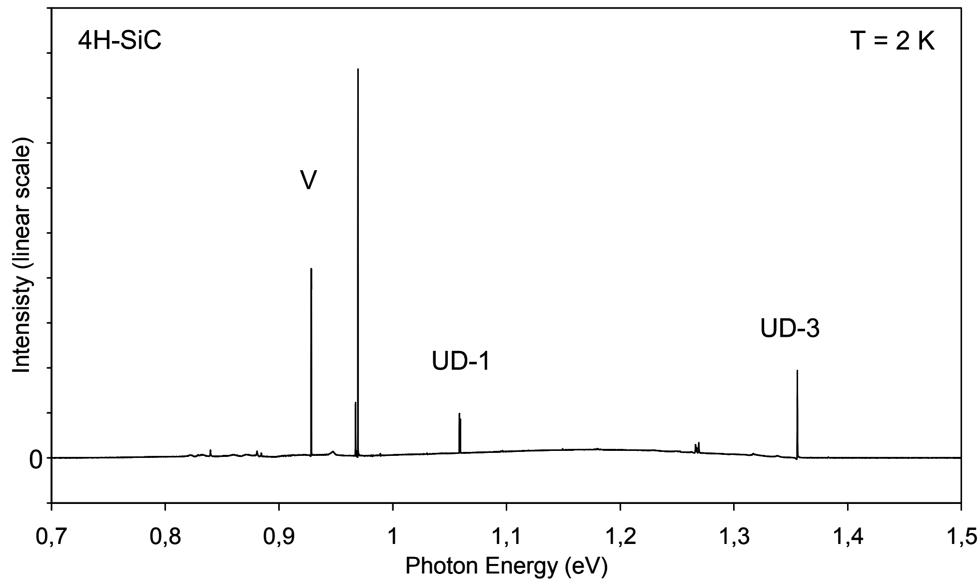

Fig. 1: Photoluminescence at low temperature from semi-insulating 4H-SiC material using above bandgap (UV) excitation.

Results and discussion

A number of different luminescence centers are detectable in semi-insulating SiC. Fig. 1 shows a photoluminescence (PL) spectrum from a semi-insulating 4H-SiC sample, measured at 2 K.

The spectrum in Fig. 1 shows vanadium, UD-1 and UD-3 signals [3]; other signals also present in as-grown semi-insulating material are the UD-2 and Cr. The concentrations of impurities are normally very low in the materials grown with the HTCVD technique. Fig. 2 shows a PL spectrum from a semi-insulating sample with vanadium clearly visible and the insert shows a SIMS spectrum from the same sample with a vanadium concentration of $1 \cdot 10^{14}$ cm^{-3}. The vanadium concentration in HTCVD material is normally close to or below $3 \cdot 10^{12}$ cm^{-3}, which is the detection limit for vanadium in SIMS measurements, but also in these samples one can detect vanadium luminescence without any problem.

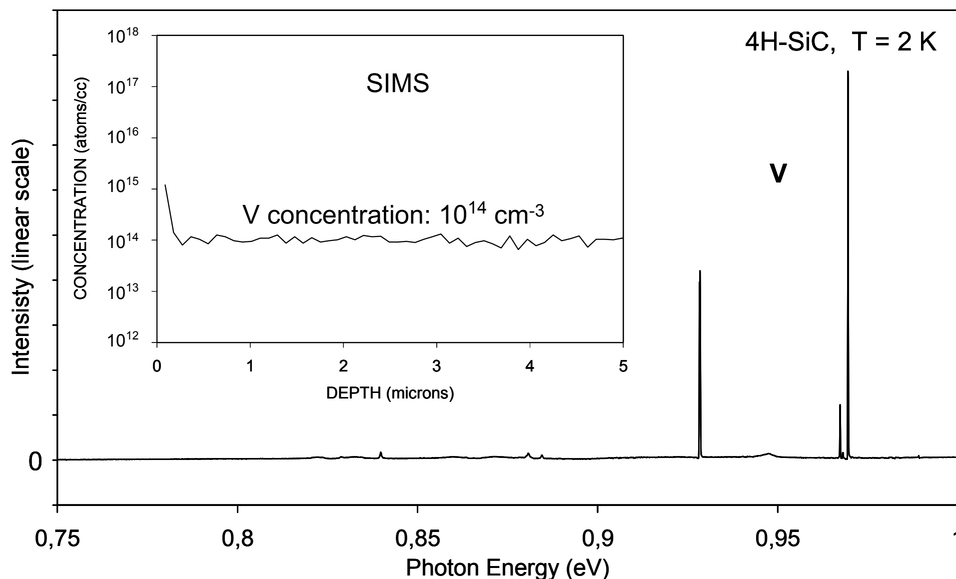

Fig. 2: Vanadium luminescence from a semi-insulating 4H-SiC sample and in the insert the vanadium concentration in the same sample as measured with SIMS.

Impurity	Measured concentration	SIMS detection limit
Fe	$1.7 \cdot 10^{14}$ cm^{-3}	$1.4 \cdot 10^{14}$ cm^{-3}
Co	$1 \cdot 10^{14}$ cm^{-3}	$4 \cdot 10^{13}$ cm^{-3}
Ni	$1.9 \cdot 10^{14}$ cm^{-3}	$8 \cdot 10^{13}$ cm^{-3}
Cr	$3.4 \cdot 10^{13}$ cm^{-3}	$2.3 \cdot 10^{13}$ cm^{-3}
Nb	$4.9 \cdot 10^{13}$ cm^{-3}	$1 \cdot 10^{13}$ cm^{-3}

Table 1: Impurity concentrations measured with SIMS.

Other impurities which sometimes can be detected are listed in Table 1, together with their SIMS detection limits.

As shown from the vanadium case, impurities can be very efficient recombination centers and give rise to strong emission even at very small concentrations. Any of the listed impurities in Table 1 could be responsible for the UD-1 or UD-3 luminescence, which are both considered as impurity related based on a number of experimental results published by Wagner et al. [4] and Magnusson et al. [3,5].

From SIMS measurements we also know the atomic concentration of impurities giving rise to shallow levels, which in the case of HTCVD grown material mainly are nitrogen (donor) and boron (acceptor). Small amounts of aluminum can also be present but normally in concentrations of $1 \cdot 10^{14}$ cm^{-3} or lower. Nitrogen and boron are found in the $1 \cdot 10^{15}$ cm^{-3} range [6]. Comparing concentrations of different impurities one realizes that nitrogen and boron are the only ones which really stand out in terms of concentration. The other impurities are only found at lower concentrations if at all. The electrical properties of the crystal would then be n-type or p-type depending on the nitrogen and boron concentration in the specific sample; this is not what is observed. The samples are semi-insulating with high resistivities - normally $>>10^5$ Ωcm - with thermal activation energies in the range from 0.6 eV up to 1.4 eV.

Using infrared excitation instead of above-bandgap excitation as for the spectrum in Fig. 1, it is possible to detect also the silicon vacancy related PL in the HTCVD grown material. The center can be observed in absorption also, as shown in the transmission spectra from a 5 mm long sample in Fig. 3a. The absorption line at 1.353 eV is the V_2 line from the silicon vacancy in 4H-SiC. Fig. 3b shows the same sample but after annealing at 1600 °C for 1 hour in a H_2 ambient. The silicon vacancy does not anneal out at this high temperature even if it decreases in intensity; this is a very important result and it has also been shown by Son et al. [7] that the carbon vacancy does not anneal out either at this high temperatures.

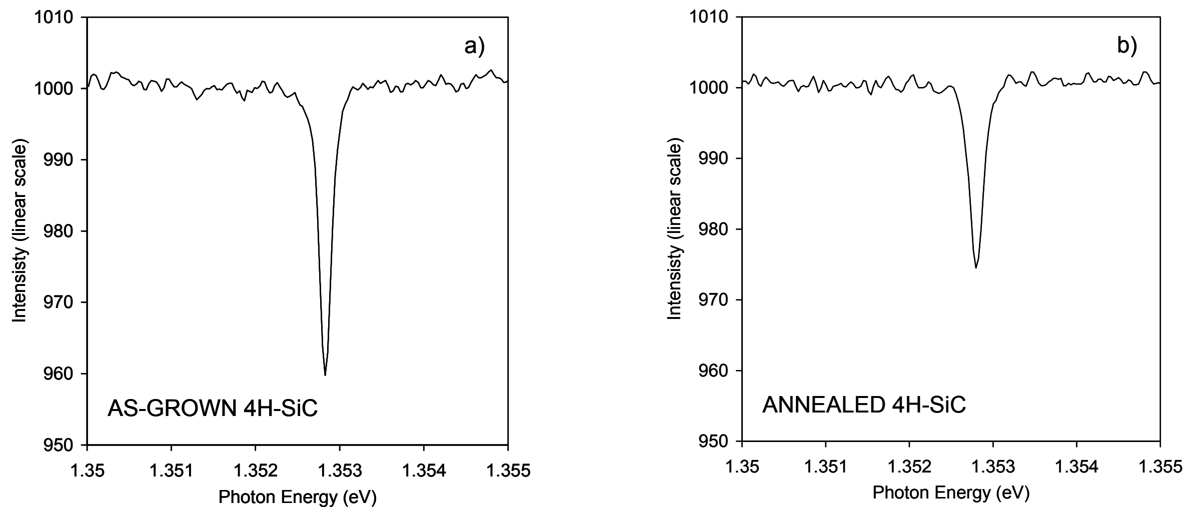

Fig. 3: Transmission spectrum of a 4H-SiC sample a) before and b) after annealing at 1600 °C.

Growth conditions: Hydrocarbon -	Rich	Poor
Resistivity	10^8 - 10^9 Ωcm	> 10^9 Ωcm
Thermal activation energy	< 0.8 eV	0.8 - 1.4 eV
Silicon vacancy absorption	Strong	Weak
Carbon vacancy signal (EPR) [7]	Weak	Strong
Resistivity after annealing	Not stable	Stable

Table 2: Properties of semi-insulating material grown under different conditions.

The semi-insulating properties of the material may thus not only be affected by impurities; also the intrinsic defects are present and stable even after high temperature annealing. Before discussing the different types of intrinsic defects and their presence, let us look at the different growth conditions which are used to grow semi-insulating samples with the HTCVD technique. Since the HTCVD is a gas-feed bulk-growth technique it is possible to change the ratio between silicon and carbon input to the system; growth conditions can therefore be either hydrocarbon rich or hydrocarbon poor [2]. The differences between the hydrocarbon rich and poor grown material are shown in Table 2.

So even if the silicon vacancy can be detected in both hydrocarbon rich and poor grown material the absorption is much stronger in the hydrocarbon rich grown material. In the case of hydrocarbon poor grown material the silicon vacancy absorption is very weak and at least 5 mm long absorption length is needed in order to detect the silicon vacancy absorption signal.

By using PAS on the same set of samples as we use for absorption we can find out further information about the open volume and the distribution of the open volume between single vacancies and vacancy clusters. PAS is an established measurement technique which relies on that positrons get trapped in vacancy type of defects since the vacancies lack a positive ion core. The lower electron density in the vacancies raise the positron lifetime above the bulk lifetime and the open volume can therefore be probed by measuring the lifetime of the positrons. Fig. 4 shows positron lifetime spectra from hydrocarbon rich grown samples (a) and from hydrocarbon poor grown samples (b) and how the lifetimes are affected by annealing. The annealing is performed at 1600 °C in a H_2 ambient.

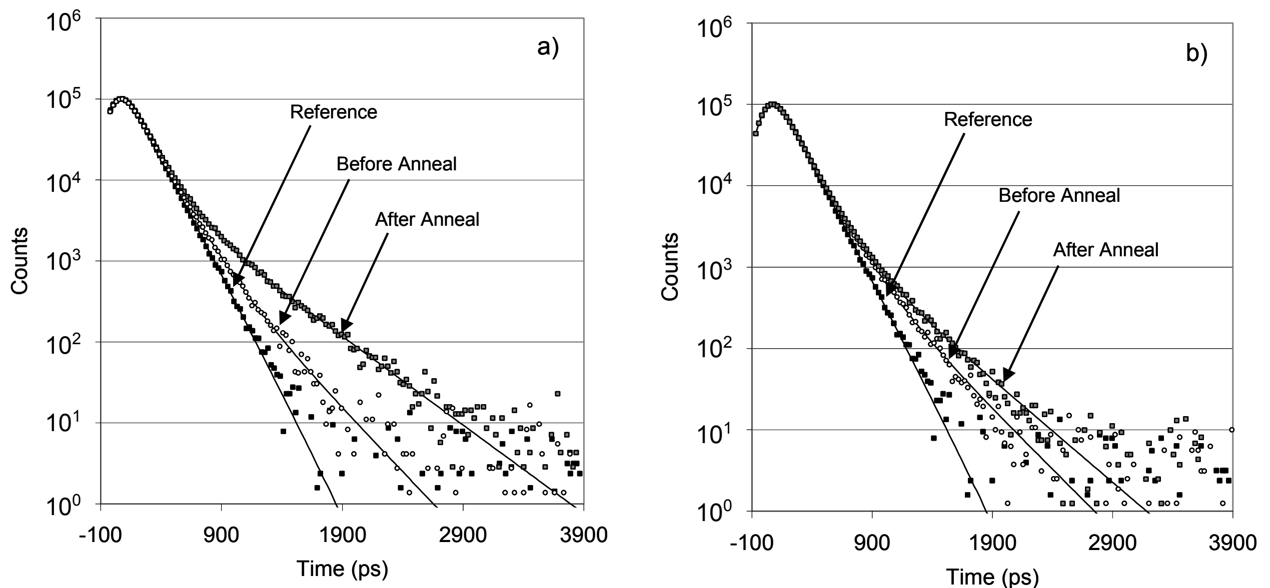

Fig. 4: Positron lifetime spectra for a) hydrocarbon rich grown samples and b) hydrocarbon poor grown samples.

The difference between as-grown and annealed samples as shown in Fig. 4 is very large. The lifetimes are clearly separated from each other and also from the SiC reference sample (p-type sample or thick epi sample with low defect concentration).

The changes measured with PAS in the hydrocarbon rich grown samples (Fig. 4a) after annealing (1h) that the distribution of the open volume in the samples changes so that more of the volume is in the vacancy clusters at the expense of the single vacancies. This is observed in the PAS spectra by the move of the kink between short and the long lifetime component to the left, i.e. the intensity of the long component increases. It is also clear that the cluster size increases since the long lifetime component increases in lifetime after the annealing. This result is consistent with the fact that the intensity of the silicon vacancy from absorption measurements shows a decrease of the vacancies after annealing (but does not disappear). The silicon vacancies are suggested to become mobile during the annealing at 1600 °C and cluster together; the process is clearly slow and all vacancies are not moved into clusters even after more than four hours of annealing at 1600 °C. The same annealed samples show decreases in both the silicon vacancy absorption and the resistivity. The drop in resistivity after 1 hour of annealing is about one order of magnitude. At the same time as the resisitivity drops the thermal activation energy of the resistivity also decreases in the sample. Moving from the hydrocarbon rich grown samples to the hydrocarbon poor grown samples one would expect different behavior since the resistivity and the thermal activation energy of the resistivity are stable upon annealing in contrast to the hydrocarbon rich grown material. In the optical absorption measurement, the silicon vacancy signal was hardly detectable, if at all, and does not show any big changes. In Fig. 4b the PAS spectra are presented for samples which were as-grown and annealed for four hours. Since fewer change were observed for the hydrocarbon poor grown samples longer annealing times were used than for the hydrocarbon rich grown samples. The distribution of the open volume in the samples before and after annealing is not changed, but the annealed samples have longer lifetime in the long lifetime component compared to the as-grown samples. So the only change is that the clusters present have grown bigger but the total open volume in the clusters is the same and the concentration of the single vacancies is also unchanged.

These results from PAS and absorption measurements on both the hydrocarbon rich and poor materials fit together since they show how the hydrocarbon rich materials have more silicon vacancies, which also are decreased after annealing at the same time as the clusters grow in both size and concentration in comparison to the hydrocarbon poor material where the single vacancy concentration and cluster concentration are almost constant after annealing. The PAS measurements also give us an idea of the concentration of missing atoms in the samples, which can be calculated with positron trapping equations [1]. Typical concentrations are clearly above 10^{16} cm^{-3} distributed on both single vacancies and vacancy clusters.

The concentrations of vacancies in the samples are very high compared to the known metal impurities, see Table 1. Also, when comparing to the nitrogen and boron concentrations the vacancy concentration is high, and will be dominating in terms of concentration. We therefore attribute the electrical properties in the semi-insulating SiC to deep levels related to intrinsic defects such as vacancies and not deep levels related to impurities. The exact compensation ratio between the nitrogen and boron is not so important since the vacancy concentration is much higher than either of the two. Another supporting argument is that when the silicon vacancy is removed (clustered together after annealing) the resistivity is decreases and the Fermi-level is moving closer to one of the two bands. So when one of the defects responsible for the semi-insulating properties is decreased in concentration the resistivity is also decreased.

Summary

Optically active centers in semi-insulating SiC originate from both impurities and intrinsic defects. By comparing results from FTIR, SIMS and PAS measurements we have found that the dominating group of defects is the vacancies and not the impurities. Comparing the different impurities we find that nitrogen and boron are present in higher concentrations compared to metals. The metals can still give rise to strong infrared luminescence, but the concentrations are still very small from SIMS measurement, typical $1 \cdot 10^{14}$ cm^{-3} or lower.

Measurements made on semi-insulating material grown under hydrocarbon rich conditions show that the material after annealing at 1600 °C has fewer silicon vacancies compared to before annealing even if they do not disappear completely. The silicon vacancies are clustered together into bigger vacancy complexes during the annealing. At the same time the resistivity in the samples decreases and the Fermi-level moves towards the band edge due to the removal of electrically active defects. In the semi-insulating hydrocarbon poor grown material the situation is very different; the silicon vacancy absorption signal is very weak, no large growth of vacancy clusters is observed, and the resistivity is stable. We attribute the semi-insulating properties of the HTCVD grown material to intrinsic defects where the silicon or carbon vacancy plays the major role depending on whether the material is grown under hydrocarbon rich or poor conditions.

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