Materials Science Forum *Online: 2012-05-14*
ISSN: 1662-9752, Vols. 717-720, pp 259-262
doi:10.4028/www.scientific.net/MSF.717-720.259

Investigation of intrinsic carbon-related defects in 4H-SiC by selective-excitation photoluminescence spectroscopy

I.G. Ivanov[1, a,*], A. Gällström[1], R. Coble[2], R.P. Devaty[2], W.J. Choyke[2,b] and E. Janzén[1,c]

[1] Linköping University, Department of Physics, Chemistry and Biology, 581 83 Linköping, Sweden

[2] University of Pittsburgh, Physics & Astronomy Department, 100 Allen Hall 3941 O'Hara Street, Pittsburgh, PA, 15260 USA

[a]ivani@ifm.liu.se, [b]choyke@pitt.edu, [c]erija@ifm.liu.se, *corresponding author

Keywords: carbon aggregates, carbon split interstitial, di-carbon antisite, photoluminescence

Abstract. Emission of carbon-related defects is investigated by means of selectively-excited photoluminescence in high purity 4H-SiC electron-irradiated with very low dose. Two new centers with clearly associated phonon replicas are observed, one of which is tentatively assigned to the carbon split interstitial at the hexagonal site. The temperature dependence of the spectrum is also studied and indicates that at least some of the observed luminescence lines arise from recombination of excitons bound to isoelectronic centers.

Introduction

Defects related to carbon interstitials in SiC have received significant attention in the past few years, because they are commonly created during implantation or electron irradiation. The ability of C interstitials to migrate in the lattice and aggregate at certain lattice sites in different configurations gives rise to a large variety of C-related defects. Several of them have been studied theoretically [1,2] and experimentally [3-6]. The theory is capable of estimating the formation energies of the defects giving us an idea of their abundance in as grown and, perhaps, irradiated material, and their dissociation energy related to the thermal stability of the defects upon annealing. Further output of the calculation is the ground-state energy, but even if no complications with charged states of the defects are involved, the accuracy of the ground state is often not better than a few tenth of an eV, obviously not enough for unambiguous comparison with experimental data from electrical or optical measurements. Fortunately, local-phonon energies can be calculated with much better accuracy [1,2], and since in many cases they are observable as shifts of phonon replicas from the no-phonon line, a rather comprehensive attempt was undertaken in [4,5] to identify some of the C-related defects by comparison of the observed energies of local (defect-specific) phonons in photoluminescence (PL) with the theoretically calculated ones. High-temperature annealing, mapping across the irradiated region, and use of n- and p-type samples were common methods used in these studies to vary and study the relative contributions of different C-related defects. However, the defects were created using relatively high dose of electron irradiation (mostly above 10^{19} cm^{-2}) that inevitably introduces severe lattice damage and large defect concentrations, which may initiate interaction between different defect centers and hinder their individual identification. We introduce a supplementary approach by using a high-purity (virtually intrinsic) sample irradiated with low dose, and using different excitation wavelengths in order to vary and distinguish the emission from different centers.

Experimental

We have studied two high-purity epitaxial layers [both unintentionally doped n-type, with $n \sim 7\ 10^{14}$ cm^{-3} (sample#1, 70 μm thick) and $n \sim 8\ 10^{13}$ cm^{-3} (sample#2, 110 μm thick), irradiated at room temperature with 1 MeV electrons at a fluence of $3\ 10^{15}$ cm^{-2}, with subsequent annealing in Argon at 1260°C (sample#1) and 1100°C (sample#2) for 30 min. Sample #2 is the main subject of this

work because it can be considered as virtually intrinsic and with the low irradiation dose applied we do not expect significant interaction between the defects or aggregation of larger carbon clusters in significant concentrations. Most of the resulting PL lines are consistent with previous observations in 4H-SiC [4,5], however, with much weaker intensity than in these references (by about 2-3 orders of magnitude judging from comparison of the relative intensities of the PL and the Raman lines). Sample #2 was prepared as a free-standing film with polished side edges used to introduce the laser beam in order to increase its path through the sample and thus the signal. All spectra with below-band-gap excitation were obtained in a geometry of near-backscattering from the polished edge of the sample. Variable excitation was obtained from a frequency-doubled Ti-sapphire laser in the CW-regime.

Results and Discussion

The no-phonon lines and their associated phonon replicas observed in this study are listed in Table 1. The following remarks are based on the data shown in the table. We have listed only lines which are prominent under certain excitation conditions (see below); not all lines are observed under, e.g., above band gap excitation. Most of these lines have been observed also in [4,5,6], except for the two centers with no phonon lines at 4695 Å and 4968 Å. We note also that our assignment of the phonon replicas of the 4718 Å center differs from that of [4].

Apart from visual analysis of the spectra obtained with about 200 different excitation wavelengths, we make use of statistical methods in order to establish correlation between different lines. We consider now the various PL centers in more detail.

The 4695 Å and 4968 Å centers, called here for brevity X- and Y-centers, respectively, have not been reported earlier, to the best of our knowledge. Their emission is very weak under above band gap excitation with a 351 nm laser, as shown in Fig.1a. The dominant emission in this case is due to the alphabet lines (not shown) and the a_0, b_0 and c_0 lines and their phonon replicas (cf. Table 1) previously associated in [5,6] with the dicarbon antisites. However, the X- and Y-centers become dominant under excitation around 3900-4000 Å (3098 – 3178 meV, Fig.1b). In addition, the X-center exhibits a sharp excited state at about 64 meV above the 4695 Å (2640 meV) no-phonon line X_0. The spectrum excited resonantly at this state, 4584.4 Å (2704 meV), is shown in Fig. 1c, and we notice the simultaneous appearance of the peak at 5084 Å (2438 meV) in Fig. 1b,c interpreted here as a phonon replica at 202 meV of the X-center (X_{202}). In previous work [4] a line at the same position as X_{202} was associated with the 189 meV phonon replica of the tricarbon antisite (the 4718 Å center, cf. Table 1). We also observe the 4718 Å no-phonon line in many of our spectra (e.g., Fig.1b and insert), hence further arguments will be given to ascertain that the line at 5084 Å observed in our work is not a replica of the former line. Firstly, confirmation of our assignment comes from the observation of the second order $2X_{202}$, cf. Fig. 1. Secondly, a correlation map built from a series of 55 spectra obtained by scanning the laser across the excitonic band gap (not shown) shows a strong correlation of the X_0 line (4695 Å) with X_{202} (5084 Å), not with the 4718 Å center. In addition, three replicas at 152, 189 and 247 meV were associated in [4] with the 4718 center, but in our series strong correlation is observed only with the 247 meV replica (cf. insert in Fig.1), and the 152 meV replica is not observed at all. Thus we conclude that the 5084 Å line observed in our measurements is indeed a phonon replica of the X-line, although overlap with the 189 meV replica of the 4718 Å center cannot be completely ruled out.

Table 1. The no-phonon PL lines and their replicas observed with different excitation wavelengths.

Notation (position)	Energy (meV)	Local phonons in meV (line position)	Assignment
a_0 (4632 Å)	2675	133 (4874 Å) 180 (4966 Å)	
b_0 (4636 Å)	2674	133 (4878 Å) 178 (4968 Å)	Dicarbon antisite $(C_2)_{Si}$ [6]
c_0 (4643 Å)	2670	132 (4884 Å) 180 (4979 Å)	
X_0 (4695 Å)	2640	202 (5084 Å)	C split interstial (tentative)
4718 (4718 Å)	2627	247 (5208 Å)	Tricarbon antisite $(C_3)_{Si}$ [4]
G_0 (4935 Å)	2512	167 (5287 Å) 170 (5294 Å)	Dicarbon antisite pair [4]
Y_0 (4968 Å)	2495	171 (5332 Å)	–

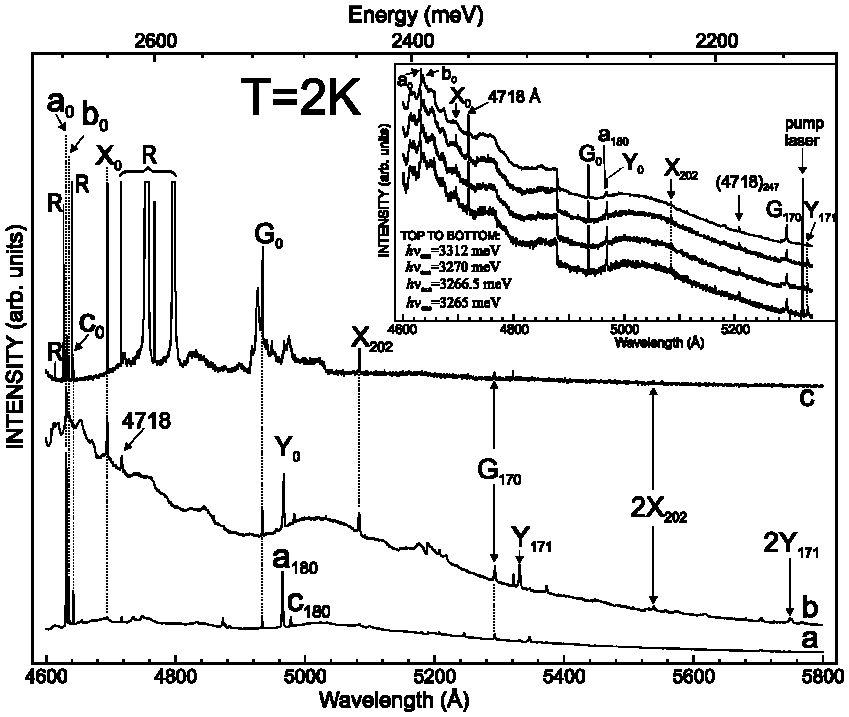

Fig. 1. The PL spectrum of sample #2 with (a) above band gap excitation, (b) excitation at 3126 meV, and (c) resonant excitation at 2704 meV. The insert illustrates the onset of the Y-center (see text). The lines marked 'R' are the Raman bulk modes.

Considering the X-center, the carbon split interstitial (at the hexagonal or cubic carbon site) might be a good candidate based on the reasonable agreement between the observed (202 meV) and calculated local phonon energy (197 [1], or 189-192 [7] meV). Indeed, the higher vibrational energy of the C-C stretch mode compared to the dicarbon antisite is stipulated by the stiffer bond between the two carbon atoms due to less space available to the pair on a carbon site compared to silicon site, and a single vibrational mode above the phonon continuum is calculated in [1]. Also, an excited state is expected due to splitting of the doubly-degenerate *e*-level in the gap originating from the non-bonding π-orbitals on the two C atoms in the lower-symmetry environment of 4H-SiC if compared to 3C-SiC. However, the energy of the experimentally determined excited state – 64 meV – is in strong disagreement with the theoretical calculation for the cubic site (0.7 eV [1]), whereas in the case of a carbon split interstitial at a hexagonal site the two levels are nearly degenerate, leaving the latter configuration a better candidate for the X-center.

Let us consider now the Y-center in more detail. The no-phonon line position Y_0 coincides within the experimental accuracy with the phonon replica b_{178} associated with the b_0 line of the dicarbon antisite [5,6], hence despite the good correlation of this line with its phonon replica Y_{171} and the observation of $2Y_{171}$ another confirmation is desirable that Y_0 is not related to b_0. Indeed, the insert in Fig. 1 displays a series of spectra obtained near the onset of the Y_0-line which show no or even decreasing contribution from b_0 while Y_0 increases more than 10 times from top to bottom in this figure. Again its increase is correlated with the appearance of Y_{171}. No other local phonon modes associated with the Y-center were observed in this study.

Finally, we discuss the G-center associated with a dicarbon antisite pair in [4]. In all our measurements we observe strong correlation of the no-phonon line at 4935 Å with its 170 meV-replica up to the second order, in good agreement with [4]. We also observe the weaker satellite of G_0 at 167 meV discussed in [4]. However, it is worth noting that the formation of antisite pairs in significant concentrations is not likely in our sample due to the low concentration of dicarbon antisites and their low mobility (high dissociation energy). It is worth noting that the structures of the G center (4935 Å) and the Y-center are very similar, both show a single phonon replica at ~170 meV, but we will not attempt identification of the Y-center at this time.

We turn now to consideration of the temperature dependence of the spectrum, some selected spectra of which are displayed in Fig. 2. The most striking feature is the remarkable growth in intensity of the a_0-b_0-c_0 triplet (dicarbon antisite [5]) by a factor of ~2, and the G-center (4935 Å line) by a factor of ~10 in the temperature range 5-40 K. We attribute this growth to the increase in the population of *free* excitons which are freed from the shallow donors and recaptured to the deeper a_0-b_0-c_0- and G-centers. Indeed, if a center possesses a charged state well within the band gap, then a particle of the opposite charge can always be bound by the Coulomb field of the charged

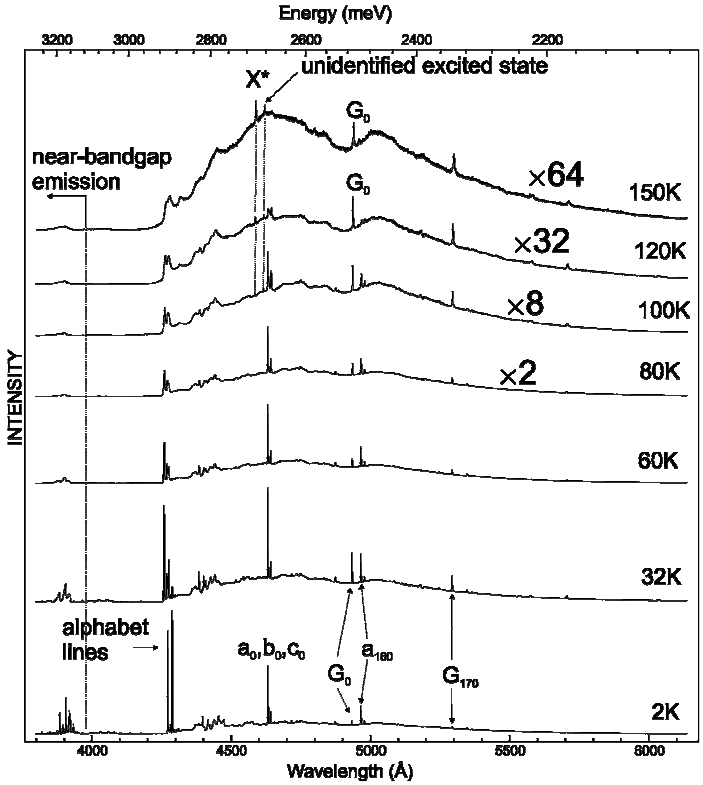

Fig. 2. Temperature dependence of the PL spectrum. All spectra are displayed so as to compare the absolute intensities, but note the scale changes which apply to individual spectra.

center. While excited states for the second particle close to its respective band are expected, the ground state of such a bound exciton need not be shallow, and the recombination lifetime need not be slow as is the case with isoelectronic atoms. Fast recombination rates have been measured in [6] for the center associated with the dicarbon antisite (a_0-b_0-c_0), which was used as an argument against the bound-exciton concept. However, this center possesses two loosely bound electrons in the two carbon π-orbitals which are available for non-radiative Auger recombination, hence short lifetime of an exciton bound to the center is expected. The bound-exciton-recombination picture, suggested originally in Ref. [1], is supported also by the excitation scan across the excitonic band gap; the luminescence of the alphabet lines, the dicarbon antisite and the G_0-center (4935 Å) grows strongly when free excitons (but no free carriers at 2K) are created with the assistance of the lowest energy phonon in 4H-SiC. It should be noted, however, that not all centers exhibit such behavior; on the contrary, the X-center for example decreases in intensity when excited above the phonon-assisted excitonic band gap, which might be an indication that the emission from this center is due to internal electronic transitions. Thus, both the temperature dependence and the scan across the excitonic band gap might provide us with tools to distinguish electronic transition within the center from emission of excitons bound to it.

We notice also that at temperatures above ~80 K two excited states are emerging at 2704 and 2686 meV, the former (X^*) quite obviously being the excited state of the X-center considered earlier. (The other is not yet associated with any of the lines observed at 2K.)

In conclusion, we observe two new luminescence centers in virtually intrinsic 4H-SiC irradiated with a very low dose of electrons. Both centers involve carbon atoms judging from the high energies of the local phonons, and we tentatively propose the carbon split interstitial at a hexagonal site as the origin of one of them (the X-center with no-phonon line at 4695 Å).

Acknowledgment. Financial support from Knut och Alice Wallenbergs Styftelse (Knut and Alice Wallenberg Foundation) and Vetenskapsrådet (VR) in Sweden is gratefully acknowledged. The University of Pittsburgh group thanks the II-VI Foundation for partial support of this research.

References

[1] A. Gali *et al.*, Phys. Rev. B 68 (2003) 125201.
[2] A. Mattausch, M. Bockstedte, and O. Pankratov, Phys. Rev. B 70 (2004) 235211.
[3] G.A. Evans *et al.*, Phys. Rev. B 66 (2002) 035204.
[4] J.W. Steeds and W. Sullivan, Phys. Rev. B 77, 195204 (2008).
[5] F. Yan *et al.*, Mat. Sci. Forum Vols 645-648 (2010) 411-414.
[6] J.W. Steeds, W. Sullivan, S.A. Furkert, and G.A. Evans, Phys. Rev. B 77 (2008) 195203.
[7] M. Bockstedte *et al.*, phys. stat. sol. (b) 245 (2008) 1281-1297.