Mechanism of the Configurational Change of Metastable Defects in Silicon

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From a detailed study of two different defects in silicon, excitonic Auger capture is shown to be an important mechanism of the configurational change of metastable defects. A free exciton interacts with the defect and recombines, transferring its energy to an electron, which will be emitted high up into the conduction band. This hot Auger electron will quickly reach the bottom of the conduction band. The liberated energy may excite the defect above the barrier between the two configurations.

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When a defect in a solid has two different atomic configurations separated by an energy barrier, the configuration highest in energy is known as the metastable configuration. Metastability is common for impurities and defects in semiconductors and in solids in general [1]. These include many important defects such as the *DX* centers in III-V compounds [2], the *EL*2 defect in GaAs [3], thermal donors [4], irradiation-induced defects [1], and H-related defects in Si [5]. However, very few such defects have been identified and understood so far. The physical mechanism causing the conversion from the stable to the metastable configuration is unclear for most metastable defects.

In earlier studies of recombination-stimulated defect reactions in compound semiconductors similar effects were clearly demonstrated [6]. The mechanism inducing the defect reaction was argued to be multiphonon recombination at defects with a large lattice relaxation [7]. The energy of the recombining carriers in that case is liberated in the form of phonons localized to the defect. Since it takes some time for the vibrational energy to migrate into the surrounding crystal, the liberated energy might be added to the thermal energy to overcome the potential barrier for transfer of a defect atom to a neighboring site. The defect reaction is athermal if the liberated recombination energy is larger than the potential barrier (if the temperature dependence of the carrier capture process to the defect is neglected).

In this Letter we will show that an important mechanism for the conversion from the stable to the metastable configuration of a metastable defect is excitonic Auger capture [8,9]. A free exciton (FE) interacts with the defect and recombines, liberating the energy in the form of an Auger particle, which in some cases can be detected. The conversion to the metastable state then occurs athermally.

We will give two examples of metastable defects in silicon. One is a C-related defect, which is found in electron-irradiated samples. Only the metastable configuration in its neutral charge state has been observed. The defect has been investigated by infrared absorption and has its lowest and strongest no-phonon line (spin singlet) at 615 meV [10,11]. The other defect is a S-Cu complex, for which both the stable and the metastable configurations have been observed [12–15]. There is strong photoluminescence (PL) from both configurations for this defect with no-phonon bound exciton (BE) lines at 968 meV (S_A^0) and 812 meV (S_B^0), respectively. Both lines are related to the neutral charge state and are spin triplets with accompanying spin singlets about 10 meV higher in energy [14].

We will show that FEs are involved in the conversion process by studying (a) the spectral dependence of the photoinduced conversion rate, (b) the influence of annealing on the conversion rate, and (c) the influence of impact ionization of FEs (due to a microwave field) on the conversion rate. We will also show that an Auger process is involved in the conversion, since (a) the conversion rate is temperature independent, and (b) an Auger particle can be detected in the EPR measurements.

We shall first describe the relevant experimental data for the two defects and thereafter discuss the conversion mechanism. We will start with the C-related defect.

As mentioned above only the metastable configuration has so far been observed for the C-related defect. Its optical absorption spectrum appears only after optical excitation at temperatures below 65 K with photon energies above or in close resonance with the band gap. At temperatures above 70 K the spectrum disappears again with a thermal activation energy of 0.21 eV [10].

The conversion rate to the metastable configuration, as measured by the growth rate of the absorption line at 615 meV, is found to be independent of temperature between 4.2 and 60 K, both for white light excitation and for 1.06 μm Nd-YAG laser light excitation. We have further investigated how the conversion rates at 10 K varied for samples exposed to different electron-irradiation doses and annealing procedures (up to 310 °C). Although the final metastable defect concentration is high for high irradiation doses, the conversion rate is extremely small (tens of hours) for unannealed samples. The annealing procedure was carried out after electron irradiation in order to decrease the concentration of other defects acting as competing recombination channels. The concentration of

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FEs during photoexcitation is thus increased. The conversion rate is increased substantially (to tens of minutes) after the annealing, but is still temperature independent.

Since the energy of the Nd-YAG laser line is actually below the band gap of silicon at the lowest temperatures it excites either FEs directly (a possible process, since the sample contains many defects) or free carriers via a two-step process, which quickly form FEs. When white light is used, on the other hand, the absorption of photons occurs in a broad energy range. If a germanium or silicon wafer, held at room temperature, was used to filter the white light (thus significantly decreasing the number of photons with energies higher than the band gap), the conversion rate was negligible. It is experimentally found that there is a linear relationship between the conversion rate and the laser power. We assume further that the concentration of FEs is proportional to the optical excitation power. Then it follows that the conversion rate is proportional to the concentration of FEs, which thus indicates the importance of FEs for the conversion as will be discussed below.

Next we summarize the corresponding experimental data for the S-Cu defect. The configuration conversion occurs either by band gap photoexcitation ($S_A \rightarrow S_B$ at $T < 40$ K) or by thermal annealing ($S_B \rightarrow S_A$ at $T > 40$ K) [13,16]. Let us start with the configuration coordinate diagram in Fig. 1 to illustrate the conversion between the configurations. Here we follow the notation used in Ref. [12], i.e., configuration 1 (stable) and 2 (metastable) for the configurations giving rise to the S_A and S_B PL spectra, respectively. From the electron binding energies of the BE (65.3 meV for S_A BE and 66.2 meV for S_B BE) [14] and the energy difference between the two BE transitions, we obtain the ground state of configuration 1 in its neutral charge state to be about 156 meV lower compared with configuration 2. Both ground states are in the lower half of the band gap. The barrier

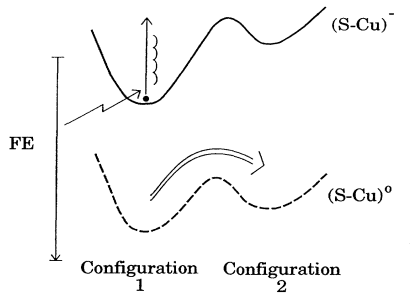

FIG. 1. Configuration coordinate diagram illustrating the conversion between the two configurations of the metastable S-Cu defect. The solid line is for the negative charge state $(S\text{-}Cu)^-$ and the dashed line for the neutral charge state $(S\text{-}Cu)^0$. FE denotes the free exciton. The excitonic Auger process is indicated by the arrows, which converts the defect from configuration 1 to configuration 2. The energy barrier for $(S\text{-}Cu)^0$ is about 0.1 eV while it is unknown for $(S\text{-}Cu)^-$.

height in the neutral charge state for thermally activated conversion from configuration 2 to configuration 1 was determined to be about 0.1 eV [16,17] from thermal quenching of S_B and the thermal recovery of S_A, after configuration 1 has been converted to configuration 2 by photoexcitation.

The ordering of the ground state energies for the negative charge state shown in Fig. 1, was based on our X-band EPR results presented in Fig. 2. After cooling down the sample (the Fermi level is in the upper half of the band gap) in darkness, a broad EPR signal (about 150 G FWHM) was observed (Fig. 2, upper left), which decreased in intensity once the above band gap photoexcitation was applied (Fig. 2, lower left). The linewidth of the EPR signal is unusually broad to be observed in silicon, about 2 orders of magnitude broader than most of the EPR signals from other defects in this material. This is in agreement with the X-band optically detected magnetic resonance (ODMR) spectra for the S_A and S_B triplets, where similar linewidths are observed. This broadening is induced by the unresolved Cu-related hyperfine structure of the defect, proven by the zero-field ODMR where a narrower ODMR linewidth is achieved [12,15]. It should be noted that this broad EPR signal was not seen in samples containing no S-Cu-related defects. Instead other more known defects are detected such as isolated S and the S pair, both giving rise to sharp EPR lines when positively charged [18]. We attribute the broad EPR signal to the unpaired electron bound in configuration 1 in the negative charge state for the following reasons.

(a) Its appearance correlates very well with the conversion kinetics, i.e., it shows up after cooling in darkness but quenches with a subsequent band gap photoexcitation. This situation is persistent unless a thermal annealing at $T \geq 40$ K is performed, in close resemblance with the configuration conversion monitored by PL ($S_B \rightarrow S_A$).

(b) It is not observed if the sample has been cooled down with applied above band-gap excitation (Fig. 2, lower right), not even if the excitation is removed at temperatures below 40 K (Fig. 2, upper right). A thermal annealing at temperatures exceeding 40 K is then required to observe the EPR signal. This again resembles

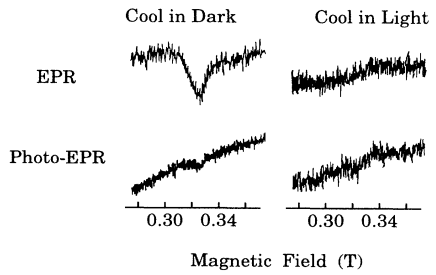

FIG. 2. EPR data at 4 K for the S-Cu defect. For details, see text.

the PL behavior, where mainly S_B is observed after cooling with band-gap excitation.

(c) The ground states of the neutral charge state for both configurations are known to be diamagnetic and EPR inactive [12–14].

The number of electrons in the conduction band increases as a result of the configuration conversion, as observed by an increasing free electron microwave absorption in the EPR spectra, partially seen by the increased overall slope (Fig. 2, lower left), when the EPR signal from the negative charge state of configuration 1 decreases. This increase in free electron concentration is persistent even after the above-band-gap optical excitation has been turned off and is equivalent to the observation of persistent photoconductivity.

We obtain no evidence for the presence of an EPR signal from the negative charge state of configuration 2. This can be explained to be due to its high energy position very close to or even resonant with the conduction band, so that the defect is in the diamagnetic neutral charge state of the configuration, see Fig. 1.

The conversion rate is independent of temperature just as for the C-related defect. We have further investigated the dependence of the conversion rate on the excitation photon energy in more detail for the S-Cu defect. The results are summarized in Fig. 3. In this case the vertical axis represents the change in S_A^0 and S_B^0 (PL intensity of configurations 1 and 2, respectively) in arbitrary units after photoexcitation at each photon energy subsequent to cooling in darkness. It should be noted that after photoexcitation at each energy the sample was heated up to room temperature to ensure a complete recovery of configuration 1, in order to achieve identical starting conditions. The curve in Fig. 3 clearly shows a similarity with the band-edge absorption spectrum [19]. The conversion rate is proportional to the excitation intensity for above-band-gap excitation and thus to the FE concentration. However, due to the high excitation intensity during the pulses some free carriers will be created also for excitation energies below the band gap via two-photon absorption. This explains the nonzero conversion (proportional to the square of the excitation intensity) between the configurations with below-band-gap excitation in Fig. 3. The very slow conversion with 1.3 μm photoexcitation reported in Ref. [20], we believe is due to creation of free carriers via a two-step process. The alternative model of directly photoionizing the defect followed by a multiphonon energy relaxation of the photoexcited carrier, which induces the configuration change, is unlikely since the excitation spectrum in that case should be different from that of band-edge absorption.

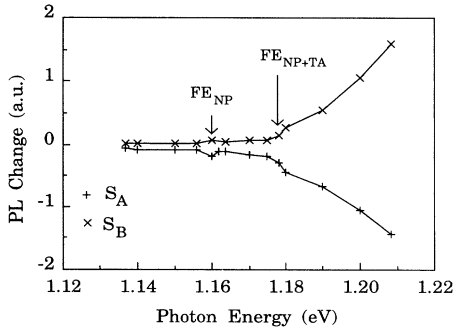

FIG. 3. The dependence of the conversion rate at 3 K on the excitation photon energy for the S-Cu defect as monitored by the photoluminescence (PL) change of S_A^0 and S_B^0. Here FE_{NP} corresponds to the no-phonon absorption of the free exciton and FE_{NP+TA} corresponds to the transverse-acoustical-phonon-assisted absorption of the free exciton. The average excitation power is 10 mW and is applied for 6 min at each photon energy (10 Hz and 5–6 ns pulses).

By applying a microwave field during the conversion from configuration 1 to configuration 2, we could decrease the conversion rate substantially. The maximum microwave power we used was 200 mW, which does not affect the temperature of the sample significantly. As shown previously [21] an electric field (such as the microwave field in this case) will impact ionize the FEs into free electrons and holes and thus reduce the number of FEs.

The experimental results of the two metastable defects presented above show that FEs are involved in the conversion to the metastable state. In the heat treated samples with the C-related defect the concentrations of defects, that act as competing recombination channels, have decreased. This means that more FEs are available for the C-related defect and the conversion rate will increase as is observed. For the S-Cu complex the conversion rate follows the band-edge FE absorption spectrum and decreases when the FEs are broken up by the microwave field. The questions are then how the energy of the FEs is transferred to the defect and how the conversion occurs.

We suggest the following plausible model: We know from the EPR measurements, that the S-Cu complex is at least partly in the negative charge state when it is in configuration 1. If the defect interacts with a FE, the exciton hole may be captured at the defect transferring the energy to the exciton electron, which will be emitted high up into the conduction band [8,9]. This hot Auger electron will quickly (within ps) reach the bottom of the conduction band. The liberated energy may excite the defect above the energy barrier between the two configurations. The EPR measurements presented above really show that electrons are transferred from the defect to the conduction band during the configuration conversion, which is consistent with the model presented here.

For the C-related defect we do not yet have any proof of the existence of a negative charge state. However, following Hangleiter [8,9] the exciton hole can still be captured at the defect, transferring the energy to the exciton

electron, which is emitted into the conduction band.

In principle it should be possible to optically excite the unpaired electron in the S-Cu complex high up into the conduction band. However, the photoionization cross section of the defect and the photon flux available are too small compared to the fundamental absorption cross section across the band gap and the Auger capture cross section [8,9]. Only the latter process gives any contribution to the conversion rate, which is consistent with the experimental data presented above.

Hangleiter [8,9] argues that excitonic Auger recombination via deep impurity levels is an important recombination mechanism in silicon. At low FE concentration the excitonic Auger capture rate is temperature independent as long as only the FE ground state is populated. In our case the conversion rate from the stable to the metastable configuration is temperature independent in a wide temperature region, which is only consistent with an excitonic Auger capture process. All other capture processes including multiphonon emission recombination [22] are bound to give some temperature dependence.

In this Letter we have shown that excitonic Auger capture is an important mechanism for the configurational change of metastable defects in silicon. The model is supported by the following experimental results: First, the conversion rate from the stable to the metastable configuration depends on the concentration of free excitons. Second, the conversion rate is temperature independent. Finally and most important, the Auger electron emitted during the excitonic Auger capture can be detected in the conduction band after the conversion to the metastable configuration.

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[1] G. D. Watkins, Mater. Sci. Forum **38-41**, 39 (1989).

[2] D. V. Lang, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach Science Publ., New York, 1986), p. 489.

[3] G. M. Martin and S. Makram-Ebeid, in *Deep Centers in Semiconductors* (Ref. [2]), p. 399.

[4] L. F. Makarenko, V. P. Markevich, and L. I. Murin, Fiz. Tekh. Poluprovodn. **19**, 1935 (1985) [Sov. Phys. Semicond. **19**, 1192 (1985)].

[5] B. Holm, K. Bonde Nielsen, and B. Bech Nielsen, Phys. Rev. Lett. **66**, 2360 (1991).

[6] D. V. Lang and L. C. Kimerling, Phys. Rev. Lett. **33**, 489 (1974).

[7] J. D. Weeks, J. C. Tully, and L. C. Kimerling, Phys. Rev. B **12**, 3286 (1975).

[8] A. Hangleiter, Phys. Rev. B **35**, 9149 (1987).

[9] A. Hangleiter, Phys. Rev. B **37**, 2594 (1988).

[10] J. H. Svensson and B. Monemar, Phys. Rev. B **40**, 1410 (1989).

[11] J. H. Svensson, B. Monemar, and E. Janzén, Phys. Rev. Lett. **65**, 1796 (1990).

[12] W. M. Chen, M. Singh, A. Henry, E. Janzén, B. Monemar, A. M. Frens, M. T. Bennebroek, J. Schmidt, K. J. Reeson, and R. M. Gwilliam, Mater. Sci. Forum **83-87**, 251 (1992).

[13] M. Singh, E. C. Lightowlers, G. Davies, C. Jeynes, and K. J. Reeson, Mater. Sci. Eng. B **4**, 303 (1989).

[14] D. J. S. Beckett, M. K. Nissen, and M. L. W. Thewalt, Phys. Rev. B **40**, 9618 (1989).

[15] A. M. Frens, M. T. Bennebroek, J. Schmidt, W. M. Chen, and B. Monemar, Phys. Rev. B **46**, 12316 (1992).

[16] 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.

[17] M. Singh, G. Davies, E. C. Lightowlers, and G. D. Watkins, in Proceedings of the 5th International Conference on Shallow Impurities in Semiconductors, Kobe, Japan (Trans Tech Publications, Clausthal-Zellerfeld, to be published).

[18] G. W. Ludwig, Phys. Rev. **137**, A1520 (1965).

[19] K. L. Shaklee and R. E. Nahory, Phys. Rev. Lett. **24**, 942 (1970).

[20] M. Singh, thesis, 1992, Departments of Physics, King's College, London.

[21] H. Weman, Q. X. Zhao, and B. Monemar, Phys. Rev. B **36**, 5054 (1987).

[22] J. Bourgoin and M. Lannoo, *Point Defects in Semiconductors II*, Springer Series in Solid State Sciences Vol. 35 (Springer-Verlag, Berlin, 1983), p. 191.