$dP_t/dt=0$ and Eq. (1) becomes

$$k_1 p_0(N_t-P_t^0)=k_2 P_t, \qquad \text{(A-6)}$$

where

$$p_0=N_v e^{-(\epsilon_F-\epsilon_v)/kT}$$

and $(N_t-P_t^0)=N_t[1-e^{-(\epsilon_F-\epsilon_t)/kT}]$. In this equation, $N_v=(2\pi mkT/h^2)^{\frac{3}{2}}$, and it is the effective density of states at the edge of the valence band. Furthermore, it is assumed that ϵ_t is far enough below ϵ_F, the Fermi level, to validate the Boltzmann approximation. By assuming $(p_1-p_0)\cong p_1$, these equations can be rearranged to give Eq. (2).

PHYSICAL REVIEW VOLUME 102, NUMBER 6 JUNE 15, 1956

Copper in Germanium: Recombination Center and Trapping Center

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(Received November 16, 1955)

The time-dependent photoconductivity of copper-doped *n*-type and *p*-type germanium bridges has been measured between 130°K and 293°K. Temporary hole traps were found in the *n*-type samples at the lower temperatures but no traps were observed in the *p* type. Trap concentrations agreed with the density of copper atoms to within a factor of two and were at least 100 times higher than undoped crystals. The trappings levels are 0.2 ev above the valence band; the capture cross section for holes, σ_p, is 10^{-16} cm^{-2} and independent of temperature while the capture cross section for electrons, σ_n, is temperature-dependent with an activation energy greater than 0.1 ev. As a result of this temperature dependence of σ_n, the 0.2-ev copper level changes from a recombination center at room temperature to a hole trap at lower temperatures.

INTRODUCTION

INJECTED minority carriers in semiconductors have been shown to interact with localized centers whose electronic energy levels lie in the forbidden gap. The kinetics of these reactions have been discussed by several authors under the two classifications of recombination[1] and trapping.[2,3] While it has been convenient for experimental and theoretical reasons to separate these processes, it has also been realized that both are closely related. In this paper, we shall present measurements of hole trapping by the 0.2-ev copper level in *n*-type germanium at low temperatures. Since this level has been shown to act as a recombination center in germanium at room temperature,[4] it will be necessary to examine the relation between recombination and trapping. In general, the results may be anticipated by considering the system represented in Fig. 1.

Recombination centers are represented by triangles within the forbidden gap and trapping centers by squares. The arrows representing transitions to both bands from the recombination centers indicate that electron and hole capture and release rates are important. In other words, an electron or hole in a recombination center has ready access to either band. An electron or hole, after capture, attracts a carrier of the opposite type resulting in a mutual annihilation. If either of the rate constants becomes very small compared to the other, a recombination center will become a trapping center. We have found that the 0.2-ev copper level changes from a recombination center at room temperature to a trapping center at low temperatures, presumably because the rate of electron capture (or hole release to the conduction band) decreases with temperature. This means the probability that a trapped hole will attract an electron is decreased and that the hole usually remains in the center until it is thermally excited back to the valence band.

DETERMINATION OF TRAPPING CENTER PROPERTIES

The trapping center properties were found to be qualitatively similar to those of the bombardment traps[5] described in the previous paper. Experimental techniques were identical with those described in reference 5. In brief, we measured the time dependence of the photoconductivity. Chopped white light was used to illuminate germanium bridges and the conductivity was measured across noncurrent carrying arms.[6] A Tektronix 514 oscilloscope and 121 pre-

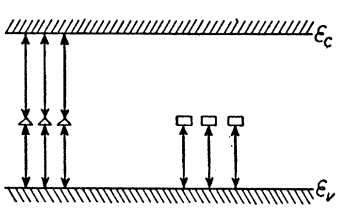

FIG. 1. Schematic energy level diagram. The arrows on the left indicate that recombination centers can capture holes from valence and conduction bands and that captured holes may be released to either band. The arrows on the right indicate that trapping centers interchange holes only with the valence band.

[1] W. Shockley and W. T. Read, Jr., Phys. Rev. **87**, 835 (1952).
[2] J. R. Haynes and J. A. Hornbeck, Phys. Rev. **90**, 152 (1953); J. A. Hornbeck and J. R. Haynes, Phys. Rev. **97**, 311 (1955).
[3] H. Y. Fan, Phys. Rev. **92**, 1424 (1953).
[4] Burton, Hull, Morin, and Severiens, J. Phys. Chem. **57**, 102 (1953).
[5] R. G. Shulman, preceding paper [Phys. Rev. **102**, 1451 (1956)].
[6] At low temperatures extreme care is necessary to prevent interference from transient photoresponses arising at the contacts. All our samples were bridges with gold-antimony bonded contacts which at low temperatures were more often ohmic than any other contacts we tried.

TABLE I. Comparison of trap density and copper concentration.

Sample number	Type	ρ (ohm-cm)	N_t	[Cu]
U-67	*n*	0.6	3.3×10^{14}	2×10^{14}
U-69	*p*	1.2	$<1\times10^{11}$	2×10^{14}
U-74	*n*	3.0	1.4×10^{14}	2×10^{14}
VIII 789	*n*	1.8	1.4×10^{14}	2×10^{14}

amplifier were modified by H. R. Moore so as to be linear from 0.1 cps to 10^7 cps and the photoconductivity measured as a function of time on the oscilloscope. Both *p*- and *n*-type copper-doped germanium bridges were examined for traps at temperatures between 120°K and 300°K. All the *n*-type samples showed trapping, but no traps were found in the *p*-type samples. The densities of trapping centers were measured by the changes in sample conductivity under strong illumination. A comparison of the densities of trapping centers and of copper is presented in Table I. The copper concentration in the grown crystals were calculated from the fraction of copper added to the melt and a distribution coefficient[7] $k=1.5\times10^{-5}$.

The analysis of trapping kinetics[2,3,5] assumes two independent trap properties. It has been convenient to choose the capture cross section of the trapping centers and their energy with respect to the valence band as the independent properties. The capture cross section is a kinetic property involving the rate of capture of carriers while the energy level is an equilibrium property. Because of the high concentrations of trapping centers all the decay curves were nonexponential, indicating multiple trapping. The formulas relating the observed rates of rise and decay of photoconductivity to the properties of the traps were derived previously[2,5]:

$$dP_t/dt=\sigma v p_1(N_t-P_t)-P_t/\tau_d, \qquad \text{(1-a)}$$

$$N_v\sigma v\tau_g=\exp[(\epsilon_t-\epsilon_v)/kT], \qquad \text{(1-b)}$$

where we consider hole traps and where σ = cross section for hole capture, v = thermal velocity of mobile holes, p_1 = hole concentration maintained in valence band by chopped light while on, τ_g = time constant for liberation of holes from traps, N_v = effective density of states at edge of valence band, $(\epsilon_t-\epsilon_v)$ = energy of trapping centers above edge of valence band, N_t = density of trapping centers, P_t = density of trapped holes, and τ_d = decay time constant which is a function of P_t.

Equation (1-a) describes the rate of change of trapped-hole density as the difference between the rate of capture and the rate of liberation. By increasing the light intensity and thereby increasing p_1 so that $\sigma v p_1 \gg 1/\tau_d$, the equation can be simplified and when integrated takes the convenient form

$$\sigma v=1/\tau_0 p_1, \qquad (2)$$

where τ_0 is the time constant of rise. In this form, the determination of σv from experiment involves measuring τ_0 and p_1. By assuming a value of $v=1.4\times10^7$ cm/sec the capture cross section for holes as a function of temperature has been derived from the experiments and is plotted in Fig. 2. The value determined at room temperature from recombination kinetics[4] is included, and it can be seen that the capture cross section of holes by the upper copper level is independent of temperature within experimental accuracy.

DETERMINATION OF TRAP ENERGY

Equation (1-b) can be used to determine $(\epsilon_t-\epsilon_v)$ in two ways. At any temperature the measured values of τ_g and σ and the calculated values of N_v and v can be substituted in the equation in order to determine the energy. Alternatively, if σ is independent of temperature, as Fig. 2 shows, then a plot of $\ln\tau_g$ *vs* $1/T$ should have a slope of $(\epsilon_t-\epsilon_v)/k$. Because of the multiple trapping, the decay of photoconductivity is nonexponential.[2] The first part of the decay, however, has a time constant τ_g, which will be the same for all samples containing the same type of trap. On the other hand, the rest of the decay curve will vary from sample to sample at the same temperature. We have measured τ_g, and typical results are plotted *vs* $1/T$ in Fig. 3. From the slope, $(\epsilon_t-\epsilon_v)=0.18$ ev, which is to be compared with the value[8] of 0.2 ev determined by Hall measurements. When one substitutes the measured values of τ_g and σv in Eq. (1-b), the same value of 0.18 ev is obtained for $(\epsilon_t-\epsilon_v)$.

DISCUSSION OF RESULTS

The transition from a recombination center to a trapping center indicates that the cross section for electron capture which is appreciable at room temperature has decreased at the lower temperatures. If we assume a relation of the form $\sigma_n=\sigma_n^0 e^{-\Delta\epsilon/kT}$, then a lower limit may be placed upon $\Delta\epsilon$. Values of τ_g of about 10^{-3} second were observed at 125°K. From this we can calculate that at this temperature $\sigma_n<3\times10^{-20}$

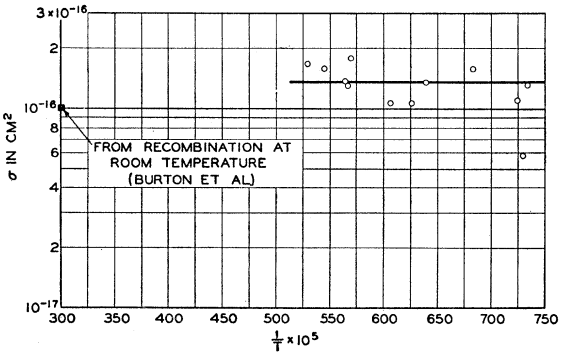

FIG. 2. Cross section for hole capture by copper traps in *n*-type germanium as a function of $1/T$.

[7] Burton, Kolb, Slichter, and Struthers, J. Chem. Phys. **21**, 1991 (1953).

[8] F. J. Morin and J. P. Maita, Phys. Rev. **90**, 337 (1953).

cm², and comparing this with the room temperature value of 10^{-17} cm² we can say that $\Delta\epsilon > 0.11$ ev. This limit upon the activation energy is in agreement with the recent report of Baum and Battey[9] who have measured this energy as 0.22 ev.

One would expect that the lifetime of minority carriers would increase as the copper centers become trapping centers and recombination through them becomes negligibly slow. We have seen some evidence of this effect as shown in Fig. 4 where the lifetime of holes is plotted *vs* $1/T$ for two different values of ambient illumination. The steady illumination was needed in order to keep the traps filled, and under illumination the exponential decay of recombination is observed. It can be seen that the lifetime has increased several-fold as the temperature is lowered from 300°K to 175°K.

These lifetimes were measured by observing the decay in photoconductivity. Measurements made with a chopped light and point contact collector on bulk samples were difficult to interpret at these low temperatures because of a "shoulder" that was invariably found on the signal *versus* light distance curve. The "shoulder" is possibly caused by channel formation. However, this increase of lifetime with decreasing temperature was not observed in all the samples and it is believed that the results are sometimes complicated by two other mechanisms.

The first complicating factor is the background impurities which are assumed to have a concentration of about 10^{13}/cm³. These may act as recombination centers and at low temperatures may limit the recombination times. Residual impurities may also contribute to the trapping, and in fact several samples showed anomalous decay curves at long times, indicating some trapping mechanism in addition to copper traps.

The second factor is the effect of minority carrier concentration upon the recombination time. As Shockley and Read[1] have predicted, and as Bemski[10] has observed in silicon, the recombination rate depends upon

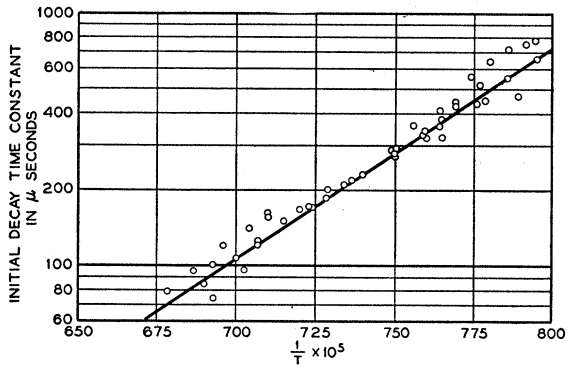

FIG. 3. Initial decay times for copper traps in *n*-type germanium as a function of $1/T$.

[9] R. M. Baum and J. F. Battey, Phys. Rev. **98**, 923 (1955).
[10] G. Bemski, Phys. Rev. **100**, 523 (1955).

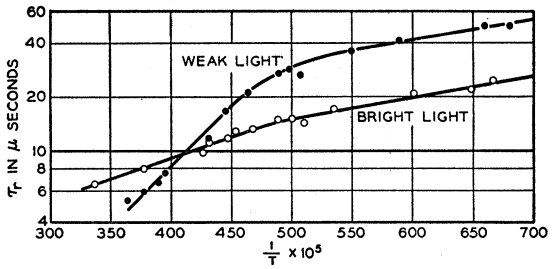

FIG. 4. Hole lifetime in *n*-type copper-doped germanium for two different hole concentrations, produced by changing the intensity of the ambient light.

the minority carrier concentration. It is necessary to inject carriers in order to fill the traps and therefore, while measuring the recombination, there is always a relatively high concentration of minority carriers. In Fig. 4 we see that increasing the illumination decreases the lifetime at low temperatures, but it is difficult to be certain that this is the only explanation of the effects observed.

A detailed examination of the electronic environment of copper atoms is beyond the scope of this paper. However, a potential barrier to electron capture might be correlated with an electron density at a radius corresponding to the 0.04-ev electron energy state.

QUANTITATIVE ANALYSIS

Once the cross section and energy for the copper traps have been determined, it is a simple matter to use these properties in order to determine copper concentrations in *n*-type samples. This method of analyzing for copper is based upon two parameters and therefore can determine the chemical nature of the centers with somewhat more assurance than Hall measurements. In 10 ohm cm germanium there is no difficulty in identifying 10^{13} copper atoms/cc. Under optimum conditions of low background trap concentrations, the method will measure as few as 10^{11}/cc. Trapping determinations of copper concentrations require that the sample be *n* type while Hall measurements can only be made on *p*-type samples. In this manner the two methods supplement each other.

CONCLUSIONS

We have shown that the upper copper level in *n*-type germanium which acts as a recombination center at room temperature becomes a minority carrier trap at lower temperatures. The properties of these traps further our understanding of the detailed electronic nature of the centers and in addition provide a means of quantitative analysis for copper in *n*-type germanium.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge that Dr. D. Navon mentioned to us, while we were planning to study it, that copper-doped germanium showed trapping.