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Dynamics of the nitrogen-bound excitons in 6*H* SiC

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We have measured the photoluminescence decay time of the *P*, *R*, and *S* bound excitons at the neutral nitrogen donors in 6*H* SiC using picosecond pulsed excitation. At 2 K the decay times are 8.0, 1.8, and 1.5 ns, respectively, which are significantly faster than previously reported values for shallow donors in other indirect-band-gap materials such as Si or GaP. Each of the observed decay times is found to be independent of the doping level in the sample, and also temperature independent at low temperatures, but decreases when the bound excitons are thermally ionized. The decay time related to different donors exhibits a strong dependence on the binding energy of the donor level. We suggest that the dominating mechanism responsible for the observed decay time is a phononless Auger process. In high-purity samples we have also measured the free-exciton decay time at low temperatures to be 12 ns.

INTRODUCTION

The growing interest in SiC during recent years is due to its potential as a material for high-performance devices in optoelectronic, high-temperature, high-frequency, and power applications. By recent efforts and achievements in crystal growth it is now possible to produce both epitaxial and bulk SiC material of high quality. SiC is also interesting as a model material for fundamental studies. The possibility to produce high-quality material of several different polytypes, which all have different band structures (and thus different band gaps ranging from 2.3 eV for 3*C* to 3.3 eV for 2*H*) makes it possible to study the behavior of fundamental electronic properties as well as properties of defects, in a way not possible in other semiconductor materials.

Today the technologically most mature polytype is 6*H* SiC, which has a band gap of about 3.0 eV at 4 K. In this paper we focus on nitrogen, the most common impurity in 6*H* SiC. In 6*H* SiC there are three inequivalent carbon sites, one hexagonal (*h*) and two cubic (*c*1 and *c*2) sites. Nitrogen atoms occupying substitutional carbon sites will therefore give rise to three different donor levels in the band gap. The energy positions of these levels have recently been determined by infrared absorption spectroscopy to be 81.0 meV (*h*), 137.6 meV (*c*1), and 142.4 meV (*c*2) below the conduction-band level.[1]

The near-band-gap low-temperature photoluminescence (PL) spectrum of *n*-type 6*H* SiC is normally dominated by sharp lines due to the recombination of excitons bound at these nitrogen donors (Fig. 1). The no-phonon (NP) lines of the donor-bound excitons (DBE's) associated with nitrogen are usually labeled P_0, R_0, and S_0. The recombination energies at 2 K are 3.0070 eV (4122 Å), 2.9924 eV (4142 Å), and 2.9906 eV (4144 Å),[2] respectively, and correspond to DBE binding energies of 16.0, 30.6, and 32.4 meV, when the free-exciton (FE) band gap is taken as 3.023 eV.[3] At slightly lower photon energies in Fig. 1 the phonon replicas of the P_0, R_0, and S_0 lines are shown. The dominant replicas are labeled in accordance with Ref. 4.

In this paper we present decay measurements of the different nitrogen-related DBE's in the 6*H* polytype of SiC. To our knowledge no time-resolved measurements of these DBE's have previously been published. However, in other indirect-band-gap materials such as Si (Ref. 5) and GaP (Ref. 6), similar DBE's have been investigated. These results all showed measured decay times less than microseconds, which are several orders of magnitude faster than expected for a radiative recombination of the exciton in an indirect-band-gap material. The observed decay time has instead been attributed to a phononless Auger recombination[5–7] of the DBE.

EXPERIMENT

A series of 6*H* SiC samples with doping concentration varied from as low as 10^{14} up to 2×10^{18} cm^{-3} has been

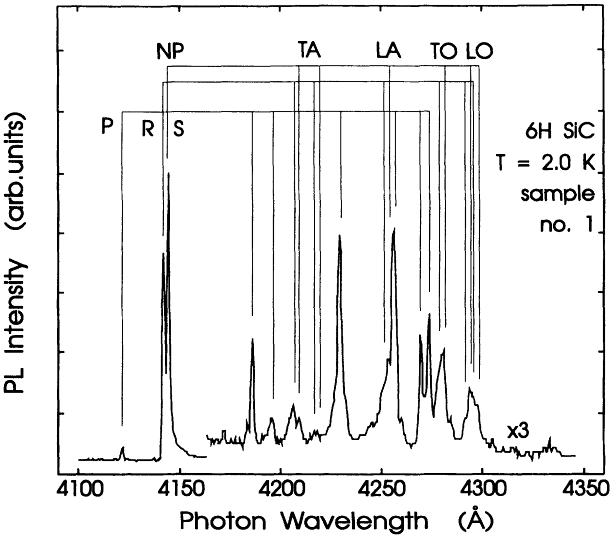

FIG. 1. PL spectrum at 2.0 K from the band-gap region of 6*H* SiC, measured in sample 1. The spectrum is dominated by exciton emission related to the *P*, *R*, and *S* nitrogen-bound excitons.

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TABLE I. A compilation of properties for the different 6*H* SiC samples used in this study. The notations are explained in detail in the text.

Sample	1	2	3	4	5	6	7
Substrate	M-Lely	M-Lely	M-Lely	M-Lely	M-Lely	Lely	M-Lely
Grade	research	research	production	research	research		research
On-/Off-axis	off	off	off	on	off	on	off
Doping n (cm^{-3})	1×10^{18}	2×10^{18}	2×10^{18}	4.4×10^{17}	2×10^{18}	$(1-2)\times10^{18}$	2×10^{18}
Epilayer	Cree						LiU
Thickness (μm)	10						10
Doping (cm^{-3})	1.7×10^{16}						$<5\times10^{14}$

used in this study. Two types of substrates were used: wafers from Russia grown by a nonseeded Lely method (Lely),[8] and wafers from Cree Research, U.S.A., grown by a seeded modified Lely method (M-Lely).[9] The latter were either of research grade (*R*) or production grade (*P*) and prepared either on- or off-axis. The epitaxial layers were either grown by Cree research or prepared for the present work (LiU).[10] The characteristics of the samples are summarized in Table I.

The PL and PL time-resolved measurements were performed using pulsed excitation from a dye laser synchronously pumped by a mode-locked Ar$^+$ laser. The pulses, with a width of < 10 ps and a photon wavelength about 7400 Å, were frequency doubled with a LiIO$_3$ crystal, producing excitation at about 3700 Å (3.5 eV). The frequency-doubled average power was of the order of 1 mW, while the repetition frequency was varied with a cavity dumper between 1 and 10 MHz depending on the decay time of the PL. Some PL spectra were also obtained with continuous-wave (cw) excitation using the uv lines from an Ar$^+$ laser.

The PL was dispersed with a 0.6 m double monochromator. The time decays were measured with a time-correlated photon-counting system with a total time resolution better than 200 ps.

EXPERIMENTAL RESULTS

The PL spectrum from a typical 6*H* SiC sample (1) obtained with cw excitation is shown in Fig. 1. The spectrum is dominated by the recombination of nitrogen-bound excitons. In addition, each exciton has a corresponding spectrum of phonon replicas involving the TA (46.3 and 53.5 meV), LA (77.0 meV), TO (95.6 meV), and LO (104.2 and 107.0 meV) phonons. The decay time of the three different excitons has been measured separately at 2.0 K and is found to be 1.5±0.1, 1.8±0.1, and 8.0±0.5 ns, for the *S*, *R*, and *P* exciton, respectively. The decay curves are shown in Fig. 2. The larger experimental error for the *P* exciton is related to difficulties in evaluating the slower and weaker signal from this exciton, which at the same time has a spectrally overlapping contribution from the faster *R* and *S* excitons. The presented value of the decay time of the *R* and *S* DBE's was measured with detection at the recombination wavelength of the NP line, while the value for the *P* exciton was measured in the strongest phonon replica (LA, 77.0 meV) since the NP line has much lower intensity. The measured decay times do not differ between samples with different doping levels.

The energy difference between the *R* and *S* excitons is relatively small (1.8 meV) and can only be resolved using high spectral resolution. To gain intensity we preferred in most measurements lower spectral resolution. The combined signal is here called the PL in the RS exciton. The observed decay times in these samples are, within the experimental errors, an average of the decay times from the *R* and *S* excitons separately.

We have measured the decay also in the NP line of the *P* exciton as well as in different phonon replicas of all the three excitons. As expected, the same value for the decay time in the NP line and in all related phonon replicas is observed. This can in fact be used to separate the sometimes overlapping phonon spectrum related to the *RS* and *P* excitons (see Fig. 3).

The decay time as a function of temperature is shown in Fig. 4. The measured decay time is found to be constant up to a certain temperature where it decreases rap-

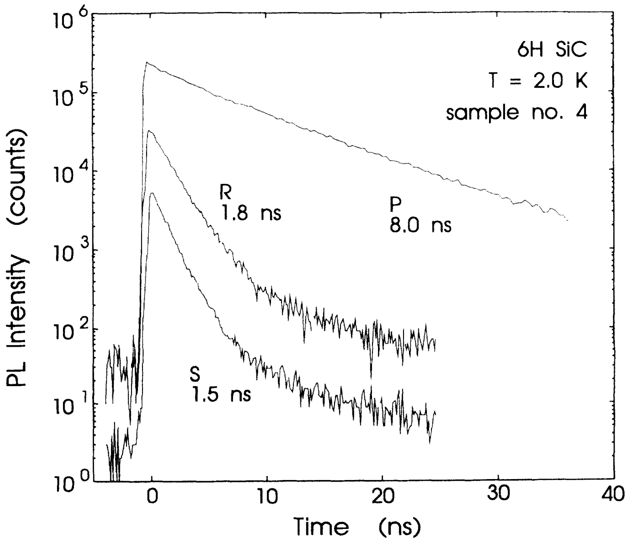

FIG. 2. Measured decay curves at 2.0 K for the *P*, *R*, and *S* bound excitons in 6*H* SiC. The corresponding decay times are shown for each curve.

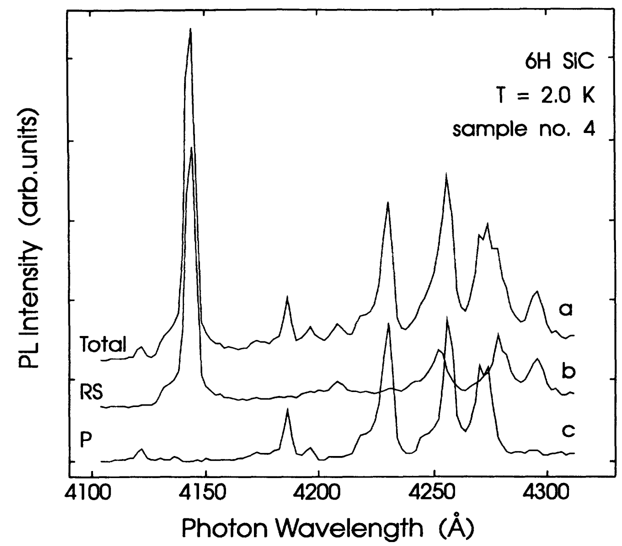

FIG. 3. Time-resolved spectra of SiC sample 4 using pulsed excitation. Curve *a* is the total time-integrated spectrum. Curves *b* and *c* are the spectral components corresponding to the emission from the *RS* and *P* excitons, obtained by a deconvolution of the decay curve at each wavelength position.

idly. This can most simply be described with the introduction of an additional temperature-activated nonradiative recombination channel. The experimentally expected decay time τ_m is then expressed as

$$\tau_m = \left[\frac{1}{\tau_{\mathrm{BE}}} + \frac{1}{\tau_{\mathrm{NR}}} \exp^{-\Delta E / k_B T} \right]^{-1} , \tag{1}$$

where τ_{BE} is the decay time of the DBE, τ_{NR} the decay time of the nonradiative channel for the DBE, and ΔE the activation energy. This model gives good agreement with the experimental values obtained from a highly doped sample such as no. 3, as shown by the solid line in Fig. 4. The line corresponding to the *RS* exciton shows the best fit of the experimental values with Eq. (1), using ΔE and τ_{NR} as variational parameters. The obtained activation energies of 30.2 and 15.3 meV for the *RS* and *P* excitons are very close to the corresponding DBE binding energy. From this we draw the conclusion that the DBE in this sample is thermally released as FE's. The expression above is valid under the assumption that the nonradiative recombination of the upper level, assumed to be the FE, is faster than the capture to the donors. In this case no recapture back to the DBE occurs. This assumption is reasonable since the FE is not observed at all in the PL spectrum in these samples.

The same good fit using Eq. (1) is not possible for a lower-doped sample as shown in Fig. 4 where the decay times for the *RS* and *P* excitons in sample 4 are represented by unfilled squares. There we expect the effective FE decay time to be longer, and that the process of recapture will be of importance. The interaction between the FE and the DBE can also be observed in sample 7, which is a high-purity epitaxial layer.[10] In this low-doped sample, the nonradiative recombination is less efficient, giving a longer lifetime of the FE, which makes it possible to observe PL recombination from the FE, as seen in Fig. 5. The PL spectrum is dominated by the different phonon replicas related to the FE. The NP line of the FE is not observed in SiC since the band gap is indirect. Figure 6 shows the decay curve of the FE measured at 2.0 K, where the decay time is found to be 12 ns.

Also shown in Fig. 6 is the decay curve of the *RS* DBE in the same sample. This decay curve has two com-

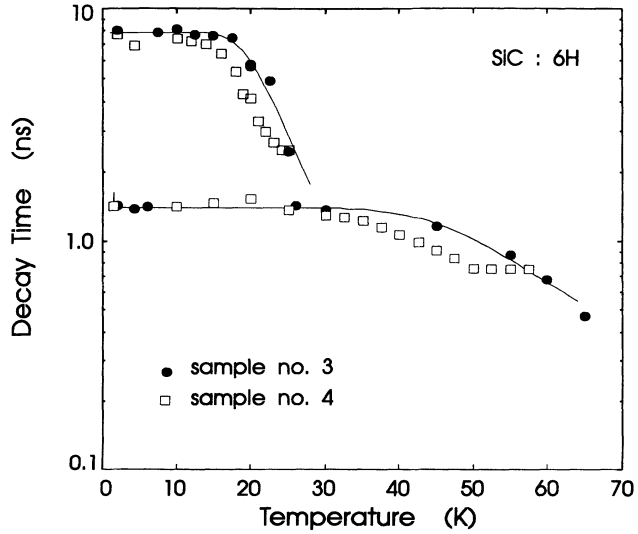

FIG. 4. Measured decay time as a function of temperature for the *RS* and *P* nitrogen-bound excitons in two different 6*H* SiC samples. The solid lines correspond to the best fit of the decay times in sample 3 according to Eq. (1).

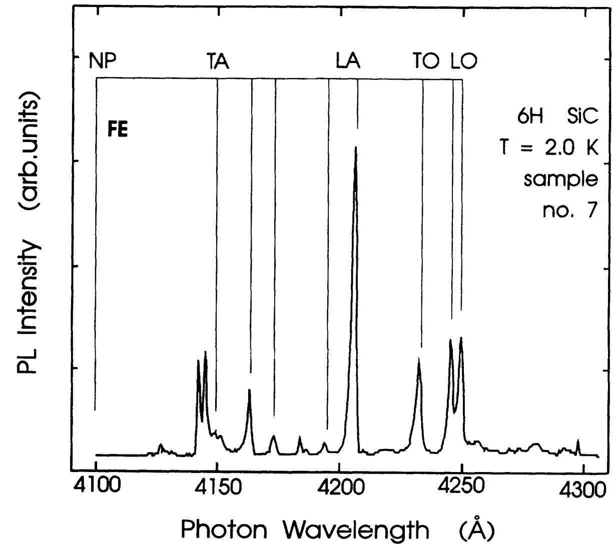

FIG. 5. Photoluminescence spectrum of sample 7, measured at 2.0 K with cw laser excitation. The PL in this low-doped sample is dominated by FE recombinations. The lines show the positions of the no-phonon line and most dominant phonon replicas related to the FE. Several of the replicas are overlapping with phonon replicas related to DBE's.

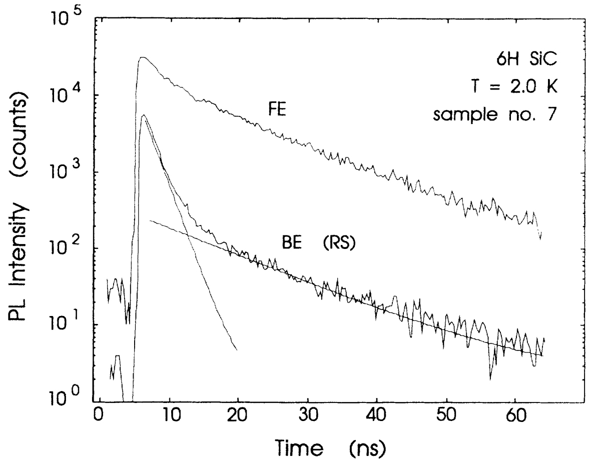

FIG. 6. Decay curves of the FE and the *RS* DBE in sample 7. The sample temperature is 2.0 K. The decay time of the FE is 12 ns. The slow (12 ns) and fast (1.5 ns) components of the *RS* decay are shown with solid lines.

ponents, where the slower decay is identical to the FE decay. This reflects the fact that the DBE is formed by capture of a FE to the neutral nitrogen donor. The creation of DBE's will continue as long as FE's exist, and, since the recombination time of the DBE is faster (1.5 ns), the observed lifetime will be determined by the lifetime of the FE population. The faster component seen in the *RS* decay curve has exactly the decay time of 1.5 ns normally observed in higher-doped samples.

The fact that we would observe this fast component is not obvious, but it can have two possible causes. First, the DBE may be formed directly from free carriers created with excitation above the band gap. The observed decay is then dominated by the normal (1.5 ns) recombination of the initially created bound-exciton population, with the additional slow component due to the capture of the FE's at the defects. The second possibility is that the two components originate from different layers, if the penetration depth of the laser excitation is longer than the thickness of the epitaxial layer. The faster component is then interpreted as being due to recombinations in the high-doped substrate, while only the slower component is coming from the epitaxial layer.

DISCUSSION

The observed values for the decay time are considerably faster than expected for a radiative recombination in a semiconductor with an indirect band gap like SiC. It seems obvious that a nonradiative recombination is the dominating mechanism that reduces the BE population. We observe the same decay time in samples with different doping. The decay time is, furthermore, independent of temperature and decreases with increasing DBE binding energy.

Our results can only be explained assuming the dominating recombination mechanism to be a phononless Auger process.[5–7] The donor-bound exciton consists originally of three particles (or four if the nitrogen "core" is included), two electrons and one hole. In the Auger process one of the electrons recombines with the hole, leaving the excess energy and momentum to the second electron. This electron, labelled as the Auger particle, is then excited up into the conduction band with an energy close to the band-gap energy and with an additional wave vector determined by the separation of the electron and hole in momentum space.

In 6*H* SiC the hole is located at the valence-band top, which is located at the Γ point in the zone center, whereas the electrons are located in the conduction-band minimum assumed to be at or close to the *M* point at the zone edge. This means that the Auger electron receives an additional wave vector corresponding to the difference in momentum space between the band minima, and that the final state of the Auger electron in *k* space will be in the vicinity of the zone center. Existing band-structure calculations[11] show that the band gap in the Γ point is close to or larger than twice the minimum indirect band gap. The exact value of the zone-center band gap is in this case very important, since the recombination rate is strongly dependent on whether the final state of the Auger particle is located below or above the Γ-point band gap. According to our measurements the recombination process is very fast (in the low nanosecond range) and we thus conclude that the direct band gap is less than twice the indirect band gap.

The nitrogen donor levels in 6*H* SiC are relatively deep, causing a strong localization for mainly the primarily bound electron. This will consequently lead to a delocalized wave function in *k* space and a larger possibility for contributions to the Auger recombination rate for final-state wave vectors different from $k=0$. This is further demonstrated by the observed decrease in decay time with increasing energy for the three nitrogen donor levels. Similar relationships have earlier been observed for DBE's in Si and GaP.[5,12]

SUMMARY

We have measured the decay time of the recombination of excitons bound at the neutral nitrogen donor in a series of 6*H* SiC samples. We have found very fast decay times at low temperatures with values of 1.5, 1.8, and 8.0 ns for the *S*, *R*, and *P* DBE's. The observed decay time is independent of temperature, at low temperatures, and independent of the doping level in the sample. We have also observed a strong relation between the decay time and the energy of the corresponding donor level, with a decrease of the decay time with increasing donor energy. From our experimental results we conclude that the dominating recombination mechanism is a phononless Auger process.

In low-doped samples, where the FE is present in PL, we have found that the observed decay time of the DBE recombination is determined by the lifetime of the FE and not by the recombination rate of the Auger process.

We have furthermore concluded that the direct band gap at the zone center must be less than twice the indirect band gap to account for the fast Auger recombination process.

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