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Nonradiative recombination via deep impurity levels in silicon: Experiment

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The nonradiative recombination of excess charge carriers via deep levels induced by transition-metal impurities in silicon is investigated experimentally. In order to reveal the recombination mechanism, the carrier lifetime is measured as a function of temperature, carrier density, and electric field. In addition, a direct proof for trap Auger recombination is given based on the highly excited Auger particles. Since our results exclude the usual models for capture into deep impurity levels, we propose a new model for deep-level recombination: The excitonic Auger recombination via deep impurity levels is shown to explain our experimental results consistently.

I. INTRODUCTION

The phenomenon of nonradiative recombination of excess charge carriers via deep impurity levels in semiconductors has attracted much interest in the past.[1–4] However, some of the basic problems remain still unsolved. Although the kinetics of the recombination process seem to be well described by the model of Shockley and Read[5] and Hall[6] (SRH), where electrons and holes can recombine by successive capture into the deep impurity level in the forbidden gap, the question of the physical mechanism of carrier capture remains unsolved within this model. Despite the large theoretical and experimental efforts exerted to answer this question there is still no satisfactory solution. From the theoretical point of view there are three models which are usually discussed in order to account for the recombination at deep impurities.[3,4] First we have to mention the so-called capture by multiphonon emission (MPE), which is well known from the study of internal transitions at defect centers in large-gap materials.[7] There the transition between two states is due to their vibronic coupling and the excess energy is dissipated in the form of localized phonons.

A second possible mechanism is the cascade capture mechanism introduced by Lax.[8] Here, the carrier being captured loses its energy by dropping through a series of closely spaced levels, emitting one phonon during each step. This mechanism is believed to be responsible for the capture of carriers into shallow impurity levels, whose hydrogenlike level scheme is ideally suited for this mechanism.

The third mechanism usually quoted is, as we shall call it throughout this paper, "classical" Auger capture of free carriers by the impurity as discussed by Landsberg *et al.*[9] or Haug.[10] In this mechanism, two independent free carriers have to meet at the impurity site, where their electron-electron interaction induces a transition of one of the carriers into a deeply bound state, while the excess energy is transferred to the other carrier which is highly excited into its respective band.

Experimentally, the situation is rather confusing. Even for one of the most intensely studied deep centers, the substitutional gold defect in silicon, the observed temperature dependence of the capture coefficients[11] cannot be explained by one of the above-mentioned models in a simple way. Electron capture into the gold donor level as well as hole capture into the acceptor level both exhibit a capture coefficient which decreases with increasing temperature according to a power law.[11] So far, one is tempted to conjecture that the cascade mechanism[8] is most likely to explain this behavior. However, at deep impurities such as gold in silicon, there is no independent evidence for the necessary closely spaced ladder of excited states. Even for the effective-mass-like excited states of charged impurities, there remains a large last step from the lowest excited state to the ground state, which can not be overcome by a single phonon.[12] Therefore this decisive step must be due to another mechanism.

Schmid and Reiner[13] have investigated the minority-carrier lifetime in gold-doped silicon at high majority-carrier densities. Their results indicated that at carrier densities around 10^{18} cm^{-3} trap Auger processes might contribute to the nonradiative recombination via the deep levels associated with gold. At lower densities, however, Schmid and Reiner[13] concluded that another recombination mechanism must be effective.

On the other hand, there are several examples where the capture coefficients show a thermally activated behavior, e.g., hole capture by the neutral interstitial iron defect in silicon,[14,15] hole capture by the neutral substitutional platinum defect in Si,[16] and carrier capture by several deep centers in GaAs and GaP as shown in the work of Henry and Lang.[17] In these cases one would conclude that in fact capture by multiphonon emission might take place.

In this paper, we shall present new experimental results on recombination via deep impurities in silicon. The experimental data as a whole will be shown to be inconsistent with any of the usually quoted models for recombination via deep impurity levels. A new model developed from these data will be outlined and discussed qualitatively. A quantitative theory of deep-impurity recombination based on our new model will be the subject of a second paper.[18] Brief preliminary reports of some of the experimental data reported here have already been given elsewhere.[19,20]

The present paper is subdivided into several sections.

First, we shall describe some basic experiments which demonstrate the capabilities of our all-optical method to observe the recombination process and which illuminate the two-step nature of the recombination via deep impurities. Based on these methods, the dependence of the carrier lifetime on various parameters such as temperature, majority-carrier density, excitation level, and an externally applied electric field will be presented. The existence of highly excited Auger particles generated by the recombination via the deep level will be shown. Our new model of an excitonic Auger recombination mechanism will then be outlined and discussed.

II. EXPERIMENTAL DETAILS

In order to obtain new insight into the recombination of free charge carriers via deep impurity levels, the recombination properties of several transition-metal impurities in silicon were investigated. Silicon was used because of its technological importance and because its properties are the best known to date. It is commercially available in a wide range of shallow doping concentrations and with concentrations of unwanted impurities below 10^{11} cm^{-3}. The competing band-to-band recombination processes such as radiative recombination[21] or band-to-band Auger recombination[22] are well known and are negligible at least at moderate shallow doping levels.

The choice of the impurity species investigated was influenced by their technological importance on one hand and by the greatest possible simplicity of their respective level scheme on the other hand. From the point of view of practical interest, gold is the obvious choice because it is widely used as a lifetime-controlling defect in silicon.[23] The substitutional gold defect in Si is usually believed to appear in three charge states, negative, neutral, and positive, and therefore to have one acceptor and one donor level within the forbidden gap.[23] However, this simple picture was questioned in a recent debate, where it was suggested that the donor and the acceptor level do not belong to the same center.[24,25]

Furthermore, the recombination centers induced by Cr or Fe were investigated. In n-type silicon, both transition metals are incorporated on an interstitial site and both give rise to only a single deep donor level.[15,26] In p-type material, both tend to form pairs with shallow acceptors which also have a single deep donor level located near the valence band.[15,26]

Our samples were prepared from single-crystal float-zone-refined silicon doped with phosphorus or boron as shallow dopants in the range $10^{12} < N_D < 10^{19}$ cm^{-3}, corresponding to an electrical resistivity between 8000 and 0.01 Ω cm. Before the diffusion process, the samples were etched in a mixture of nitric and hydrofluoric acid and stored in methanol to prevent the adsorption of oxygen or nitrogen at the silicon surface. The elemental metals were then deposited on the sample surface either by evaporation in vacuum or by scratching. The actual diffusion process was carried out in a vertical silica furnace tube in evacuated quartz ampoules at temperatures between 850 and 1250 °C. After diffusion, the ampoules were rapidly cooled in water in order to quench-in the fast-diffusing metals. All specimens were then polished mechanically and chemically to remove the alloy layer.

In order to certify that only those recombination centers introduced intentionally were active in the samples, we also made reference samples which ran through all steps of sample preparation apart from the evaporation of the dopant. In addition the samples were characterized by deep-level transient spectroscopy (DLTS) and photoluminescence measurements, where no unwanted impurities were detected.

The observation of the electron-hole recombination process was accomplished by a purely optical method. Electron-hole pairs were generated in the samples by excitation with short laser pulses. For this purpose, either a cavity-dumped mode-locked argon-ion laser operating on the green Ar line (514.5 nm) with a pulse width of about 150 ps or a Q-switched Nd-YAG laser (1.06 μm, pulse width 300 ns, where YAG is yttrium aluminum garnet) were used. The choice of the laser system was mainly determined by the actual time constants of the sample being studied. The short green light pulses of the Ar laser are well suited to observe carrier lifetimes below $\simeq$300 ns, but above this value the small penetration depth of the green light [$\simeq 1$ μm (Ref. 27)] together with the larger diffusion length of the carriers leads to an increasing influence of surface recombination on the observed decay of the carriers. The decay curves are distorted by surface recombination and therefore the evaluation of the bulk lifetime becomes difficult.[28,29] On the other hand, the infrared radiation of the Nd-YAG laser is only weakly absorbed in silicon [penetration depth $\simeq 1$ mm at 300 K (Ref. 30)]. For the usual sample dimensions of about $5 \times 5 \times 1$ mm^3 a large portion of the sample volume can be filled with electron-hole pairs so that surface recombination becomes negligible, and the bulk recombination properties can be easily determined. However, because of the relatively large width of the Q-switched laser pulse, the application of this laser was limited to carrier lifetimes larger than about 50—100 ns in our case.

The nonradiative recombination of the optically injected carriers is observed by monitoring the radiative band-to-band recombination luminescence. Although the radiative recombination in silicon is negligible compared to the nonradiative processes,[21] it is well suited as a probe to observe the decay of the excess carrier density due to the dominant nonradiative recombination.

The luminescence emitted by the sample was focused onto the entrance slit of a 0.75-m grating monochromator and detected by a highly sensitive cooled photomultiplier with S1-type cathode. The signal was processed by a time-correlated single-photon counting[31] setup interfaced with a computer. The overall time resolution of this system (with the Ar laser) was mainly determined by the response time of the photomultiplier and was about 400 ps. For the measurements, the samples were mounted in a variable-temperature "vapor bubble" cryostat,[32] filled either with liquid helium or liquid nitrogen as a coolant, thus allowing variation of the sample temperature between 4 and 400 K. The actual temperature was measured using calibrated carbon or platinum resistors and was kept constant by a proportional integrating-differentiating (PID) temperature controller.

III. BASIC PROPERTIES OF DEEP-LEVEL RECOMBINATION

The kinetics of the recombination via deep impurity levels are governed by the two-step nature of this process as described by the SRH model (Fig. 1). The differential equations for transient recombination at a single-level donorlike deep impurity have been given by Sandiford[33] and may be written as follows:[34]

$$\frac{d\delta n}{dt} = -\alpha_n[N^+\delta n - (n_0+n_1+\delta n)\delta N] , \quad (1)$$

$$\frac{d\delta p}{dt} = -\alpha_p[N^0\delta p + (p_0+p_1+\delta p)\delta N] , \quad (2)$$

$$\delta N = \delta p - \delta n . \quad (3)$$

Therein, N^0 and N^+ are the equilibrium concentrations of neutral and positively charged impurities, α_n and α_p are the capture coefficients for electrons and holes, $\delta n, \delta p$ are the nonequilibrium densities of electrons and holes, whereas n_0, p_0 are the equilibrium carrier densities given by the shallow doping level, and n_1, p_1 are the carrier densities for the Fermi level lying at the energy level of the trap and are introduced by detailed-balance considerations:[34]

$$n_1, p_1 = n_i \exp\left[\pm\frac{E_T - E_i}{kT}\right] . \quad (4)$$

The solutions of the above system of nonlinear differential equations are especially interesting in several limiting cases. The usual minority-carrier lifetime is obtained from (1)–(3) if the excess minority-carrier density δn or δp is much lower than the majority-carrier density n_0 or p_0. For example, for $p_0+p_1 \ll \delta n, \delta p \ll N_0+n_1$ (1)–(3) yield (low-injection lifetime):

$$\tau_L = \frac{1}{\alpha_p N^0} . \quad (5)$$

On the other hand, if the high-excitation limit is considered, one obtains the high-injection lifetime:

$$\tau_H = \frac{\alpha_n+\alpha_p}{\alpha_n\alpha_p N} . \quad (6)$$

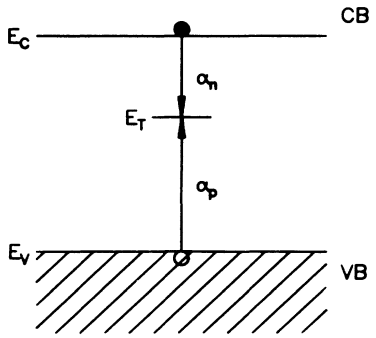

FIG. 1. Recombination of excess charge carriers via deep impurity level by a two-step SRH process (Refs. 5 and 6).

The transient decay of the excess carrier density is exponential in both limits, but the decay times may differ substantially. In the example given above, there are two possible outcomes: If the majority-carrier capture coefficient (α_n) is much larger than the minority-carrier capture coefficient (α_p), there is no difference between the high-injection and the low-injection lifetime. On the contrary, if the minority-carrier capture coefficient is larger than the one for majority carriers, the high-injection lifetime becomes larger than the low-injection lifetime. That means that after excitation to the high-injection regime, the decay starts slowly governed by the high-injection lifetime. The excess carrier density is reduced by the recombination and reaches the transition region between the high- and low-injection regions, where the recombination speeds up finally reaching the low-injection lifetime limit.

This transition between the high and low injection regions can be excellently observed by the time-resolved photoluminescence method used in this work. Figure 2 depicts the luminescence decays in p- and n-type gold-doped silicon samples at room temperature. Although the single-level description outlined above in principle is not applicable to a two-level system such as gold in silicon, the concept of high- and low-injection lifetimes remains valid. In the p-type sample shown in the upper part of the figure, where the gold donor level should dominate the recombination at low injection,[23] no change in decay time occurs at the high-to-low-injection transition. On the contrary, there is in fact a change in decay time by a factor of 5.5 in the n-type sample, where the recombination is expected to go via the gold acceptor level at low injection.[23] Therefore, it can be concluded that for the gold acceptor level, as well as for the donor level, the hole-capture coef-

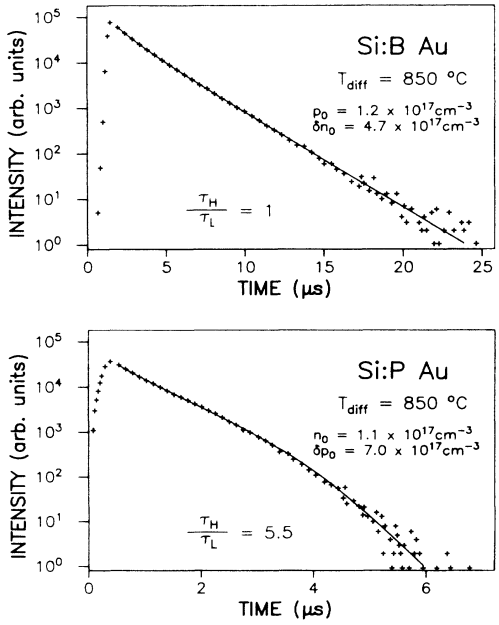

FIG. 2. Consequences of the SRH statistics (Refs. 33 and 34) on the transient decay of the carrier density as observed by the decay of the band-to-band luminescence.

ficient is larger than the electron-capture coefficient. This fact has also been observed in direct measurements of the capture coefficients by Wu and Peaker.[11] Interestingly, the high-injection lifetime is the same in n- and p-type material. Since under high-injection conditions n- and p-type material looks alike, one would expect the same high-injection lifetime if the same center is responsible for the recombination in both material types. Therefore, our lifetime measurements support the view that the same center, presumably the substitutional gold, is responsible for the recombination in gold-doped n- and p-type silicon.

The temperature dependence of the carrier lifetime is mainly determined by the temperature dependencies of the capture coefficients α_n and α_p. However, if the equilibrium Fermi level is located near the impurity energy level, the concentration of occupied impurity states will depend on temperature, thereby strongly influencing the low-injection carrier lifetime [see (5)]. These cases may be easily identified by looking at the injection dependence of the lifetime, since at high injection the lifetime depends only on the total number of deep centers. Therefore, if the low-injection lifetime becomes larger than the high-injection lifetime, which is only possible if there is a thermal ionization of the deep level, a careful examination of the temperature dependencies can yield some additional information about the depth of the recombination center.

IV. RESULTS OF LIFETIME MEASUREMENTS

In this section, we shall discuss the results of our measurements of the carrier lifetime in silicon doped with deep recombination centers. In order to get some criteria for the valuation of the theoretical models for deep-level recombination, we have investigated the dependence of the carrier lifetime on various parameters such as temperature, majority-carrier density, excitation level, and an electric field.

A. Temperature dependence of the carrier lifetime

The temperature dependence of the carrier lifetime will be discussed in two parts. First, the high-temperature region $50\ \text{K} < T < 400\ \text{K}$ is considered, where shallow impurities are mostly ionized and where high-injection as well as low-injection conditions can be realized. Figure 3 shows the measured carrier lifetimes for the high-temperature region in p- and n-type silicon doped with chromium, iron, or gold as recombination centers. The lower lifetime shown in all cases represents the low-injection (minority-carrier) lifetime. In the cases of Au in n-type Si, Cr in p-type Si (CrB pairs), or Fe in p-type Si (FeB pairs) the high-injection lifetime, being considerably larger than the low-infection lifetime is also included in Fig. 3. Figure 3 shows that for all recombination centers investigated, the carrier lifetime increases with temperature approximately obeying a power law $\tau \sim T^{\nu}$.

By comparison of the data from samples with different shallow doping levels, we have certified that these temperature dependences were not influenced by any effect of the SRH statistics, such as thermal ionization of the deep level. Therefore the measured temperature dependence of the carrier lifetime gives us the real temperature dependence of the capture coefficients for electrons and holes. Consequently, the capture coefficients derived from these data in the high-temperature range decrease with increasing temperature like $\alpha \sim T^{-\nu}$.

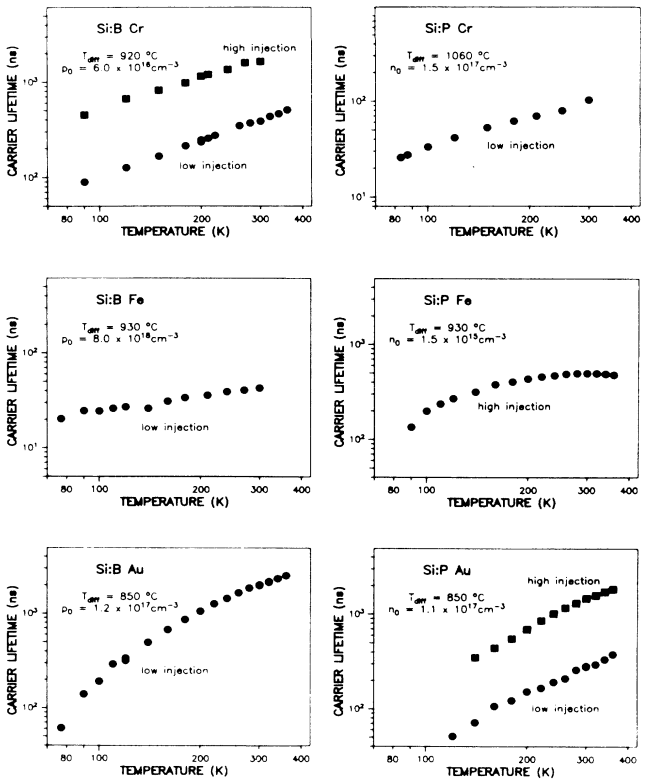

FIG. 3. Measured temperature dependencies of the carrier lifetime ($T > 70$ K) in p- and n-type silicon doped with Cr, Fe, or Au as recombination centers.

The absolute values of the capture coefficients can be estimated from lifetime measurements if one has additional information about the concentration of the recombination centers. We estimated the trap concentration in our samples by several methods. An upper bound for the center density is given by the maximum solid solubility of the metal atoms in silicon at a known diffusion temperature, given, e.g., by Weber.[35] Since the trap density enters into the relation between lifetime and capture coefficients inversely, such a procedure yields a lower bound for the capture coefficients.

Further information on the trap density was gained from room-temperature resistivity measurements on diffused samples, which originally had a high resistivity. In the case of gold, where the special diffusive behavior[36] leads to a strongly inhomogeneous gold distribution in the samples at reasonable diffusion times, neither of the above methods can be applied. For this reason, we normalized the largest of the gold-capture coefficients (hole-capture coefficient of the acceptor level) to the value published by Wu and Peaker.[11] The results for the capture coefficients at room temperature and at liquid-nitrogen temperature as determined from our lifetime measurements are summarized in Table I.

TABLE I. Experimental results for the electron- and hole-capture coefficients of the deep centers investigated and their temperature dependencies represented either by a power law $\alpha \sim T^{-\nu}$ or by an exponential $\alpha \sim \exp(E_A/kT)$ (α_n and α_p are given in $cm^3 s^{-1}$).

	300 K		77 K			
Defect	α_n	α_p	α_n	α_p	ν	E_A (meV)
Cr_i		1×10^{-7}		5×10^{-7}	1.1	
CrB	6×10^{-7}	2×10^{-7}	2×10^{-6}	7×10^{-7}	1.2	
Fe_i		2×10^{-8}		6×10^{-8}	0.6	
FeB	3×10^{-7}	3×10^{-8}	7×10^{-7}		0.6	
Au_{acc}		5×10^{-8}		6×10^{-7}		30
Au_{don}	6×10^{-9}		2×10^{-7}			30

Interestingly, all the experimentally determined capture coefficients are comparable at 77 K having absolute values between 10^{-7} and 10^{-6} $cm^3 s^{-1}$. Caused by the slightly varying temperature dependencies, the spread at room temperature is somewhat larger.

Unfortunately, apart from the gold case, only a few of these capture coefficients have been measured by other methods before. Since we have no direct measure for the recombination center density in the case of gold, we can only compare relative values of the capture coefficients. At liquid-nitrogen temperature our electron capture coefficient of the gold donor level is larger by a factor of 2.5 than the one published by Wu and Peaker.[11] The temperature dependencies found by them are also weaker than ours by a factor of about 2.

The only other among the centers considered here, where data on the temperature dependence of the capture coefficients can be found in the literature, is interstitial Fe. The hole-capture coefficient of Fe_i determined from the carrier lifetime in n-type Si at 300 K is more than 10 times larger than the value measured with DLTS by several groups.[15,37] Even more, we find a capture coefficient increasing with increasing temperature, whereas the DLTS investigations yields a thermally activated capture coefficient increasing with temperature. The reason for this discrepancy will be discussed in Sec. VIII.

Let us now compare the lifetimes under high- and low-injection conditions and the capture coefficients for electrons and holes derived from these. For all Cr- or Fe-related centers (Cr_i,CrB,Fe_i,FeB), the electron-capture coefficient is reasonably larger than that for holes. Although the energetic distance of the deep levels of CrB and FeB from the conduction band (0.87 eV, 1.05 eV) is much larger than the distance from the valence band [0.28 eV (Ref. 26), 0.1 eV (Refs. 15 and 36)], their electron-capture coefficient is larger by a factor of 3 or 10, respectively, than their hole-capture coefficient.

On the contrary, for both deep levels associated with gold the hole-capture process is more efficient than the electron capture. This follows from the fact that in gold-doped n-type silicon the high-injection lifetime is larger than the low-injection lifetime by a factor of about 5.5 (at room temperature), whereas in p-type Si the lifetime is virtually independent of the injection level.

In the temperature region below 60 K, special low-temperature states of the carriers such as excitons bound to neutral shallow dopants may show up, which might disturb the evaluation of the carrier lifetime due to recombination via deep impurities. Therefore, in order to avoid such complications, the samples investigated in this temperature range were made from ultrapure silicon with a resistivity of 8000 Ω cm ($\simeq10^{12}$ cm^{-3} B). As above, Cr, Fe, or Au was diffused into the specimen in order to introduce deep recombination centers. Because of the extremely low shallow doping level in these samples, virtually no sites for bound exciton formation are available. Therefore the true carrier lifetime due to the deep recombination centers at low temperature can be measured.

The lifetime measurements on these samples shown in Figs. 4 and 5 reveal that the capture coefficients of the deep centers are independent of temperature in this region. In the Cr- and in the Fe-doped high resistivity samples there is virtually no change in carrier lifetime between 4 and 50 K (Fig. 4). At a first glance, the gold-doped sample (Fig. 5) shows a contradicting behavior.

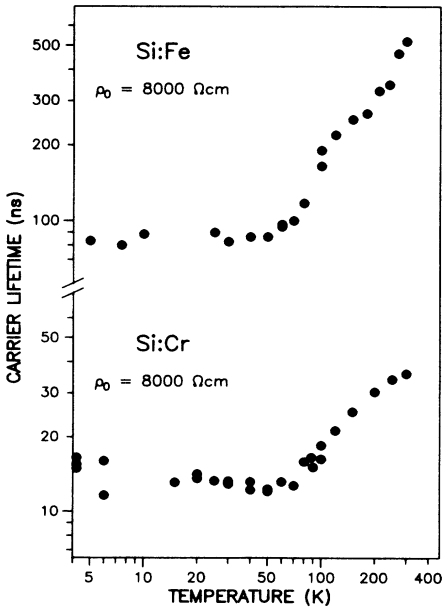

FIG. 4. Measured temperature dependence of the carrier lifetime in undoped Si diffused with iron or chromium showing that the carrier lifetime is independent of temperature below 60 K.

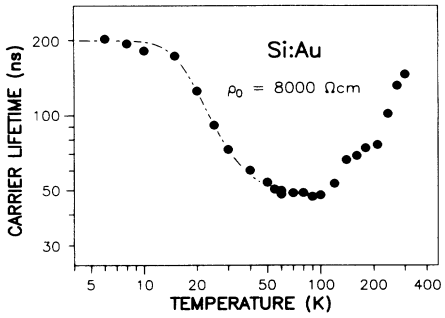

FIG. 5. Carrier lifetime versus temperature in gold-doped silicon. The dashed-dotted line is a fit taking into account the influence of a shallow excited level on the recombination (see the text).

This different behavior, however, can be well understood on the basis of known properties of the deep centers under discussion.

On one hand, the deep levels associated with isolated chromium or iron are both donor levels with an electron-capture coefficient being much larger than the hole-capture coefficient. Therefore, under high-injection conditions as realized at low temperature, the centers are neutral most of the time since the hole capture is the slowest step in the recombination process. The hole and the neutral donor interact only via the strongly localized defect potential. There is no additional Coulomb interaction which could lead to weakly bound hydrogenlike states.

On the other hand, both deep levels associated with gold in Si have larger cross sections for hole capture than for electron capture. Consequently, under high-injection conditions, the gold center will be in the positive charge state for most of the time, since under these circumstances the gold donor level is the dominant recombination level. Such a positively charged center is capable of binding an electron in shallow, hydrogenlike states in addition to the deeply bound defect ground state. If a gold center has captured an electron into such a shallow level, the center is neutral and therefore cannot capture another electron directly into the deep ground state.

Therefore we can easily understand the deviating behavior of gold-doped Si if we assume that the transition rate between the shallow excited states and the deep ground state is small. At low temperature, i.e., $kT \ll E_{\text{shallow}}$, many gold centers will come into an inactive excited state with an electron weakly bound. The number of positively charged active recombination centers is reduced leading to a relatively large carrier lifetime. At higher temperature, when the shallow levels can be ionized thermally, the number of active recombination centers increases and as a consequence the carrier lifetime decreases.

These phenomena can be described quantitatively by solving a set of rate equations similar to those valid in the case of a bound exciton competing with free-carrier recombination.[38] A fit to our experimental data drawn in Fig. 5 as a dashed-dotted line yields a binding energy of the shallow level of about 5—10 meV, which is reasonable for a $2s$ or $2p$ Coulombic level.[39] This also compares reasonably well with the effective-mass-like excited states of the gold acceptor level recently observed by Armelles *et al.*[40] by infrared absorption spectroscopy.

The increase in carrier lifetime above 100 K is already known from other recombination centers and from gold-doped samples with shallow doping. It seems to be a fundamental property of the recombination via deep impurity levels.

Let us now briefly summarize our results for the temperature dependence of the carrier lifetime. For temperatures above 60 K, the carrier lifetime due to deep-level recombination increases with temperature. At lower temperature, the mechanism for deep-level recombination itself yields a constant carrier lifetime. However, this simple behavior can be complicated by the formation of bound excitons at shallow dopants or by a weakly bound carrier at the deep center. In addition we concluded that the transition of a shallow bound carrier to the deep ground state is much less efficient than the direct capture of the carrier into the ground state.

B. Dependence on majority-carrier density

The dependence of the minority-carrier lifetime on the majority-carrier density is primarily interesting as a well-known criterion to identify Auger-type processes.[13] Since a classical Auger capture process into an impurity with only one charge state requires two free carriers, the respective capture coefficients will increase linearly with majority-carrier density.[9,10]

The results of our measurements of the minority-carrier lifetime as a function of majority-carrier density in silicon doped with Au or Cr as recombination centers are depicted in Fig. 6. Apart from the steep decrease of the lifetime

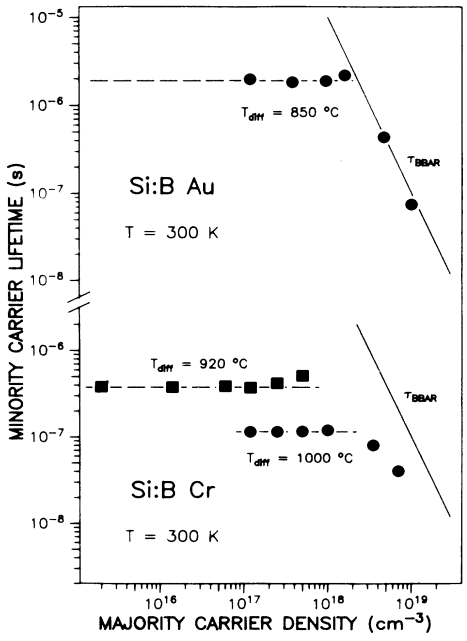

FIG. 6 Measured dependence of the minority-carrier lifetime in Au- or Cr-doped Si on majority-carrier density at 300 K.

at carrier densities above 10^{18} cm^{-3} due to band-to-band Auger recombination,[22] the minority-carrier lifetime is essentially independent of carrier density in the range 10^{15}–10^{18} cm^{-3}. The mechanism of recombination via the deep levels appears to be insensitive to variations of the majority-carrier density. Considering the criterion for trap Auger processes given above, this seems to rule out a significant contribution of Auger capture processes to the recombination via the deep impurities investigated.

C. Excitation dependence at low temperature

At low temperature, an interesting new property of deep-level recombination shows up. Below the critical temperature T_c for the formation of electron-hole droplets (EHD) [$T_c = 23$ K (Ref. 41)], where the high-density EHD and a low-density excitonic phase can coexist, the influence of deep recombination centers on the the EHD and on free excitons is considerably different. Whereas the exciton lifetime is strongly reduced by the impurities, the EHD decay remains basically unaltered [$\tau \simeq 137$ ns (Ref. 42)].

The experimental result above T_c is shown in Fig. 7(a) for iron-doped silicon. At low excitation the excess carriers decay exponentially corresponding to a carrier lifetime independent of carrier density. At high excitation, the initial decay is slower and gets gradually faster with decreasing carrier density. Finally the decay time reaches the same values as in the low-excitation case. The slower decay at high excitation is accompanied by a change in the luminescence spectrum [Fig. 7(b)]: Whereas at low excitation the spectrum is exciton like, it becomes free-carrier-like at high excitation as indicated by the low-energy tail of the luminescence line.[43] This transition between free excitons (FE's) and an electron-hole plasma (EHP) due to the screening of the Coulomb interaction at high carrier densities is called the "Mott transition."[44,45]

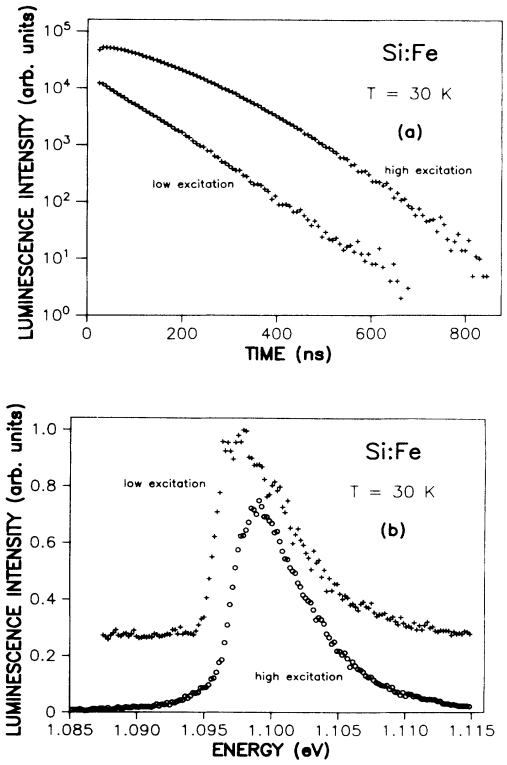

FIG. 7. (a) Comparison of luminescence decay in Si:Fe at 30 K for high and low excitation. (b) Luminescence spectra of Si:Fe in the free exciton region for high and low excitation as in (a).

The experimentally observed slowdown of the recombination via the deep impurities at high carrier densities is therefore due to a transition between free excitons and an electron-hole plasma. This interpretation is supported by the fact that the region of slower recombination is shifted towards higher carrier density at higher temperatures, which is also expected for the Mott transition.[45]

These experimental observations suggest that recombination via deep impurity levels at low temperature is more efficient for the free excitons occuring at low carrier densities than for a high-density electron-hole plasma (EHD or EHP). This is a first indication that the excitonic binding of the carriers plays an important role in the recombination process.

D. External electric field

The influence of free excitons on the recombination process was also investigated by applying an external electric field to the samples. For that purpose, two contacts were evaporated onto the surface of the samples and the exciting laser beam was focused on the gap between them (Fig. 8). In this configuration, the decay of the excess carriers was observed by two methods: The band-to-band luminescence was used as a measure of the density of excitons and free carriers, whereas the time dependence of the photocurrent yielded information about free carriers only. At sufficiently high voltage, impact ionization of excitons will occur and the thermal equilibrium between excitons and free carriers is shifted towards the free-carrier side.[46–48]

Figure 9 shows a typical measurement of the decay of both the luminescence and the photocurrent in chromium doped silicon. Without voltage, the luminescence decays exponentially with a time constant of about 12 ns deter-

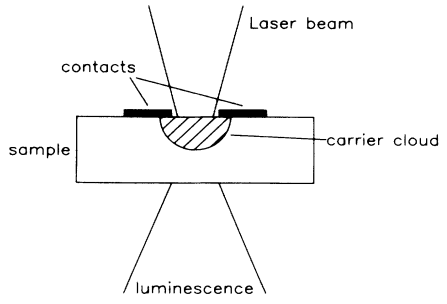

FIG. 8. Schematic plot of the setup used for investigating the influence of an electric field on the recombination.

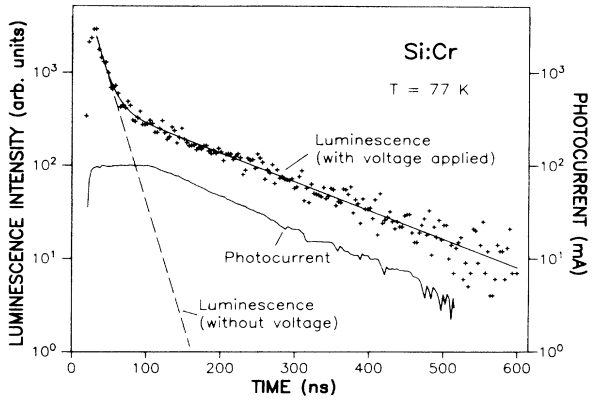

FIG. 9. Decay of the luminescence and the photocurrent in Si:Cr at 77 K with and without electric field. The field applied was about 800 V/cm.

mined by the chromium concentration. If a voltage of about 80 V is applied, the luminescence decay becomes biexponential, with an initial decay time of $\simeq$12 ns and a slower component decaying with about 150 ns. The photocurrent also decays slowly exactly following the slow component of the luminescence.

This is particularly interesting, since only free carriers contribute to the photocurrent, whereas the luminescence is mainly due to free excitons, which have a considerably larger radiative transition probability than free carriers.[49] Therefore, the experiment clearly shows that the free carriers detected by the photocurrent decay much slower than the free excitons.

The dependence of the two decay times derived from the biexponential decay of the luminescence on the applied voltage is depicted in Fig. 10. The fast decay is independent of the applied voltage. The slower decay time increases with voltage and appears to reach a limiting value at or above 80 V. This observation suggests that the increasing degree of ionization of the excitons with increasing voltage is the reason for the increase in decay time. At low voltages, the carriers decay with the fast decay time of free excitons, whereas in the high voltage limit the lifetime of free carriers determines the effective decay time.

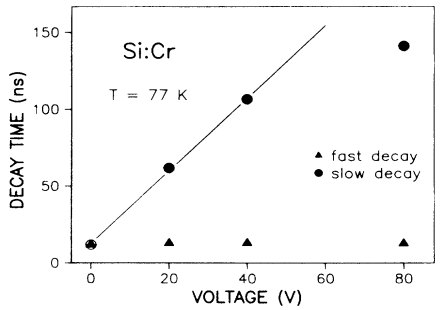

FIG. 10. Field dependence of the two decay times derived from Fig. 9.

This experiment also indicates that the recombination via deep impurity levels is much more efficient for free excitons than for free electrons and holes. The excitonic binding of the carriers seems to lead to a strong enhancement of the recombination probability.

V. AUGER SPECTROSCOPY

All the experiments on the recombination kinetics described above have in common that they give only indirect evidence for the mechanism of the capture of carriers into deep impurity levels. For an interpretation of the experimental data, it is generally necessary to compare them with the predictions derived from theoretical models. In the case of Auger capture processes, however, there is a fundamental difference to other processes allowing an unambiguous identification of Auger processes: Contrary to single or multiphonon capture, where the excess energy of the captured carrier is directly emitted in form of phonons, Auger processes involve an intermediate electronic state, the highly excited Auger particle, which is temporarily storing the excess energy. Only when this Auger particle is relaxing back to the band minimum, is its energy gradually transferred to the lattice.

This unique property of Auger recombination processes can be utilized to prove the existence of Auger processes. For the case of band-to-band Auger recombination in electron-hole droplets (EHD) this has already been done by Betzler.[50] He utilized the fact that the highly excited Auger particle can recombine radiatively with another carrier of opposite charge in its respective band minimum thereby emitting a high-energy luminescence near twice the bandgap energy. Since the hot particles are rapidly relaxing back to the band minimum, there is a quasithermal distribution of hot carriers below their maximum energy determined by the Auger process.

For the analogous case of Auger capture into a deep impurity level, the relevant processes are sketched in Fig. 11. We assume that an electron is captured by the impur-

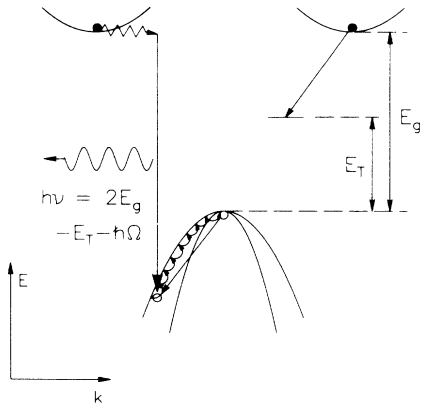

FIG. 11. Auger capture of an electron into a deep impurity level in Si and subsequent radiative recombination of the highly excited hole. The "Auger luminescence" is used to prove the existence of the Auger process.

ity and that a hole takes over the excess energy. The highly excited hole is now subject to two different energy-loss mechanisms: Mainly, the hole relaxes back to the valence-band maximum emitting optical phonons. On the other hand, at any time, even after emitting some phonons. the hole can recombine radiatively with a second electron in the conduction band. In general, this radiative transition requires a momentum-conserving phonon of energy $\hbar\Omega$. The photon emitted in this transition has a maximum energy given by

$$h\nu_{\max}=2E_g-E_T-\hbar\Omega\ . \tag{7}$$

Since the hot holes are subject to such a radiative recombination during every stage of the relaxation process, one expects a broad luminescence band extending from the band edge up to a maximum energy determined by the depth of the impurity level and given by Eq. (7).

In fact, using an improved version of the experimental setup described by Betzler *et al.*[51] we were able to observe the "hot" luminescence from highly excited carriers generated by Auger capture processes into deep impurity levels.[19] Figure 12 shows the luminescence spectrum obtained for Au-doped p-type silicon in the range 1.75—2.55 eV at a temperature of 80 K. As is well known, at about 2.3 eV the two-electron transition shows up. This transition was first observed by Betzler *et al.*[52] It is due to a phononless simultaneous radiative recombination of two electron-hole pairs yielding a photon with an energy $h\nu=2E_g$. The luminescence band due to the hot Auger particles is found at lower energies. As expected, we observe a broad luminescence band with a high-energy cutoff depending on the impurity species contained in the sample.

For the case of gold-doped silicon, this high-energy cutoff is at 1.85 eV. Using $2E_g=2.28$ eV as obtained from the two-electron transition and a mean phonon energy[53] of 0.06 eV (radiative band-to-band transitions in Si are mainly coupled to TO phonons[54]), Eq. (7) yields the energetic depth of the trap level $E_T=0.37\pm0.03$ eV. This is in excellent agreement with the energy of the well-known gold donor level[55] at $E_v+0.35$ eV suggesting that an Auger process is involved in the recombination via this level. The observed Auger particles therefore correspond to the electron capture into this level. Unfortunately, Auger particles corresponding to the respective hole-capture process, expected to occur below 1.45 eV, could not be observed for experimental reasons: The low-energy cutoff of the photomultiplier used for the detection of the Auger luminescence at about 1.7 eV prohibits their observation.

Interestingly, the appearance of the Auger luminescence is independent of the majority-carrier density of the samples. More than that, the hot luminescence is even observed from samples in a majority-carrier density range where the carrier lifetime is independent of majority-carrier density. At a first glance, there appears to be a contradiction between our experiments. On one hand, the independence of the carrier lifetime of majority-carrier density seems to rule out any significance of Auger processes for deep-level recombination. On the other hand, the observation of the hot Auger luminescence corresponding to the deep levels contained in the samples clearly shows that Auger processes play an important role in the recombination via the deep impurity levels. This apparent contradiction will be resolved by the new model for the recombination mechanism discussed below.

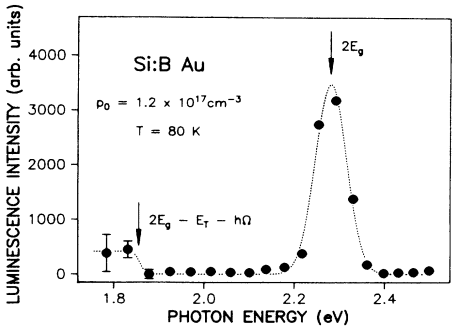

FIG. 12. Luminescence spectrum near twice the band-gap energy in gold-doped silicon. The steplike band at about 1.8 eV is due to hot Auger particles. The increasing error bars at low photon energies are due to the decreasing sensitivity of the photomultiplier.

VI. INADEQUACY OF THE CLASSICAL MODELS

The experimental results reported in this paper clearly demonstrate that the "classical" models for the capture of carriers into deep impurity levels fail to explain the observed properties of the recombination process. Radiative capture would imply that a strong luminescence corresponding to the depth of the deep level would be observed. In silicon, however, in most cases there is no deep luminescence at all. Even at those impurities, which give rise to characteristic luminescence lines,[26,56–58] the luminescence is far too weak to explain the recombination quantitatively.

Multiphonon capture,[7] which seems to be the most reasonable model from the theoretical point of view, is also excluded since it predicts an incorrect temperature dependence of the capture process: In the weak-coupling limit, as realized at the impurities considered here,[59,60] multiphonon capture processes should lead to a thermally activated behavior of the capture coefficients, i.e., they should increase with temperature. Experimentally, we observe a decrease of the capture coefficients with increasing temperature (see Sec. IV A).

Cascade capture processes,[8] although qualitatively yielding the correct temperature dependence,[61] cannot account for the experimental results either: In contrast to shallow impurities, where the hydrogenlike level scheme meets the requirements for this kind of capture,[12,38] deep impurities usually have only a few energy levels in the gap being several phonon energies apart. Even the capture into attractive charged deep centers expected to have hydrogen-like excited states near the band edge cannot be explained by this model: In general there remains a large last step from the lowest excited state to the ground state which can never be overcome by a single phonon.[12]

Finally, an Auger-type capture process[9,10] has to be

considered. The direct experimental evidence for the hot Auger particles occurring just at the right energy given above, is in favor of this type of capture process. However, the impurity Auger processes usually discussed in the literature[9,10] cannot explain some other features of the experimental results. Auger capture of a free carrier into a center with only a single charge state requires a second free carrier to take over the excess energy.[9,10] Therefore a quadratic dependence of the recombination rate on carrier density is expected, which is clearly in contradiction to our experiments. Another possible Auger process, which involves two localized carriers,[62] would work only with those deep centers having two charge states (He-like centers). In addition, for such an Auger process, the energy of the hot Auger particles should yield trap energies different from the single-particle levels. For both Auger processes, the theory predicts a very weak temperature dependence, in contrast to the distinct temperature dependence observed in our experiments. The above considerations clearly show that none of the classical models is adequate to explain the experimentally observed properties of deep-level recombination in silicon.

VII. BASIC ASPECTS OF A NEW MODEL

The time resolved measurements on the kinetics of deep-level recombination reported in Sec. IV of this paper, give some valuable hints on the real recombination mechanism. The excitation dependence of the recombination, the experiment on recombination under the influence of an electric field, and the temperature dependence of the carrier lifetime suggest a strong influence of free excitons on the recombination process. The high-excitation experiment, where the Coulomb interaction is screened by free carriers and the formation of free excitons is prevented, shows that at high excitation the recombination efficiency of the deep centers is clearly reduced compared to the low-excitation case, where nearly all carriers are bound forming free excitons. The application of an electric field accelerating the free carriers then being able to break up free excitons by impact ionization, also leads to a considerable increase in carrier lifetime. The free electrons and holes generated by the impact ionization of free excitons apparently have a much lower probability of recombination via the deep impurities than the free excitons dominating at vanishing electric field.

Interestingly, the temperature dependence of the carrier lifetime may be interpreted in a similar way. At low temperature ($T<60$ K), almost all carriers are bound as free excitons; in this region the carrier lifetime remains constant. At higher temperature ($T>60$ K) the excitons become thermally ionized and an increasing portion of the carriers exists as free electrons and holes. In the same temperature region, the measured carrier lifetime increases corresponding to a decreasing efficiency of the recombination mechanism. Therefore it may also be concluded that the recombination of free carriers via deep impurity levels is less efficient than that of free excitons.

On the other hand, the optical detection of hot Auger particles with an energy corresponding to the depth of the recombination centers reveals that some kind of Auger process involving the deep levels takes place.[19] Thereby a decisive role of Auger processes is strongly suggested.

The above considerations led us to our new model of an excitonic Auger recombination via deep impurities. The basic idea of this model is sketched in Fig. 13. Primarily, the model is based on the spatial localization of an electron-hole pair subject to an attractive Coulomb interaction thus forming a free exciton.

The capture of an electron into a deep level by an excitonic Auger process is depicted in Fig. 13(a). When a free exciton meets the impurity, the electron out of the exciton may be captured into the deep level, whereas the hole takes the excess energy and is highly excited into the valence band. Analogously, a hole may be captured into the impurity [Fig. 13(b)]. In this case the electron is excited into the conduction band. For a complete recombination of an electron-hole pair, two excitonic Auger processes are required, just as in the usual SRH model.

The excitonic Auger capture process is markedly different from a classical Auger process of free carriers as usually discussed in the literature.[9,10] Since in an exciton an electron and a hole are tied together, the transition probability varies linearly with exciton density. This corresponds to a capture coefficient being independent of carrier density. The spatial correlation of the electron and the hole within the exciton is equivalent to a strongly enhanced "local carrier density," which, especially at low carrier densities, leads to a strongly enhanced transition probability. For the excitonic process, the effective capture coefficient becomes temperature dependent, since the composition of the carrier system of excitons and free carriers varies due to thermal ionization of the excitons.

The transition probability for an excitonic Auger capture process can be estimated by the following simple argument. Within an exciton, the electron and the hole are mostly comprised within a sphere with a radius equal to the excitonic Bohr radius a_0. Using a Bohr radius $a_0=4.6$ nm for silicon,[63] the exciton corresponds to a carrier density of about $n=2\times10^{18}$ cm^{-3}. Therefore the transition probability for the excitonic Auger capture may be approximated by the transition probability of a classical impurity Auger process at a carrier density of 2×10^{18} cm^{-3}. Using the trap Auger coefficient given by Haug[64]

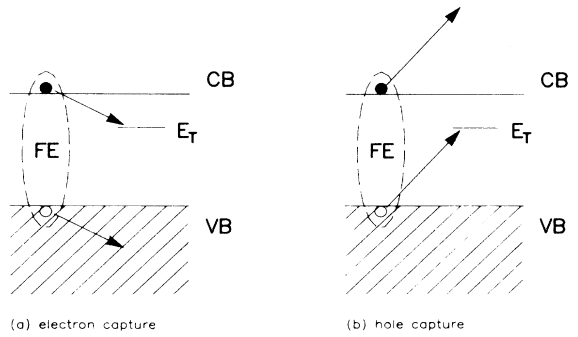

FIG. 13. Excitonic Auger capture processes into deep impurity level.

($T \simeq 0.5 \times 10^{-26}$ cm^{6}s^{-1}) this procedure yields a capture coefficient $\alpha \simeq 10^{-8}$ cm^{3}s^{-1}, which is only slightly lower than the experimental values ($\alpha \simeq 10^{-7}$ cm^{3}s^{-1}). The properties of excitonic Auger recombination via deep impurities will be investigated quantitatively in a forthcoming paper.[18]

VIII. DISCUSSION

Qualitatively, our new model is in good agreement with the expermental results reported in this paper. The temperature dependence of the carrier lifetime is governed by the thermal ionization of the free excitons. With increasing temperature, the excitonic portion of the total carrier density becomes smaller, and therefore the efficient excitonic recombination mechanism becomes less important. In fact, for all recombination centers investigated, the carrier lifetime increases with increasing temperature, in good agreement with an excitonic Auger recombination.

The experimentally observed independence of the carrier lifetime on majority-carrier density is actually an inherent property of the excitonic recombination mechanism. Due to the spatial correlation of the electron and the hole in the exciton, the capture coefficients are independent of density.

Of course, the excitation dependence of the recombination and the influence of the electric field as well as the occurrence of hot Auger particles are well explained by the excitonic Auger recombination mechanism since they served as a starting point for the development of our new model.

Actually, the enhancement of recombination processes by the excitonic localization of electron-hole pairs is a frequently observed phenomenon especially for Auger-type recombination processes. The recombination of excitons bound to neutral shallow donors or acceptors in silicon[65] and in GaP,[66] for example, is governed by a localized Auger process. An increasing depth of the impurity level leads to an increasing localization of the bound exciton in real space *and* to an increasing delocalization of the exciton wave function in k space. Both effects lead to an increase of the Auger transition probability and to a strong decrease of the bound exciton lifetime for large binding energies.[65,66]

An enhancement of band-to-band Auger recombination (BBAR) in silicon by the spatial correlation of electron-hole pairs has also been reported.[67] The recombination in electron-hole droplets (EHD) which is governed by BBAR, yields Auger coefficients distinctly larger than those obtained for highly doped silicon.[22] This difference is due to the Coulomb correlation of electrons and holes within the EHD as described by the enhancement factor g.[67] The variation of the enhancement factor with carrier density has been investigated by Schmid[68] and Wagner.[69] Interestingly, they found that the enhancement factor varies like $g \sim n^{-0.5}$—n^{-1}. For comparison, the binding of electrons and holes in free excitons just corresponds to an enhancement factor $g \sim n^{-1}$. This suggests that even at high carrier density strongly correlated electron-hole pairs are involved in the Auger recombination.

Another recombination process known to be strongly enhanced by the excitonic localization is the radiative band-to-band recombination. As shown for Si by Schlangenotto *et al.*,[49] the temperature dependence of the radiative recombination is mainly determined by the ionization of free excitons. Due to the spatial correlation, the excitons have a much larger radiative recombination probability than free electrons and holes. Even at room temperature, the radiative recombination rate is enhanced by excitonic effects by more than a factor of 10.[49]

Our new model of an excitonic Auger recombination via deep impurity levels has some important consequences. Since the efficient excitonic capture mechanism requires electron-hole pairs, this mechanism works only under minority-carrier injection conditions, i.e., if the sample is excited optically or by a forward biased *pn* junction. On the other hand, if no minority carriers are generated in the sample as in a typical DLTS experiment, capture into deep levels has to occur by other mechanisms such as the multiphonon mechanism or the cascade mechanism. Therefore, one should expect that under different experimental conditions, different capture mechanisms will be effective.

In fact, the experimental data available in the literature support this view. First of all, our own data concerning the temperature dependence of deep level recombination are gained from experiments with optical injection of electron-hole pairs. Obviously, under these conditions the

TABLE II. Capture coefficients of deep centers as measured by DLTS by various groups. The temperature dependence tends to exhibit a thermally activated behavior.

Defect	Type	Method	Capture coefficient at 300 K (cm^{3}s^{-1})	Temperature dependence	Ref.
Ti	$h \rightarrow Ti^0$	DLTS	1.5×10^{-8}	const	69
V	$h \rightarrow V^0$	DLTS	1.5×10^{-8}	const	70
CrB	$h \rightarrow CrB^0$	DLTS	1.2×10^{-7}	?	26
Fe_i	$h \rightarrow Fe_i^0$	DLTS	2×10^{-9}	$\exp(-48\ \text{meV}/kT)$	37
				$\exp(-32\ \text{meV}/kT)$	15
Au	$e \rightarrow Au^0$	DLTS	2×10^{-9}	const	11
Pt	$e \rightarrow Pt^0$	DLTS	1.4×10^{-7}	const	16
	$h \rightarrow Pt^0$	DLTS	4×10^{-8}	$\exp(-7.3\ \text{meV}/kT)$	16

TABLE III. Capture coefficients of deep centers under minority-carrier injection conditions found in the literature. These capture coefficients decrease with increasing temperature.

Defect	Type	Method	Capture coefficient at 300 K ($cm^3 s^{-1}$)	Temperature dependence	Ref.
Ti	$e \rightarrow Ti^+$	Minority-carrier injection	2.6×10^{-7}	$T^{-0.01}$	70
Fe_i	$e \rightarrow Fe_i^+$	Minority-carrier injection	4×10^{-7}	T^{-2}	14
Au	$e \rightarrow Au^+$	Minority-carrier injection	1×10^{-8}	T^{-2}	11
	$h \rightarrow Au^-$	Minority-carrier injection	1.6×10^{-7}	$T^{-1.3}$	11
	$h \rightarrow Au^0$	Minority-carrier injection	8×10^{-8}	T^0	11

excitonic mechanism predominates. The literature data mostly gained from DLTS-like experiments may be divided into two groups. The first group, compiled in Table II, contains all experiments where only majority carriers were present whose capture into the deep levels was investigated. For this group, to our knowledge, a thermally activated behavior of the capture coefficients (including zero activation energy) was found in all cases (Refs. 11, 15, 16, 26, 37, 70, and 71). In these cases, the multiphonon mechanism is most likely to be responsible for the capture.

The other group (Table III) consists of those DLTS experiments, were minority carriers were injected in order to study minority carrier capture. This group revealed capture coefficients decreasing with increasing temperature thereby following a power law.[11,14,70] These results suggest that in the experiments of the second group the excitonic Auger capture might be the dominating capture mechanism.

IX. CONCLUSION

In this paper, we have presented an extensive experimental study of nonradiative recombination via deep impurity levels in silicon. Our results on the temperature dependence, the dependence on carrier density, and on the influence of an electric field cannot be explained by one of the classical theoretical models for capture into deep levels.

Instead, our experiments clearly show that Auger processes are responsible for the recombination and that the Coulomb correlation of electrons and holes plays a decisive role. This led us to the development of our new model of an excitonic Auger recombination via deep impurity levels. We have shown qualitatively that this model is in fact able to explain our experimental results consistently. The model will be discussed in a more quantitative manner in a forthcoming paper.

ACKNOWLEDGMENTS

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