Direct Determination of the Electron-Electron-Hole Auger Threshold Energy in Silicon

W. M. Chen, B. Monemar, and E. Janzén
Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden

A. M. Frens, M. T. Bennebroek, and J. Schmidt
Department of Physics, Huygens Laboratory, University of Leiden, P.O. Box 9504, 2300 RA Leiden, The Netherlands
(Received 27 June 1994)

The threshold energy E_a for the electron-electron-hole (eeh) Auger recombination process in silicon is determined, for the first time, by a novel experimental approach. The E_a value of 5 meV obtained for the defect-mediated eeh Auger process is shown to be the upper limit for E_a in the case of the intrinsic eeh Auger process. This provides direct experimental evidence that the eeh Auger threshold energy in silicon is indeed very small, and consequently this Auger process must be dominated by the direct (phononless) mechanism.

PACS numbers: 72.20.Jv, 71.25.Rk

The physical processes of carrier recombination in semiconductors are of fundamental importance, since they determine carrier lifetimes in a variety of devices. The most important recombination processes are known as such [1], but even in our most commonly used semiconductor, i.e., silicon, the recombination process governing the carrier lifetime in a specific sample or device is in general unknown, in spite of intense studies over the last four decades. This is true for both intrinsic and extrinsic (i.e., impurity- or defect-related) mechanisms.

An important recombination process is the Auger process, where two carriers recombine, giving the released energy to the third particle which is excited into a higher energy state. Such processes are assumed to be commonly occurring in semiconductors [1], in bulk [1,2] as well as in quantum structures [3,4]. Both intrinsic and defect-related processes are important [1]. The intrinsic Auger process in n-doped silicon has recently attracted considerable attention theoretically [5,6], motivated by the assumption that this process is dominating carrier recombination in many important devices such as power devices under high injection levels.

The primary intrinsic and defect-mediated Auger recombination process in n-silicon, the electron-electron-hole (eeh) process, is depicted in Fig. 1 in the extended Brillouin zone scheme. In the case of moderate defect concentrations, both energy and momentum are assumed to be conserved in the process. This requirement will in general lead to a threshold kinetic energy E_a for the carrier in the band [and also for the free exciton (FE) when the electron-hole correlations are taken into account [6]]. Above this threshold E_a the Auger transition is possible without phonon participation (Fig. 1). For the eeh process in silicon E_a is expected to be quite small, in the range 0–50 meV, from the knowledge of the band structure [7]. The value of E_a is very important, since it determines whether a direct or indirect (phonon-assisted) Auger process will dominate, the latter assumed to be considerably weaker than the former [5]. Clearly, if the average energy of the electrons in the conduction band (and also FEs) exceeds E_a at a specific temperature and carrier injection level, a direct Auger process will dominate.

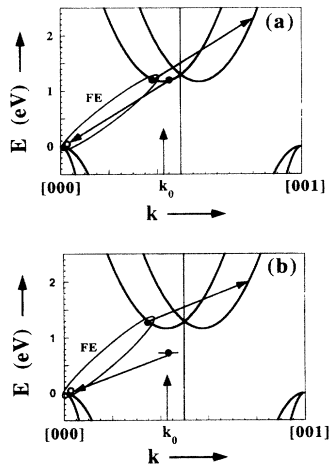

FIG. 1. Schematic diagrams for the intrinsic (a) and defect-mediated (b) excitonic eeh Auger recombination process in silicon in the **k** space. See text for the definition of the notations. The binding energy of the defect is exaggerated for clarity.

Unfortunately no direct spectroscopic determination of E_a in silicon has so far been demonstrated, and existing experimental data used to obtain indirect information of the nature of the Auger process have offered conflicting conclusions as to whether the eeh Auger process in silicon is direct or indirect (phonon assisted) [8]. Band structure calculations lack the accuracy needed (on a few meV scale) for determination of E_a in this case. The most recent calculations of the eeh Auger rate at room

 0031-9007/94/73(24)/3258(4)$06.00

temperature assume a direct process [5], which is relevant if E_a is indeed small.

In this Letter, we apply a novel experimental approach such that the eeh Auger process can be selectively studied. The success of the new experimental approach is greatly attributed to our recent discovery of the excitonic Auger process as the dominant processes inducing configurational changes of a metastable defect in silicon [9]. For the particular defect studied, a S-Cu-related complex defect in silicon, the eeh Auger process was shown to govern the conversion of the defect from its stable configuration to the metastable configuration. This is despite the fact that the eeh Auger process is by far not the dominant mechanism in carrier recombination in the lightly doped samples studied. By measuring the conversion rate as a function of the excitation photon energy, E_a can be determined directly, as will be demonstrated below.

The samples used were from a single crystal silicon wafer, grown either by the Czochralski (Cz) or by the float-zone (FZ) method. They were originally either undoped or lightly n- or p-type doped. The sulphur doping was done either by a high temperature diffusion process at (1000–1200) °C or by ion implantation followed by a high temperature annealing. A postannealing was then carried out at about 800 °C for a few seconds, followed by a rapid thermal quenching to room temperature [10].

Two independent experiments were carried out, one by using a cw laser and the other by using a pulsed laser; both are tunable over the spectral range close to the silicon band gap. The photoluminescence (PL) experiments with the cw laser were carried out in an Oxford ESR-10 continuous flow He cryostat, where the sample temperature could be varied from room temperature down to 4 K. A cylindrical TE_{011} X-band microwave cavity, with optical access from all directions, was incorporated with the optical cryostat for contactless microwave photoconductivity measurements. A coherent Ti:sapphire cw tunable laser with the near infrared (930–1100 nm) mirror set was used as the optical excitation source. The PL emissions from the samples were first dispersed by a Jobin-Yvon 0.25-m grating monochromator and then collected by a cooled Ge detector. The PL experiments with the pulsed laser were performed with the sample immersed in liquid helium at 3.1 K. The pulsed laser was generated by pumping a Spectra Physics PDL-3 dye laser, operating with Rhodamine-590, by the frequency doubled output of a Spectra Physics GCR-3 Nd:YAG laser (530 mJ/pulse, 10 Hz at 532 nm). The output of the dye laser is focused into a Raman shifter (RS) filled with H_2 gas at a pressure of 40 bars. By taking the second Stokes-shifted output of the RS we obtain pulsed infrared radiation (10 Hz, 1 mJ/pulse) in the range of 1087.5 to 1024.6 nm. PL was dispersed by a 1-m Spex 1704 monochromator and subsequently detected by a cooled Ge detector.

Upon above band-gap optical excitation, the samples give rise to two characteristic PL emissions S_A and S_B, with the zero-phonon line S_A^0 at 0.968 eV and S_B^0 at 0.812 eV at 4 K [10,11], respectively. These two PL emissions arise from bound exciton recombination at the S-Cu defect in two configurations, i.e., S_A from the stable configuration and S_B from the metastable configuration. The excitonic Auger process [9] converts the defect from the stable to the metastable configuration, evident from a decrease of the S_A PL intensity and a corresponding increase of the S_B PL intensity with the photoexcitation above the FE energy. The released Auger electron can be monitored by a persistent photoconductivity.

The detailed nature of the Auger process involved is in fact a genuine eeh Auger process (see Fig. 1), where the hole of the FE annihilates the electron at the negatively charged S-Cu defect, and the released energy is given to the third particle (i.e., the electron of the FE) which is excited high up in the conduction band. The excess energy of the Auger electron thereafter promotes the configurational change of the defect [9]. Therefore the eeh Auger process can now be conveniently singled out from the other processes if only the configuration conversion process of the S-Cu defect is monitored. The eeh Auger threshold energy, if present, should be reflected from the dependence of the conversion rate on the excitation photon energy.

In this work we carried out a detailed study of the configuration conversion rate of the S-Cu defect, thus the eeh Auger process, as a function of the excitation photon energy at a fixed excitation level. This was done by two independent experiments carried out in our two laboratories, one by using the tunable pulsed laser and the other by using the tunable cw laser, to reach a more reliable and unambiguous conclusion. The conversion rate was determined from the decrease of the S_A PL upon optical excitation. The samples were heated up to above 100 K after each measurement at a specific excitation photon energy in order to restore the defect back to the stable configuration, since the conversion from the metastable to the stable configuration is known to be thermally activated at $T > 40$ K [11]. Therefore an identical initial condition was achieved before each measurement.

In Fig. 2 we show as examples such curves of the S_A decrease with two different excitation photon energies. As can clearly be seen, the decrease of S_A, and thus the efficiency of the eeh Auger process, exhibits a significant difference depending on whether an optical excitation of the energy above or below the FE energy was applied. A considerable decrease of the S_A PL intensity was observed with the excitation of the photon energy above the FE energy. In contrast, no noticeable decrease was observed with the excitation below the FE energy. Correspondingly, the released Auger electron can be observed by the change of the microwave photoconductivity, as shown in Fig. 2, when the excitation photon energy is above the FE energy. This change is persistent unless a thermal anneal-

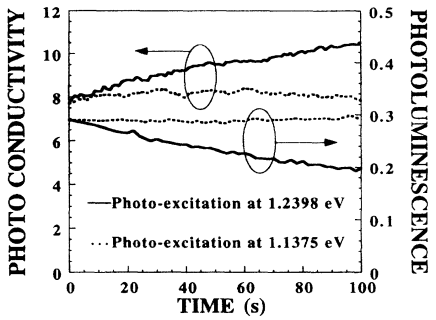

FIG. 2. Temporal dependence of the S_A PL intensity (the two lower curves) and the microwave photoconductivity (the two upper curves) at two different excitation photon energies. The excitation level was fixed at about 0.2 W/cm^2. Both the PL intensity and the photoconductivity are given in arbitrary units.

ing above 40 K is undertaken which converts the defect back to the stable configuration. No change of the photoconductivity could be detected with excitation below the FE energy. In other words, the eeh Auger process was only activated with excitation above the FE energy.

The results from the so-obtained conversion rate as a function of the excitation photon energy are summarized in Fig. 3 by curves (a) and (b), where the pulsed and cw lasers were used, respectively. The conversion rate follows that of the fundamental FE absorption, but with

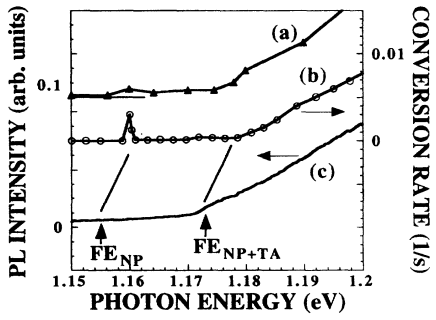

FIG. 3. Curve (a) shows the relative change in the S_A PL intensity, induced by the eeh Auger process, as a function of the excitation photon energy. It was obtained after 6 min of exposure by the pulsed laser (10 Hz and 5–6 ns pulses) at an average power of 10 mW. Such a change in the S_A PL intensity scales with the configurational conversion rate of the defect. Curve (a) is shifted in the vertical direction for clarity, with the zero level marked by the horizontal line. Curve (b) illustrates the defect configurational conversion rate, induced by the eeh Auger process, as a function of the excitation photon energy. The conversion rate was deduced from the decrease of the S_A PL emission under the cw laser excitation at 50 mW during 200 s. Curve (a), due to a smaller number of the experimental data points as marked by the solid triangles, has a lower resolution in the photon energy, as compared to curve (b) where the experimental data points are marked as the open circles. Curve (c) shows the excitation spectrum of the S_A PL emission. Here FE$_{NP}$ denotes the no-phonon transition of the FE and FE$_{NP+TA}$ denotes the transverse-acoustical-phonon-assisted transition of the FE.

a consistent and noticeable blueshift in energy by 5 ± 1 meV from the two independent sets of the experiments. Great care has been taken in calibrating the photon energy of the tunable lasers, and the blueshift was assured not to be just an artifact.

To further ensure that the blueshift is not due to any other possible unknown effect, we performed a PL excitation (PLE) study of the S_A PL emission in the same samples with experimental conditions identical to those of the experiments discussed above. In the case of a true band structure perturbation, the PLE spectrum of the S_A and any other PL emissions present in the crystal should display a corresponding blueshift with the same magnitude. The PLE spectrum is shown as curve (c) in Fig. 3. It follows exactly the fundamental FE absorption in silicon and no energy shift could be detected. The blueshift in the eeh Auger process is therefore not due to a distorted band structure, but is rather attributed to the inherent property of the eeh Auger process, i.e., the consequence of the threshold energy E_a. It should be pointed out that the reason why the PLE spectrum of S_A did not show the blueshift is that the defect monitored in this case remains in the stable configuration and no eeh Auger process is involved, in contrast to the process of the S_A decrease which is the consequence of the eeh excitonic Auger process.

Though the results on E_a were obtained via the defect-mediated Auger process in this work, it actually provides a profound implication to the general intrinsic eeh Auger process. In fact, the Auger process discussed here becomes equivalent to the intrinsic eeh Auger process when the defect level approaches the bottom of the conduction band, i.e., when the binding energy of the defect vanishes. It is therefore critically important to know how E_a varies with E_b, where E_b denotes the energy level of the defect with respect to the conduction band minimum. Such information can be obtained from the general requirements of the energy and momentum conservation for the eeh Auger process, i.e., $\mathbf{k}_i = \mathbf{k}_f$ and $E_i = E_f$. Here the subscripts i and f denote the initial and the final state of the Auger process, respectively. The eeh Auger threshold, when the excitonic effect is included and only transitions along the [001] direction in the reciprocal-lattice space (i.e., the $\mathbf{k}$ space) are considered as an example, can be obtained analytically as

$$E_a = \frac{\hbar^2}{4am_{v\parallel}}\left[b^2 - 2ac - b\sqrt{b^2 - 4ac}\right],$$

where

$$a = \frac{m_{v\parallel}}{m_{c\parallel} + m_{v\parallel}}, \qquad b = 2(3k_0 - K_{001}),$$

$$c = (3k_0 - K_{001})^2 + \frac{2m_{c\parallel}}{\hbar^2}(E_b - E_{\mathrm{FE}}^0).$$

Here $m_{c\parallel}$ is the longitudinal electron effective mass, and $m_{v\parallel}$ is the hole effective mass tensor component

in the [001] direction. k_0 denotes the position of the conduction band minimum, and K_{001} is the minimum nonzero reciprocal-lattice vector in the [001] direction. E_{FE}^0 is the ground state energy of the free exciton. The dispersion of the bands in the vicinity of the extrema is assumed to be parabolic in this case. It can be shown that the relation $dE_a/dE_b > 0$ holds for any value of E_b, or, equivalently, E_a should monotonously decrease with the decrease of E_b. The value of 5 meV, obtained with a finite value of the defect binding energy in this work, therefore represents the upper limit for E_a in the case of the intrinsic excitonic eeh Auger process. The intrinsic free carrier eeh Auger process, on the other hand, corresponds to the case described above when the excitonic effect is neglected, i.e., when E_{FE}^0 increases up to the band-gap energy E_g (with a vanishing binding energy for the free exciton). From the above expression, E_a can be shown to monotonously decrease with the increase of E_{FE}^0. The value of 5 meV, therefore, also gives the upper limit for E_a in the case of the intrinsic free carrier eeh Auger process. This is true even when different dispersions in **k** space for the free exciton and free carriers are taken into account [12]. A complete theoretical calculation should sum over reciprocal-lattice vectors (the so-called "umklapp terms") [5], and is beyond the scope of the present work. The simple model discussed above, however, provides a proper physical insight of the processes.

It should be noted that an estimate based on the above simple theoretical model gives a much larger value of E_a, more than 20 meV. This indicates that the assumption of a constant effective mass cannot accurately describe the conduction band minimum in silicon, in the energy range ($\sim$1 eV) of the Auger electron. Studies of the Auger threshold energy can in fact provide a convenient and accurate way to probe the band structure in a range of the energy spectrum, by studying defects with varying binding energies E_b and thus the energy of the Auger electron. The prerequisite is that the momentum in the defect-mediated Auger process should be preserved, which is true for shallow effective-mass-like states of impurities. The electron state of the negatively charged S-Cu defect studied in this work apparently belongs to this category.

It is also interesting to note that the zero-phonon transition of the FE in the Auger process could be observed, in contrast to the case of normal PLE. The zero-phonon transition of the FE is generally forbidden due to the strict selection rule for the indirect band gap of silicon. This selection rule can, however, be relaxed by the scattering of the FE with defects inherent in the defect-mediated Auger process, resulting in the appearance of the zero-phonon transition of the FE. The no-phonon FE transition has previously been weakly observed in absorption in doped silicon samples [13].

In summary, we have directly determined the threshold energy for the eeh Auger process in silicon, for the first time, by a novel experimental approach. We have shown that the E_a value of 5 meV obtained for the defect-mediated eeh Auger process gives the upper limit for E_a in the case of the intrinsic eeh Auger process. This provides direct experimental evidence that the eeh Auger threshold energy in silicon is indeed very small, and consequently this important Auger process must be dominated by the direct (phononless) mechanism. The results from this work are therefore expected to resolve the controversies on the subject, and lead to a better understanding of both the fundamental carrier recombination processes and the band structure in silicon.

We thank M. E. Braat for experimental assistance in the pulsed laser experiments. This work was financed in part by the Swedish Council for Engineering Sciences (TFR). This work is also part of the research program of the "stichting voor Fundamenteel Onderzoek der Materie (FOM)" financially supported by the "Nederlandse Organisatie voor Wetenschappelijk Onder zoek (NWO)." Further support was obtained from the European Community Science Program through Grant No. SC 1000363.

[1] P. T. Landsberg, *Recombination in Semiconductors* (Cambridge University Press, Cambridge, 1991).
[2] A. Hangleiter, Phys. Rev. Lett. **55**, 2976 (1985); Phys. Rev. B **35**, 9149 (1987); **37**, 2594 (1988).
[3] M. Potemski, R. Stepniewski, J. C. Maan, G. Martinez, P. Wyder, and B. Etienne, Phys. Rev. Lett. **66**, 2239 (1991).
[4] P. O. Holtz, M. Sundaram, J. L. Merz, and A. C. Gossard, Phys. Rev. B **41**, 1489 (1990).
[5] D. B. Laks, G. F. Neumark, A. Hangleiter, and S. T. Pantelides, Phys. Rev. Lett. **61**, 1229 (1988).
[6] A. Hangleiter and R. Häcker, Phys. Rev. Lett. **65**, 215 (1990).
[7] L. Huldt, Phys. Status Solidi (a) **8**, 173 (1971).
[8] J. Dziewior and W. Schmid, Appl. Phys. Lett. **31**, 346 (1977); A. Haug and W. Schmid, Solid State Electron. **25**, 665 (1982); J. Vaitkus and V. Grivitskas, Fiz. Tekh. Poluprovodn. **15**, 1894 (1981) [Sov. Phys. Semicond. **15**, 1102 (1981)]; K. G. Svantesson and N. G. Nilsson, J. Phys. C **12**, 5111 (1979).
[9] W. M. Chen, J. H. Svensson, E. Janzén, B. Monemar, A. Henry, A. M. Frens, M. T. Bennebroek, and J. Schmidt, Phys. Rev. Lett. **71**, 416 (1993).
[10] D. J. S. Beckett, M. K. Nissen, and M. L. W. Thewalt, Phys. Rev. B **40**, 9618 (1989).
[11] M. Singh, E. C. Lightowlers, G. Davies, C. Jeynes, and K. J. Reeson, Mater. Sci. Eng. **4**, 303 (1989); A. Henry, W. M. Chen, E. Janzén, and B. Monemar, in *Proceedings of the 20th International Conference on the Physics of Semiconductors,* edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 545.
[12] W. M. Chen, B. Monemar, E. Janzén, A. M. Frens, M. T. Bennebroek, and J. Schmidt (unpublished).
[13] P. J. Dean, J. R. Haynes, and W. F. Flood, Phys. Rev. **161**, 711 (1967).