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Recombination Properties of Gold in Silicon

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The presence of gold atoms in the silicon lattice decreases the lifetime of excess electrons and holes in p- and n-type material. The capture of electrons in p-type silicon occurs through the gold donor level with a capture cross section, σ_{n0}, of 3.5×10^{-15} cm^2 (at 300°K). This capture cross section varies as $T^{-2.5}$ between 200° and 500°K. In n-type silicon the electron capture cross section, σ_{n0}, is 5×10^{-16} cm^2 at 300°K and is temperature independent; the hole capture cross section, σ_{p0}, is 1×10^{-15} cm^2 at 300°K and varies as T^{-4}. The capture in this case occurs through the gold acceptor level.

INTRODUCTION

GOLD is one of the few elements outside columns III and V known to be electrically active in silicon. A donor level at 0.35 ev from the valence band and an acceptor level at 0.54 ev from the conduction band have been reported.[1,2]

The present paper describes experiments whose purpose was to determine the recombination properties of gold in silicon single crystals.

NATURE OF GOLD LEVELS

Collins *et al.*,[2] in their investigation on the properties of gold in silicon, concluded that the same gold center gives rise to both of the observed energy levels, since within their experimental errors the concentrations of the donor levels and the acceptor levels agree. Since this result is important for the interpretation of the recombination process, an additional check has been made by comparing the gold concentration with the concentration of donor levels introduced in p-type silicon.

Several gold-doped crystals have been grown by the Teal-Buehler technique[3] (0.001 inch per second, 50 rpm). The gold concentration has been calculated from the distribution coefficient[2] and has been measured by a neutron activation analysis. The concentration of donor levels has been obtained from conductivity measurements. The results are listed in Table I. Within experimental error, a one-to-one correlation of donor levels is found. This result substantiates the conclusion of Collins *et al.*[2] A neutral gold atom, therefore, can either accept or donate one electron. In other words, in the presence of an ionized gold donor level the acceptor does not exist, and vice versa. The position of the Fermi level in the silicon determines, therefore, the type of the active levels. As a result of this, in n-type material only the acceptor level at 0.54 ev from the conduction band is active and in p-type material only the donor level at 0.35 ev from the valence band is active.

The behavior of gold in silicon is therefore similar to that found in germanium, where it has been shown by Dunlap[4,5] and by Woodbury and Tyler[6] that a gold atom gives rise to one donor and three acceptor levels.

MEASUREMENTS

The lifetime of excess minority carriers has been measured in gold-doped silicon as a function of the conductivity type, resistivity, and gold concentration.

The gold concentration has been obtained by one of the two methods mentioned before or from a determination of the concentration of levels as obtained from conductivity measurements.

The lifetime has been measured by the injection-extraction method[7] or with a Van de Graaff accelerator, using the technique described by Wertheim.[8] For several samples, the lifetime has been measured as a function of temperature and as a function of injection density.

RESULTS

Since a different gold level is active in n-type and p-type silicon, respectively, recombination processes in these two types can be considered separately and each can be described in terms of the single-level recombination theory.[9,10] The injection-extraction method[7] can yield the steady-state lifetime, particularly if the plateau

TABLE I. Comparison of gold concentration with the concentration of gold donor levels in p-type silicon crystals.

Sample	Gold concentration (cm^{-3})		Donor concentration (cm^{-3})
	Determined from activation analysis	Calculated from distribution coefficient	
1	6.5×10^{14}	6×10^{14}	6×10^{14} [a]
2	5×10^{14}	6×10^{14}	6×10^{14} [b]
3	7×10^{13}	6×10^{13}	6×10^{13} [a]

[a] Obtained from temperature dependence of resistivity.
[b] Obtained from resistivity change between gold-doped and undoped portions of the crystals.

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[1] E. A. Taft and F. H. Horn, Phys. Rev. **93**, 64 (1954).

[2] Collins, Carlson, and Gallagher, Phys. Rev. **105**, 1168 (1957).

[3] G. K. Teal and E. Buehler, Phys. Rev. **87**, 190 (1952).

[4] W. C. Dunlap, Jr., Phys. Rev. **100**, 1629 (1955).

[5] W. C. Dunlap, Jr., Phys. Rev. **97**, 614 (1955).

[6] H. H. Woodbury and W. W. Tyler, Phys. Rev. **105**, 84 (1957).

[7] R. H. Kingston, Proc. Inst. Radio Engrs. **42**, 829 (1954).

[8] G. K. Wertheim and W. M. Augustyniak, Rev. Sci. Instr. **27**, 1062 (1956).

[9] W. Shockley and W. T. Read, Jr., Phys. Rev. **87**, 835 (1952).

[10] R. N. Hall, Phys. Rev. **87**, 387 (1952).

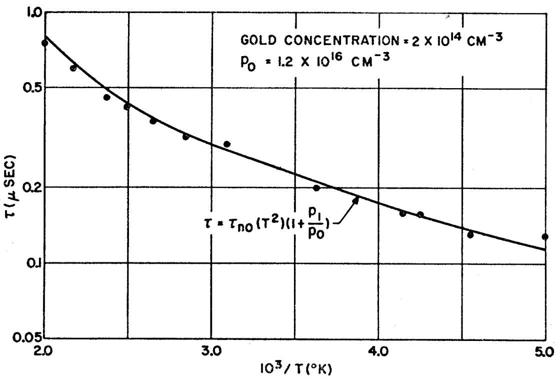

FIG. 1. Lifetime *vs* temperature in *p*-type silicon measured by the injection-extraction technique. The electron capture cross section, σ_{n0}, varies as $T^{-\frac{5}{2}}$ with temperature.

portion of the pattern is observed. This plateau can be adjusted to be of a duration several times shorter than the lifetime itself and is proportional to the time during which the injected carriers diffuse back to the junction. Accordingly, the plateau length measures the steady-state minority carrier density under conditions of forward bias. Similarly to the photoconductivity case, the Van de Graaff method gives the transient lifetime. The solutions for the two cases have been obtained by Shockley and Read[9] and by Sandiford,[11] respectively. For the case of a *p*-type semiconductor and low injection density, they are

$$\tau_{\text{st. state}}=\frac{\tau_{p0}(n_0+n_1)+\tau_{n0}[p_0+p_1+N(1+p_0/p_1)^{-1}]}{p_0+N(1+p_0/p_1)^{-1}(1+p_1/p_0)^{-1}}, \quad (1)$$

and

$$\tau_{\text{tr}}=\frac{\tau_{p0}[n_0+n_1+N(1+n_0/n_1)^{-1}]+\tau_{n0}[p_0+p_1+N(1+p_0/p_1)^{-1}]}{p_0+N(1+p_0/p_1)^{-1}(1+p_1/p_0)^{-1}}, \quad (2)$$

where τ_{p0} and τ_{n0} are the lifetimes (mean lives) in strongly *n*-type and *p*-type material, n_0 and p_0 are the equilibrium concentrations of electrons and holes, n_1 and p_1 are the densities of electrons and holes for the case that the Fermi level coincides with the recombination level, and N is the density of gold levels. In *n*-type semiconductors, n_0 and n_1 are exchanged with p_0 and p_1.

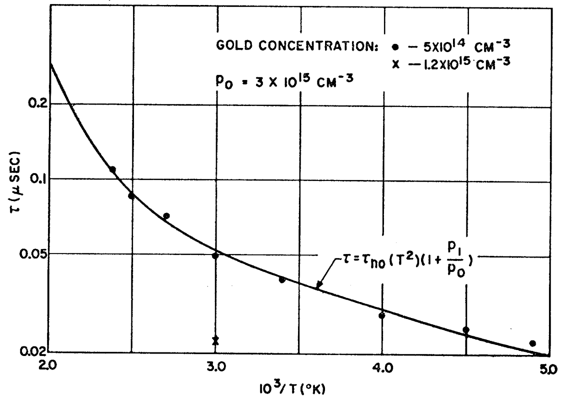

FIG. 2. Lifetime as a function of temperature in *p*-type silicon measured by the Van de Graaff method.

The only difference between these two equations lies in the fact that in the steady-state solution the density of centers, N, appears explicitly in the numerator only in the term describing the capture of the majority carriers, while in the transient case N is present symmetrically in both the majority and minority carrier capture terms. Under high injection the density of excess carriers, δn, needs to be considered. For the case in which the densities N in the foregoing equations are negligible, the steady-state lifetime takes the form

$$\tau=\frac{\tau_{p0}(n_0+n_1+\delta n)+\tau_{n0}(p_0+p_1+\delta n)}{n_0+p_0+\delta n}. \quad (3)$$

The quantities τ_{n0} and τ_{p0} in all of these expressions are related to the capture cross sections, σ_{p0} and σ_{n0}, by

$$\tau_{p0}=\frac{1}{v_pN\sigma_{p0}} \quad \text{and} \quad \tau_{n0}=\frac{1}{v_nN\sigma_{n0}},$$

where v_p and v_n are the thermal velocities of the carriers. From measurements of lifetimes and the knowledge of N, one can obtain the capture cross sections σ_{p0} and σ_{n0}.

p-TYPE SILICON

Data were obtained on four *p*-type, gold-doped crystals of varying resistivities. Typical results showing the temperature dependence of the lifetime are shown in Fig. 1. For this particular crystal the concentrations are $N=2\times10^{14}$ cm^{-3} and $p_0=1.2\times10^{16}$ cm^{-3}. The data were obtained by the injection-extraction method with injection densities of the order of 10^{14}-10^{15} cm^{-3}. It can easily be verified that the terms in N [Eq. (1)] can be neglected; and since δn is not negligible Eq. (3) applies. It can be simplified because

$$\delta n<p_0, \quad \delta n>n_0, \quad \delta n>n_1, \quad p_0>p_1,$$

and

$$\delta n>p_1 \text{ (at all temperatures up to 500°K)}.$$

Equation (3) therefore becomes

$$\tau=\tau_{n0}+\tau_{p0}(\delta n/p_0), \quad (4)$$

with $\delta n/p_0\approx10^{-2}$-$10^{-1}$. Since no dependence of lifetime on δn was found, we conclude that in the temperature range between 200°K and 500°K the second term in (4) is smaller than the first one. This implies that $\tau_{p0}<\tau_{n0}(p_0/\delta n)$, which puts a lower limit on σ_{p0}.

The observed increase of τ with temperature must therefore be due to the temperature dependence of τ_{n0}.

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[11] D. J. Sandiford, Phys. Rev. **105**, 524 (1957).

The best fit to the data is obtained with a T^2 dependence of τ_{n0}, which implies that σ_{n0} is proportional to $T^{-\frac{5}{2}}$, since v_n varies as $T^{\frac{1}{2}}$. Figure 2 gives results obtained on a crystal with $N=5\times10^{14}$ cm^{-3} and $p_0=3\times10^{15}$ cm^{-3}. The lifetime was measured by the Van de Graaff technique. We have in this case

$$N(1+p_0/p_1)^{-1}<p_0,$$

and

$$p_0>n_0.$$

Hence the transient solution (2) yields

$$\tau=\tau_{n0}(1+p_1/p_0)+\tau_{p0}N/p_0. \tag{5}$$

Since $N/p_0=5\times10^{-2}$, the second term is even smaller than in the case of Fig. 1. A good fit to the data is obtained with the same, T^2, temperature dependence of τ_{n0} and neglecting the second term. The average value for σ_{n0} (300°K) from all four p-type crystals is 3.5×10^{-15} cm^2. We also conclude that $\sigma_{p0}(300°\text{K})\geq10^{-16}$ cm^2.

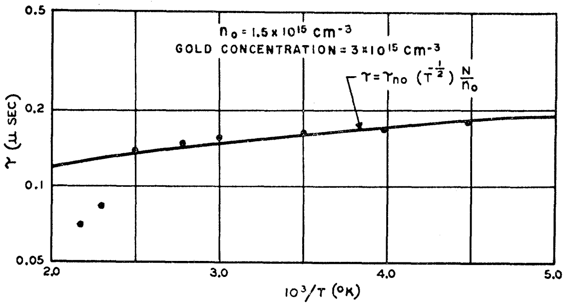

FIG. 3. Lifetime as a function of temperature in n-type silicon measured by the Van de Graaff technique. The electron capture cross section, σ_{n0}, is temperature independent.

n-TYPE SILICON

Figures 3–5 represent the temperature dependence of the lifetime in three n-type, gold-doped silicon crystals. The transient measurements in Fig. 3 are for the case of $N=3\times10^{15}$ cm^{-3}, $n_0=1.5\times10^{15}$ cm^{-3}, thus,

$$\begin{gathered} n_0>p_0,\quad n_0>n_1,\quad n_0>p_1,\quad p_0<p_1,\\ p_0<N(1+n_0/n_1)^{-1}(1+n_1/n_0)^{-1}, \end{gathered} \tag{6}$$

and δn small.

Accordingly, Eq. (2) reduces to

$$\tau=\tau_{p0}+\tau_{n0}(N/n_0),$$

with $N/n_0=2$. From these results alone it is not possible to separate the relative contributions of τ_{n0} and τ_{p0}. The separation will be possible from results on different crystals.

Figure 4 represents results of a steady-state measurement with $N=1\times10^{15}$ cm^{-3}, $n_0=1.2\times10^{15}$ cm^{-3}, and $\delta n\approx5\times10^{14}$ cm^{-3}. The steady-state Eq. (2) becomes

$$\tau=\tau_{p0}+\tau_{n0}\delta n/(\delta n+n_0), \tag{7}$$

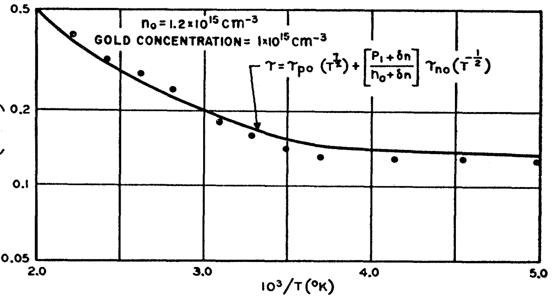

FIG. 4. Lifetime as a function of temperature in n-type silicon measured by the injection-extraction method. The theoretical curve is drawn for σ_{n0} independent of temperature and σ_{p0} varying as T^{-4}.

with $\delta n/(\delta n+n_0)\approx0.3$. In this case a variation of τ with δn is observed, which indicates that both terms are significant.

To obtain a better separation of the two terms, a high-resistivity crystal has been grown, with $N=6\times10^{14}$ cm^{-3} and $n_0=8\times10^{13}$ cm^{-3}. The lifetime has been measured by the injection-extraction technique with $\delta n\approx6\times10^{14}$ cm^{-3}. Since $n_0/n_1\approx10^3$, and N [Eq. (1)] can be neglected, Eq. (3) applies and simplifies in this case to

$$\tau=\tau_{p0}+\tau_{n0}. \tag{8}$$

The data are shown in Fig. 5. The lifetime τ is found to be independent of δn as required by (8).

The three n-type crystals give us three experimental situations in which the τ_{p0} term is smaller than the τ_{n0} term as in Figs. 3 or 5, or predominates as in Fig. 4. In all three cases a fit is obtained with $\sigma_{n0}(300°\text{K})=5\times10^{-16}$ cm^2 and $\sigma_{n0}(T)$ temperature independent, and $\sigma_{p0}(300°\text{K})=1\times10^{-15}$ cm^2 and $\sigma_{p0}(T)$ varying as T^{-4}.

DISCUSSION

The room-temperature values of the capture cross sections and their temperature dependence, are tabulated in Table II. It is apparent that:

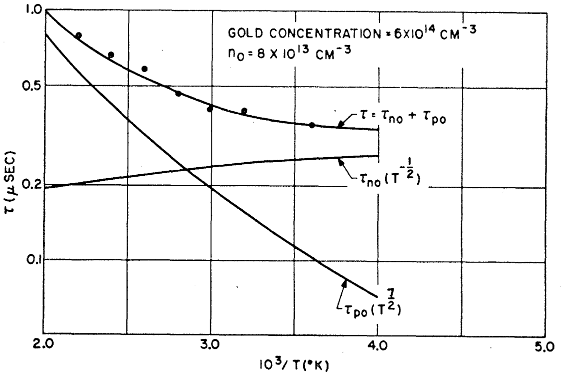

FIG. 5. Lifetime as a function of temperature in high-resistivity n-type silicon measured by the injection-extraction method. The temperature variations of σ_{n0} and σ_{p0} are consistent with those of Fig. 3 and Fig. 4.

TABLE II. Capture cross sections for electrons and holes in n-type and p-type, gold-doped, silicon.

	n-type		p-type	
	σ_{n0}(cm^2)	σ_{p0}(cm^2)	σ_{n0}(cm^2)	σ_{p0}(cm^2)
300°K values	5×10^{-16}	1×10^{-15}	3.5×10^{-15}	$\geq10^{-16}$
Temperature dependence	Independent	T^{-4}	$T^{-2.5}$	
Capture at	Au^0	Au$^-$	Au$^+$	Au^0

(1) The capture of excess carriers by oppositely charged gold atoms shows a pronounced temperature dependence, while capture at neutral atoms does not.

(2) In n-type silicon at temperatures below 300°K the hole capture cross section due to negatively charged gold exceeds considerably the electron capture cross section at neutral gold atoms.

These two facts are consistent with the notion that the existence of either of the gold levels depends on the position of the Fermi level. They are also in accordance with Lax's[12] prediction that a charged center ought to exhibit a temperature dependence of the capture cross section in the form of T^{-n}, where n can be between 1 and 4, and that a neutral center should have a weaker temperature dependence.

The values of the capture cross sections when extrapolated to 77°K agree quite well with those observed by Davis,[13] particularly in the case of charged centers.

ACKNOWLEDGMENTS

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[12] M. Lax, Second Symposium of Semiconductors, Washington, D. C., October, 1956 (unpublished).

[13] W. D. Davis (private communication): at 77°K, in n-type, $\sigma_{n0}\equiv4\times10^{-15}$ cm^2, $\sigma_{p0}\equiv3\times10^{-13}$ cm^2; in p-type, $\sigma_{n0}=10^{-13}$ cm^2, $\sigma_{p0}=4\times10^{-15}$ cm^2.

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Optical Properties of n-Type InP

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Measurements of the intrinsic absorption edge of n-type InP at 77°K and 300°K are reported. Differences are found in the spectra of samples of differing origin. The effects are believed due to impurities. Reflection and absorption spectra in the vicinity of the reststrahlen peak are shown. The reststrahlen wavelength is 30.5 μ, the static and high-frequency dielectric constants are $\epsilon_0=15$ and $\epsilon_\infty=10.6$. Free-carrier absorption and reflection spectra are shown. A brief discussion of the implications of the various optical and electrical measurements as regards the conduction band structure is given.

INTRODUCTION

THIS note reports some of the optical properties of n-type InP. The material used came from two sources: a polycrystalline ingot prepared at the Battelle Memorial Institute (BMI) containing a free-carrier concentration at room temperature of $n=5\times10^{15}$/cm^3, and polycrystalline ingots prepared at this laboratory having room-temperature carrier densities between 2×10^{16} and 5×10^{18}/cm^3. None of the ingots were intentionally doped; the carriers presumably resulted from the presence of uncontrolled and unidentified impurities. The state of compensation of the impurities is also unknown.

A. Intrinsic Electronic Absorption

Figure 1 shows the intrinsic electronic absorption spectra of InP at 300° and at 77°K.[1] This is the absorption process which is due to the excitation of an electron from the valence to the conduction band. The data were taken using a Perkin-Elmer monochromator incorporating a diffraction grating for high dispersion. The spectral resolution was between 2×10^{-4} and 1×10^{-3} ev for the data shown.

Consider first the spectra for the BMI material. At both 77°K and 300°K the curves show a break at an absorption coefficient of about 10 cm^{-1}. Above the break point the slope of the curve is steeper than below. The slopes above the break are of the same magnitude as the slopes at comparable absorption coefficients and temperatures for such materials as InSb.[2] For the latter, calculations have indicated that the transitions are direct.[3,4] The absorption above the break point in the BMI InP, in all probability, may be regarded similarly as due to direct processes. How-

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[1] F. Oswald, Z. Naturforsch. **9a**, 181 (1954).

[2] V. Roberts and J. E. Quarrington, J. Elec. **1**, 152 (1955); G. W. Gobeli and H. Y. Fan, Bull. Am. Phys. Soc. Ser. II, **2**, 121 (1957).

[3] H. Ehrenreich, J. Phys. Chem. Solids **2**, 131 (1957).

[4] E. O. Kane, J. Phys. Chem. Solids **1**, 249 (1957).