Photoluminescence upconversion in 4H–SiC

Mt. Wagner,[a] I. G. Ivanov, L. Storasta, J. P. Bergman, B. Magnusson,[b] W. M. Chen, and E. Janzén
Department of Physics and Measurement Technology, Linköping University, SE-581 83 Linköping, Sweden

(Received 23 April 2002; accepted 12 August 2002)

Efficient photoluminescence upconversion is observed in 4H–SiC samples containing both the UD-3 defect and the titanium impurity. In this process, the titanium photoluminescence emission with no-phonon (NP) lines at 2.848 eV (A_0) and 2.789 eV (B_0) can be excited by tuning the laser to the NP line of UD-3 at 1.356 eV. In samples containing either only UD-3 or only titanium, a different photoluminescence upconversion process can be observed, which occurs at photon energies higher than ~1.5 eV without exhibiting sharp features. At least one of the two processes generates both free electrons and free holes and can, therefore, be a candidate for an important recombination channel. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1511813]

Photoluminescence (PL) upconversion has been reported in several semiconductors and is usually associated with two-stage transitions via deep-level defects, which are important for carrier recombination. These defects can be intrinsic like the EL2 defect in GaAs (Ref. 1) or impurities like chromium in GaP.[2] In SiC, observation of a photoluminescence system at photon energies higher than the laser energy has been reported upon excitation with the 488 nm line of an Ar^+ laser.[3] In addition, two-photon absorption spectra have been obtained in 6H–SiC both directly[4] and via associated thermoluminescence.[5]

SiC is a promising material for future devices, mainly for high-temperature, high-power, and high-frequency applications. A thorough understanding of the properties of intentionally or unintentionally introduced defects is mandatory for achieving reproducibly high material quality. However, many defects are still poorly understood. In particular, the role of deep-level defects for minority carrier recombination should be investigated carefully. The upconversion processes we report on here may be important in this context since the defect(s) involved in the upconversion may also constitute an efficient recombination channel.

Two different photoluminescence upconversion processes in 4H–SiC are presented in this letter. In semi-insulating samples containing both the UD-3 defect[6] and the titanium impurity, excitation of the titanium related luminescence via UD-3 was found to be very efficient. Samples, in which either the UD-3 defect or the titanium impurity is missing, exhibit a different kind of upconversion with greatly reduced efficiency.

A series of several bulk semi-insulating 4H–SiC samples grown by the high temperature chemical vapor deposition (HTCVD)[7] technique was used in this study. In addition, one commercially available semi-insulating 4H substrate grown by physical vapor transport (PVT)[8] has been investigated.

In PL, PL excitation (PLE), photoconductivity, and photo-Hall experiments, the 351 nm line of an Ar^+-ion laser was used for above band-gap excitation and a Ti:sapphire laser tunable between 700 and 1000 nm was employed for below band-gap excitation. The resulting luminescence was spectrally dispersed with a monochromator and detected with a photomultiplier tube, a silicon avalanche photodiode, or a GaAs photomultiplier in photon counting mode. Time resolved PL-decay measurements were performed using the second harmonics ($\lambda = 530$ nm) from a diode pumped pulsed YAG laser. The signal was detected with an IR sensitive photomultiplier tube and recorded using photon counting techniques.

Photoconductivity and Hall measurements were performed in the van der Pauw configuration. Ohmic contacts were prepared by growing a thin (typically 200 nm) n^+-CVD layer (typical nitrogen doping 1×10^{19} cm^{-3}) on top of the sample. CVD growth was performed at a temperature of 1600 °C and a pressure of 1 atm, resulting in a growth rate of 2 μm/h. The growth time was 6–8 min. TiPtAu metal contacts were patterned on top of the n^+-layer using lithography and were annealed at 500 °C.

The UD-3 defect gives rise to one no-phonon (NP) PL line at 1.356 eV in 4H–SiC. The defect has the symmetry of a substitutional lattice site (C_{3v}), and the radiative transition occurs between a ^1E excited state and a $^1A_1$ ground state. The chemical identity of the defect is not clear at this point. Details of the UD-3 emission are presented separately.[9] Figure 1(a) shows a PLE spectrum at $T = 2$ K with the detection energy fixed to UD-3. The lines V1 and V1′ originate from the emission of the silicon vacancy overlapping with the UD-3 emission. The silicon vacancy is not involved in the PL upconversion.

Upon resonant excitation at UD-3, its excited states, or the phonon replicas, samples containing both UD-3 and titanium emit bright green light. This emission is due to the well known titanium related luminescence[10,11] with NP lines at 2.848 eV (A_0) and 2.789 eV (B_0) and a broad phonon-assisted sideband with peak energy at 2.45 eV. PL spectra are shown in Fig. 2(a) under above band-gap excitation and under excitation at UD-3 (1.356 eV). In order to prove that the apparent photoluminescence upconversion in Fig. 2(a) is truly related to the UD-3 defect, another PLE scan was ob-

[a]Electronic mail: matwa@ifm.liu.se
[b]Also at Okmetic AB, SE 583 30 Linköping, Sweden.

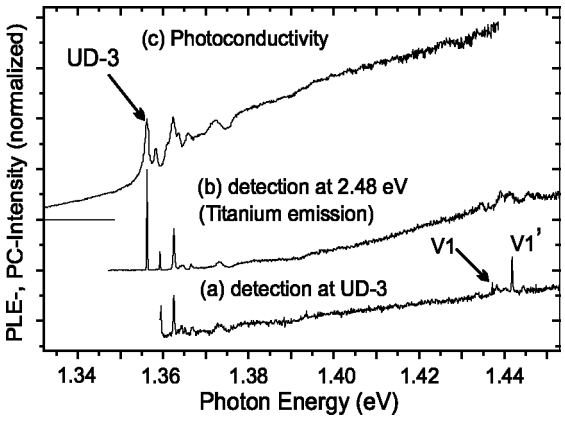

FIG. 1. PLE spectra in 4H–SiC (a) detecting the UD-3 emission at 1.356 eV ($T=2$ K), and (b) detecting the titanium emission at 2.48 eV ($T=8$ K). The lines V1 and V1′ in spectrum (a) originate from the emission of the silicon vacancy overlapping with the UD-3 emission. The silicon vacancy is not involved in the PL upconversion; (c) excitation spectrum of the photoconductivity at $T=20$ K.

tained detecting the peak energy of the titanium emission at 2.48 eV [Fig. 1(b)].

The efficient photoluminescence upconversion process was observed in all samples containing both UD-3 and titanium. In one HTCVD grown sample, the UD-3 emission and the upconversion process via UD-3 were not observable. The PVT grown sample does contain UD-3. However, the titanium emission cannot be detected, and the efficient upconversion process is absent. Visible PL due to the titanium emission in the HTCVD sample and a donor–acceptor pair (DAP) recombination centered at 2.93 eV in the PVT sample are, however, still observable under excitation with photon energies lower than the emission, but only with the highest available power density (~ 80 W/cm^2). This represents a different photoluminescence upconversion process, in which the signals apparently disappear for photon energies smaller than ~ 1.5 eV without exhibiting sharp features (Fig. 3). This is consistent with the threshold energy of 1.56 eV reported for thermoluminescence in 6H–SiC.[5] It is therefore quite probable that the same physical process is responsible for both excitation of the thermoluminescence and the second photoluminescence upconversion observed here. It is quite likely that this second upconversion process is also present in the samples containing both UD-3 and titanium, but is obscured by the dominant features due to UD-3.

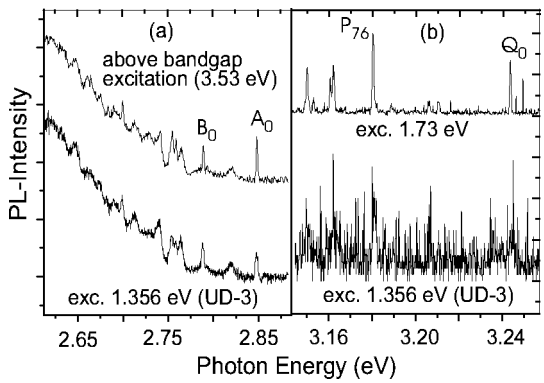

FIG. 2. (a) Titanium PL emission in 4H–SiC at $T=2$ K excited with above band-gap laser light (upper spectrum), and excited resonantly on the NP line of UD-3 at 1.356 eV (lower spectrum). (b) Near-band-gap emission at $T=2$K in 4H–SiC excited with infrared laser light at 1.73 eV (upper spectrum) and resonantly at UD-3 (lower spectrum).

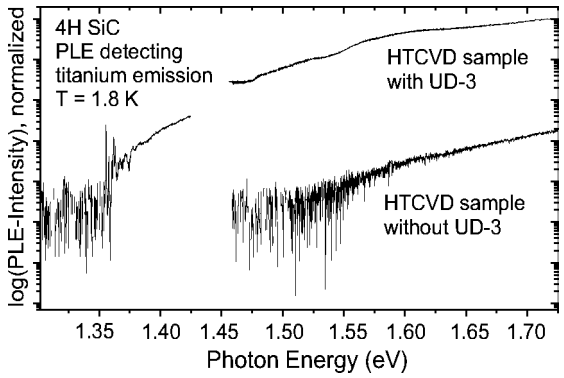

FIG. 3. PLE spectra detecting the titanium emission in 4H–SiC at $T=1.8$ K. Upconversion via UD-3 dominates in the sample containing UD-3. In the sample, in which UD-3 cannot be observed, the second upconversion process is found at energies higher than ~ 1.5 eV without exhibiting any sharp features.

Under above band-gap excitation, several lines due to recombination of free and nitrogen-bound excitons can be observed in all 4H–SiC samples investigated. These lines are also clearly present under IR excitation at 1.73 eV [Fig. 2(b), upper spectrum]. However, when the Ti:sapphire laser is tuned to UD-3, this near-band-gap emission is barely visible [Fig. 2(b), lower spectrum]. At this point, due to the extremely weak PL signal strength, it is not clear whether the excitons are resonantly excited via UD-3 in a similar way as the titanium emission or whether the tail of the second upconversion process extends down to the energy of UD-3.

In order to elucidate the excitation processes underlying the upconversion, photoconductivity (PC) experiments were performed at low temperature (5 and 20 K). The PC excitation spectra [Fig. 1(c)] resemble the PLE results. In particular, sharp transitions due to UD-3 and its excited states are observed. No difference in the relative intensities of the peaks are found between 5 and 20 K. The only difference in PC compared to PLE is the presence of an unstructured background photocurrent extending to energies below UD-3. Probably shallow levels not related to UD-3 contribute to the photoconductivity in this range.

In order to observe sharp transitions in PC experiments, a second step from the excited state of UD-3 to the valence or conduction band must be involved. The energy for this step can be supplied either thermally or optically. Thermal activation from an excited state to the conduction band has been reported for the shallow nitrogen donor in photothermal ionization spectroscopy (PTIS).[12] In this case, the relative intensities of the peaks due to the various excited states depend on measurement temperature. Excited states at greater distance to the band edge become visible at elevated temperatures. This is not the case in our experiments as the observed excited states of UD-3 are far from the band edge.[9] An alternative model explaining the sharp transitions involves a two-step excitation via the excited state of UD-3. In this model, a carrier is first excited into this state and then transferred into the band. Such a process can only be efficient if the lifetime of the excited state is quite long and the lifetime of UD-3 was found to be ~ 50 μs at $T=1.8$ K.

Hall experiments revealed that the main contribution to the photocurrent seems to be due to photoexcited electrons. No contribution of the holes could be observed, which may be due to their lower mobility compared to the electrons.

A surprising feature of the efficient photoluminescence upconversion process is that the highest lying NP line A_0 at 2.848 eV of the titanium emission has an energy larger by 136 meV than two times that of UD-3 (1.356 eV). This difference cannot be accounted for by any thermal process at the low temperatures used in the experiments (down to 1.8 K). Therefore, it must be assumed that three photons are absorbed in the upconversion process. Such a three-photon excited PL signal with near cubic power dependence has recently been reported in GaN.[13] In our experiments, the power dependence is $I \sim P^{\gamma}$ with $\gamma \approx 2.5$ at low laser powers. The coefficient γ decreases with increasing power and becomes consistent with the value found in the photoconductivity experiments ($\gamma \approx 1.5$).

In at least one of the two upconversion processes reported here, free electrons and holes are created as evident from the observed near-band-gap emission. One possible three-step upconversion process consists of a deep-level defect with one charge state in the band gap, e.g., $0/+$. When the level is empty, an electron can be transferred from the valence band to this level. The next photon excites the defect into a metastable excited state. In this long-lived state, the electron can absorb another photon and end up in the conduction band, with the defect returning into its original charge state. The reverse process is also possible; it may, therefore, constitute an important recombination channel.

At this point, it is not clear whether the efficient upconversion process involving UD-3 is of the same nature since this process is apparently absent in the PVT sample even though it contains UD-3. A direct charge transfer process between UD-3 and titanium cannot be excluded. Further investigations are necessary to clarify this point.

In summary, two different photoluminescence upconversion processes have been observed in 4H–SiC. In samples containing both the UD-3 defect and the titanium impurity, an efficient upconversion process via UD-3 has been found. The existence of both defects may be required for the process to occur, indicating a possible direct link between the two defects in the process. The second upconversion process occurs at photon energies higher than ~ 1.5 eV without exhibiting sharp features. It is present in all the samples studied, which do not show the first upconversion process. The observation of the near-band-gap emission indicates creation of free electrons and holes in at least one of the two upconversion processes, showing its possible role as an important recombination channel via the defects involved.

The authors would like to thank Okmetic AB for kindly supplying the samples used in this study and Thales for help with sample processing.

[1] E. J. Johnson, J. Kafalas, R. W. Davies, and W. A. Dyes, Appl. Phys. Lett. **40**, 993 (1982).
[2] B. Clerjaud, F. Gendron, and C. Porte, Appl. Phys. Lett. **38**, 212 (1981).
[3] J. W. Steeds, F. Carosella, G. A. Evans, M. M. Ismail, L. R. Danks, and W. Voegeli, Mater. Sci. Forum **353–356**, 381 (2001).
[4] M. P. Lisitsa, N. R. Kulish, and A. V. Stolyarenko, Fiz. Tekh. Poluprovodn. (Leningrad) **14**, 2037 (1980) [Sov. Phys. Semicond. **14**, 1208 (1980)].
[5] O. V. Vakulenko and B. M. Shutov, Fiz. Tekh. Poluprovodn. (Leningrad) **12**, 1013 (1978) [Sov. Phys. Semicond. **12**, 603 (1978)].
[6] E. Janzén, A. Henry, J. P. Bergman, A. Ellison, and B. Magnusson, Mater. Sci. Semicond. Process. **4**, 181 (2001).
[7] A. Ellison, B. Magnusson, C. Hemmingsson, W. Magnusson, T. Iakimov, L. Storasta, A. Henry, N. Henelius, and E. Janzén, Mater. Res. Soc. Symp. Proc. **640**, H1.2.1 (2001).
[8] S. G. Müller, R. C. Glass, H. M. Hobgood, V. F. Tsvetkov, M. Brady, D. Henshall, J. R. Jenny, D. Malta, and C. H. Carter, Jr., J. Cryst. Growth **211**, 325 (2000).
[9] Mt. Wagner, B. Magnusson, W. M. Chen, and E. Janzén, Phys. Rev. B (to be published).
[10] D. R. Hamilton, W. J. Choyke, and L. Patrick, Phys. Rev. **131**, 127 (1963).
[11] L. Patrick and W. J. Choyke, Phys. Rev. B **10**, 5091 (1974).
[12] C. Q. Chen, J. Zeman, F. Engelbrecht, C. Peppermüller, R. Helbig, Z. H. Chen, and G. Martinez, J. Appl. Phys. **87**, 3800 (2000).
[13] C. K. Lee, F. K. Kao, S. C. Wang, and C. L. Pan, Jpn. J. Appl. Phys., Part 1 **40**, 6805 (2001).