Experimental Proof of Impurity Auger Recombination in Silicon

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Direct experimental proof of impurity Auger recombination in silicon is given by measurement of the weak luminescence from highly excited carriers which are produced in the Auger process. Gold, iron, and chromium used as deep impurities have been identified spectroscopically by the energetic shift from the $2E_g$ emission corresponding to their levels in the gap.

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The physical mechanism of nonradiative recombination of free charge carriers via deep impurity levels in semiconductors is not yet fully understood. The main problem is of which way the excess energy of the recombining carriers is dissipated. In the recent literature, most authors assume capture of carriers into the deep impurity levels by processes involving the emission of single or multiple phonons, such as the cascade mechanism[1] or the multiphonon capture mechanism.[2]

Lifetime studies on excitons bound to neutral shallow impurities[3] and on high-density carriers subject to band-to-band Auger recombination[4] have demonstrated the importance of Auger recombination processes. However, only in a few cases has Auger recombination via deep impurities been reported.[5]

Probably, the main reason for the insufficient knowledge of the recombination mechanism is that the recombination mechanism is usually deduced from experiment in an indirect way, e.g., by means of the temperature dependence of the capture coefficients or by reaction-rate arguments. However, since these arguments are based on the predictions of theoretical models, they do not permit an unambiguous identification of the recombination mechanism.

In this Letter, the first direct evidence for Auger recombination via deep impurity levels in silicon is presented. Experimentally, I use the unique attribute of Auger processes that the excess energy is stored in an intermediate electronic state before being transformed into phonons by relaxation. The highly excited particles generated by an impurity Auger process are detected by means of their radiative recombination for the first time.

Several years ago, Betzler[6] succeeded in detecting the hot carriers originating from band-to-band Auger recombination in electron-hole droplets in highly excited silicon at low temperature. He observed an extremely weak luminescence band below twice the band-gap energy, which was due to the radiative recombination of a "hot" Auger particle with a "cold" particle of opposite charge. LO-phonon–assisted relaxation of the Auger particles in their band gave rise to a weak multiple structure in the luminescence spectra.

In a similar way, I have been able to observe the "hot" charge carriers produced by an impurity Auger process for the first time. The processes giving rise to such high-energy luminescence are depicted in Fig 1(a) in the silicon band structure. The highly excited hole, which has taken over the electron-capture energy, may recombine radiatively with a second electron in the conduction band while it relaxes back to the valence-band maximum. This process requires the participation of a momentum-conserving phonon. Therefore, one expects a broad luminescence band with a weak structure as determined by the details of the relaxation process; this band extends from the band-gap energy up to a maximum energy depending on the trap energy,

$$h\nu_{\max} = 2E_g - E_T - \hbar\Omega . \quad (1)$$

Here, $\hbar\Omega$ is the energy of the phonon involved in the radiative transition.

The samples investigated were made from high-purity (floating zone) p-type silicon (boron doped) which was diffused with Au, Fe, or Cr at 850–950 °C. This treatment resulted in a concentration of recombination centers of 10^{13}–10^{14} cm^{-3} and in a low injection-carrier lifetime of 10–100 ns at 80 K. Before the measurements, the samples were etched in a mixture of nitric and hydrofluoric acid in order to decrease the surface-recombination velocity. The experimental setup used for the luminescence measurements was similar to that described by Betzler, Weller, and Conradt,[7] but the sensitivity was improved substantially. The samples, mounted on a cold finger and kept at liquid-nitrogen temperature, were excited by the 850-nm light of a three-diode stacked GaAs laser array. The laser was also cooled to 80 K and was operated at a pulse length of $\simeq 2\ \mu$s, yielding a peak power of $\simeq 12$ W. The luminescence was dispersed by a double-prism monochromator and detected by a cooled S11-type photomultiplier, which reached a dark count rate of about 0.5 s^{-1}. The pulses from the photomultiplier were processed by a digital-boxcar technique,[7] allowing the detection of extremely weak luminescence signals at count rates as low as 0.1 photon/min. The spectra were measured several times

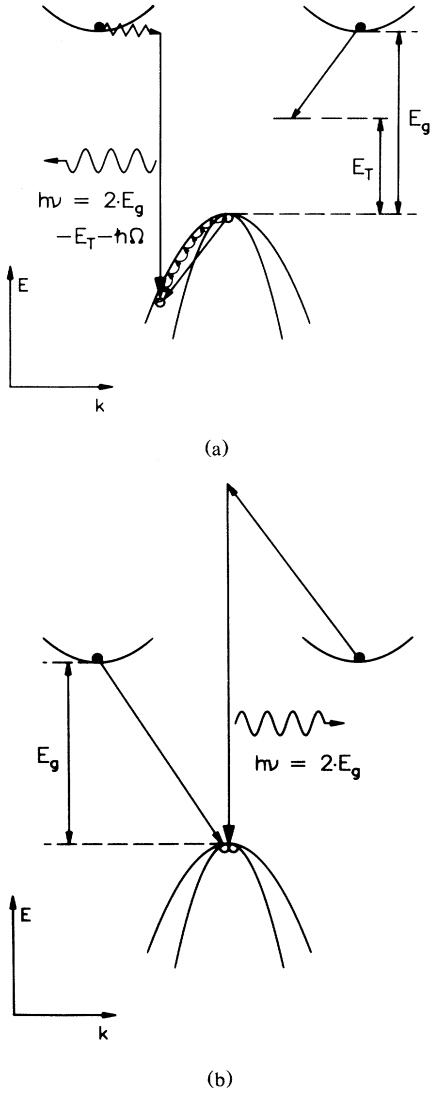

FIG. 1. Radiative transitions far above the principal band edge in silicon. (a) Auger capture of an electron into a deep impurity level and subsequent radiative recombination of the highly excited hole. (b) Simultaneous radiative recombination of two electron-hole pairs.

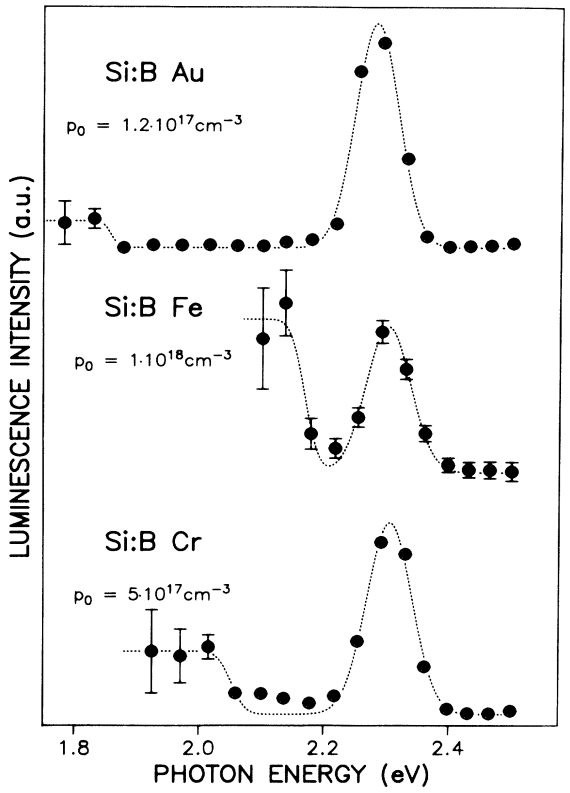

FIG. 2. Luminescence spectra near twice the band-gap energy in silicon doped with deep recombination centers. The steplike bands on the low-energy side are due to hot Auger particles (the absolute magnitudes of the three spectra are strongly different).

and averaged, yielding a total measuring time of up to 3 weeks.

Figure 2 shows the luminescence intensity versus photon energy for Au-, Fe-, and Cr-doped Si in the range 1.75–2.55 eV at 80 K. The dominant feature of the spectra is a relatively sharp luminescence line at about 2.3 eV. This line is the $2E_g$ band previously observed by Betzler *et al.* at 300 and 77 K,[8] and at 2 K in electron-hole droplets.[9] It originates from the phononless simultaneous radiative recombination of two electrons and two holes [Fig. 1(b)]. This transition can be utilized as a mark for twice the band-gap energy.

At lower photon energies the steplike onset of emission bands appears with a high-energy cutoff clearly depending on the impurity species contained in the sample. These luminescence bands are due to the radiative recombination of the highly excited Auger particles. The sharp onset of the bands corresponds to the maximum possible energy of the Auger particles, which produce the broad band towards lower energy upon relaxation to the band edge. Contrary to the band-to-band Auger-recombination case at low temperature in Ref. 6, no structure of the Auger luminescence could be resolved in the present experiments. This is probably due to the present higher temperature and to the poor instrumental resolution which had to be used because of the extremely weak luminescence. From the high-energy cutoff of the Auger luminescence the energy of the impurity level involved in the Auger process can be evaluated by means of Eq. (1).

Let us perform this evaluation for the case of gold-doped silicon. The $2e$ transition is centered at 2.28 eV, and the high-energy cutoff of the Auger luminescence

is at 1.85 eV. Since radiative band-to-band transitions in silicon are preferentially coupled to TO phonons,[10] the momentum-conserving phonon amounts to about 0.06 eV.[11] From these data we obtain an energetic distance of the trap level from the nearest band edge of 0.37 ± 0.03 eV. This is in good agreement with the energy of the well-known donor level of gold in silicon at $E_v + 0.35$ eV,[12] expected to be the dominant recombination level in gold-doped p-type silicon. Similarly, in iron-doped Si, I obtain a trap energy of 0.08 eV below the band edge, which compares well with the donor level of the iron-boron pairs at $E_v + 0.1$ eV.[13]

In chromium-doped Si, the cutoff of the Auger luminescence yields a defect level at $E_v + 0.20$ eV, which has also been derived from measurements of the temperature dependence of the carrier lifetime on the same series of samples.[14] This level energy has to be compared with the results of deep-level transient-spectroscopy (DLTS) investigations on Cr-doped Si, which yielded a donor level at $E_v + 0.28$ eV for the Cr-B pairs.[15]

There are several possible causes for the significant difference between the present result and that from DLTS. First, the present samples could have been contaminated with other impurities. This seems unlikely, since the samples have been characterized by DLTS and by infrared photoluminescence measurements, and no unwanted impurities have been detected.

Possibly, a recent observation of Chantre and Bois[16] is helpful to understand this difference. They observed different DLTS signals depending on the charge state of Fe-Al pairs in Si during the cooling down of the samples. This observation was explained by the difference in Coulombic energy of differently oriented interstitial-substitutional pairs. In our case of Cr-B pairs, The $E_v + 0.28$ eV level is ascribed to $\langle 111 \rangle$-oriented pairs.[15] From the difference in Coulombic energy, a level at $E_v + 0.21$ eV is expected for $\langle 100 \rangle$ pairs. Since this energy coincides with the present measured energy of the dominant recombination level in Cr-doped p-Si, one would conclude that the recombination occurs mainly via $\langle 100 \rangle$-oriented Cr-B pairs.

The experiments reported here clearly show that the recombination of nonequilibrium carriers in Au-, Fe-, or Cr-doped silicon is due to an Auger-type process. An Auger process involving two bound carriers, as at doubly ionizable (He-like) centers,[17] can be excluded since it would lead to a considerably lower energy of the hot Auger particles. The measured energy of the Auger particles is consistent with an impurity Auger process of one bound and two free carriers (H-like center) as treated theoretically by Landsberg, Rhys-Roberts, and Lal[18] and by Haug.[19]

The classical picture of such an Auger process predicts a quadratic dependence of the Auger recombination rate on carrier density. Experimentally, however, the impurities considered here lead to a carrier lifetime independent of majority-carrier density in the range 10^{15}–10^{18} cm^{-3}.[14] On the other hand, the present experiments clearly show that an Auger process is involved in the recombination. This contradiction suggests that the simple classical picture of an impurity Auger process has to be modified. From the recombination kinetics in silicon doped with the same impurities as used here, I deduced a strong influence of excitonic effects on the recombination even at room temperature[14,20]: The probability of an Auger-capture process is strongly enhanced by the excitonic localization of the electron-hole pairs.[14]

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