Carrier Capture Probabilities in Nickel Doped Germanium*

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Nickel has been diffused into germanium in order to study the carrier capture probabilities of the two nickel acceptor levels. Measurements of minority carrier lifetime as a function of temperature show that the electron capture probability of low-resistivity p-type samples is temperature-independent. The electron capture probability of high-resistivity p-type samples increases exponentially with increasing temperature, as does the hole capture probability of high-resistivity n-type samples. Possible interpretations of the results are discussed.

I. INTRODUCTION

In a previous publication[1] we have discussed the recombination of minority carriers in germanium through the agency of recombination levels. The levels were introduced into the forbidden energy gap by copper atoms in the germanium lattice. The expression for the electron lifetime that is pertinent to this work has been given as[2]

$$\tau_n=\frac{(1/C_p)(n_0+n_1)+(1/C_n)[p_0+p_1+N_t(1+p_0/p_1)^{-1}]}{n_0+p_0+N_t(1+p_0/p_1)^{-1}(1+p_1/p_0)^{-1}}, \quad (1)$$

where N_t is the density of recombination levels; C_p is the product of the trap density and the probability per unit time of an individual trap capturing a hole, averaged over the holes in the valence band; C_n is the product of the trap density and the probability per unit time of an individual trap capturing an electron, averaged over the electrons in the conduction band; n_0 and p_0 are the equilibrium electron and hole densities; and n_1 and p_1 are the values the equilibrium electron and hole densities would have if the Fermi level were located at the same position in energy as the recombination traps.

In a copper-doped sample, the recombination proceeds through the upper acceptor level located 0.30 ev above the top of the valence band. In this instance C_p is known to be much larger than C_n. If the sample is doped in such a fashion that the upper copper level is partially populated, then the term in the numerator of (1) involving $1/C_p$ is negligible compared to the one involving $1/C_n$. Since n_0 in the denominator is small compared with p_0, $\tau_n \simeq 1/C_n f_{pt}$, where f_{pt} is the probability that the upper copper level is empty. When the carrier concentration is small compared to N_t, then f_{pt} is virtually constant, and the temperature dependence of C_n is given by the reciprocal of the lifetime. A study of τ_n *vs* temperature showed that the principal temperature dependence of C_n is $\exp(-E/kT)$, where $E=0.22$ ev. The proposed interpretation of this result was that only electrons of energy greater than 0.22 ev above the bottom of the conduction band can get into the traps.

In this paper, we wish to present evidence that similar phenomena occur in nickel-doped germanium. The selectivity in the electron capture process may be due to a Coulombic repulsion between the negatively charged acceptor sites and the incoming electrons. Evidence is also obtained for qualitatively similar selectivity in the hole capture process by nickel atoms. The explanation in this instance cannot be due to Coulombic repulsion.

It has been shown that nickel introduces two acceptor levels in germanium, one at 0.22 ev above the top of the valence band,[3-5] the other at 0.30 ev below the bottom of the conduction band.[3] It is not clear whether the upper level exists at its observed energy before the lower level is filled, or whether the lower level exists at

TABLE I. Sample properties before and after nickel diffusion. The nickel atom concentration was calculated by locating the Fermi level, F, from the experimental carrier concentration determined at a suitable temperature. The carrier concentration was equated to $2(2\pi mkT/h^2)^{\frac{3}{2}}\exp[-(E_c-F)/kT]$ for n-type samples, and $2(2\pi mkT/h^2)^{\frac{3}{2}}\exp[-(F-E_v)/kT]$ for p-type samples, where E_c is the bottom edge of the conduction band and E_v is the top edge of the valence band. The population of the nickel levels was next calculated. The nickel atom concentration was then obtained from the carrier concentration before and after nickel diffusion.

	Before nickel diffusion		After nickel diffusion		
Sample	N_D-N_A (cm^{-3})	τ_{Av} (μsec) at room temperature	τ_{Av} (μsec) at room temperature	Nickel atom concentration (cm^{-3})	Diffusion temperature (°K)
BB–10	8.0×10^{14}	10	0.20	4.4×10^{14}	1010
BB– 8	5.4×10^{14}	150	0.25	3.0×10^{14}	990
BB–12	7.9×10^{13}	45	2.0	3.7×10^{13}	920
BB– 6	1.0×10^{15}	180	0.60	1.1×10^{15}	1033
BB– 3	9.3×10^{14}	140	0.20	9.8×10^{14}	1005
BB– 7	N_A-N_D 4.5×10^{15}	20	0.60	1.8×10^{14} [a]	962

[a] Obtained from reference 5.

* This work was begun at Sylvania Electric Products, Ipswich, Massachusetts.

[1] R. M. Baum and J. F. Battey, Phys. Rev. **98**, 923 (1955).

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

[3] Tyler, Newman, and Woodbury, Phys. Rev. **98**, 461 (1955).

[4] Burton, Hull, Morins, and Severiens, J. Phys. Chem. **57**, 853 (1953).

[5] F. van der Maessen and J. A. Brenkman, Philips Research Repts. **9**, 225 (1954).

its observed energy after the upper level is filled. It is not presently known for a given resistivity and temperature whether the recombination goes predominantly through the upper or lower nickel level. However, if the recombination goes through a negatively charged atom, C_n should vary exponentially with temperature. If the recombination goes through an uncharged atom, no temperature dependence of C_n would be expected.

II. SAMPLE PREPARATION

It has been shown that nickel diffuses very rapidly in germanium at elevated temperatures.[3–5] 99.99% pure nickel was electroplated on the germanium samples, which were then sealed in evacuated vycor capsules. The nickel was diffused into the germanium by holding the samples at an appropriate temperature for such a time as to closely approximate the solubility limit of nickel in germanium[5] throughout the sample. Thereafter the samples were quenched. The concentration of nickel introduced into the various samples referred to in this paper is shown in Table I.

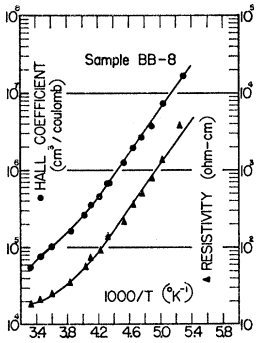

FIG. 1. Resistivity and Hall coefficient as a function of temperature for a high-resistivity n-type nickel-doped germanium sample.

In samples that were strongly p-type before diffusion due to group III acceptor doping, the introduction of nickel leads to no perceptible change in carrier concentration, as indicated by Hall coefficient and resistivity measurements. In samples that were originally n-type due to group V donor doping, the carrier concentration decreased and in some instances converted to p-type with the introduction of nickel.

Samples that were changed to high-resistivity n-type showed the existence of an acceptor level approximately 0.30 ev below the bottom of the conduction band, as is evident from Fig. 1. This is in agreement with the results of Tyler *et al.*[3] The concentration of nickel was calculated for such samples from the carrier concentration before and after diffusion under the presumption that each nickel atom introduces two acceptor levels, one or both of which are filled.

For samples that were converted to high-resistivity p-type, Hall coefficient and resistivity data showed the existence of an acceptor level approximately 0.22 ev above the top of the valence band in agreement with previous measurements.[3–5] This is shown in Fig. 2. In these samples the concentration of nickel was

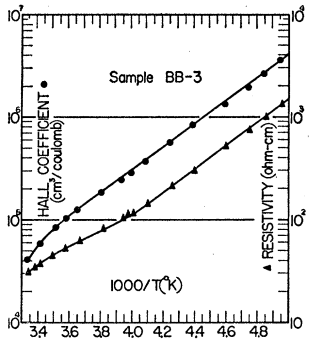

FIG. 2. Resistivity and Hall coefficient as a function of temperature for a high-resistivity p-type nickel-doped germanium sample.

calculated from the carrier concentration before and after nickel diffusion by assuming that each nickel atom accepts either one or no electrons. The solubilities calculated in this fashion agree within better than a factor of two with the data published by van der Maessen and Brenkman.[5] The small discrepancies are probably due to the lack of precise knowledge of sample temperature during diffusion.

The acceptor concentrations introduced were small compared to the solubility of copper. Also, the lifetime of the material following the heat treatment was much too short to be attributed to copper atoms in concentrations that are consistent with the observed resistivity changes, or even with the solubility limit of copper at the diffusion temperatures in question. For all samples that are discussed in this paper, the room temperature lifetime was reduced by more than an order of magnitude by the nickel doping.

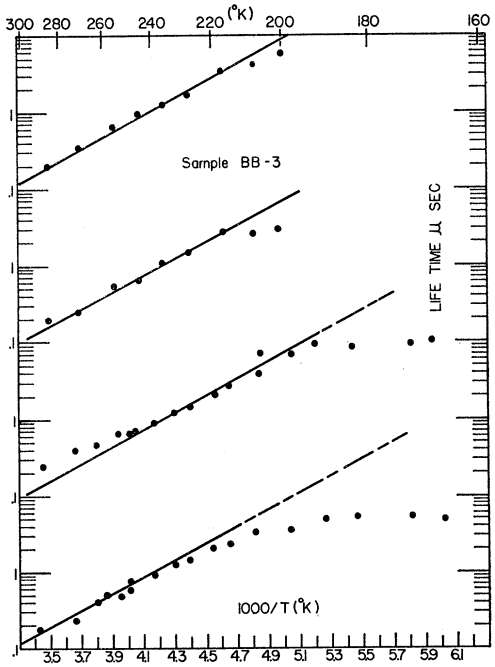

FIG. 3. Electron lifetime as a function of temperature for the high-resistivity p-type nickel-doped germanium sample for which Hall coefficient and resistivity data are shown in Fig. 2.

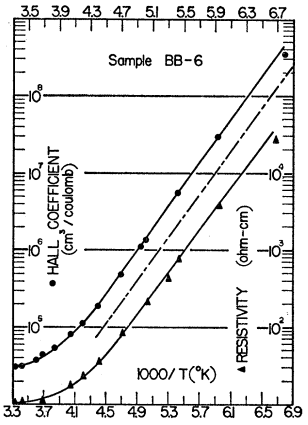

FIG. 4. Resistivity and Hall coefficient as a function of temperature for a high-resistivity p-type nickel-doped germanium sample which presumably also contains a small amount of copper. The broken line indicates the theoretically calculated slope of the carrier concentration for a sample that contains 1.0×10^{15} group V donors, 1.1×10^{15} nickel atoms, and 1.1×10^{14} copper atoms per cm³.

III. RECOMBINATION PROCESSES

A. p-Type Samples

Figure 3 shows plots of electron lifetime *vs* reciprocal temperature for the p-type sample for which Hall coefficient and resistivity data are shown in Fig. 2. The method of lifetime measurement has been previously described.[1] If it is again presumed that the first term in the numerator of Eq. (1) is small compared to the second term, then, as in the copper case, C_n has the temperature dependence of $1/\tau_n$. It will be seen that again C_n varies as $\exp(-E/kT)$, with E approximately 0.23 ev. If Coulombic repulsion is to provide the explanation for the exponential temperature dependence of C_n, then it must be presumed that the electrons are being captured in the upper nickel levels by already singly charged nickel atoms, rather than through the lower nickel levels by uncharged atoms. It would be expected that a p-type sample in which the lower nickel level is virtually completely populated has a larger ratio of charged to uncharged atoms. Hence it would be expected that such a sample would again show the same temperature dependence of minority carrier lifetime as is seen in Fig. 3. On the other hand, for very p-type samples the lower nickel level is virtually empty, and the nickel atoms are uncharged. In this case, one would not expect any temperature dependence of C_n due to Coulombic repulsion between the nickel atoms and electrons about to be captured. For sufficiently p-type samples, the lifetime is equal to $1/C_n$, as can be seen from Eq. (1). However it may be that the C_n in this instance is to be associated with the lower nickel level.

In Fig. 4, Hall coefficient and resistivity curves are shown for a sample which approximately fulfills the requirement of having the lower nickel level completely populated. The Hall coefficient curve shows an activation energy of about 0.26 ev. All other high-resistivity p-type samples showed an activation energy of 0.22 ± 0.01 ev. The higher activation energy of 0.26 ev is what would be expected if a small amount of copper were introduced into the sample in addition to the relatively large amount of nickel, and further, if the group V donor concentration was sufficient to partially populate the upper copper level and nearly completely populate the lower nickel level. Figure 5 shows plots of electron lifetime *vs* reciprocal temperature for this sample. The anticipated exponential dependence of lifetime on reciprocal temperature is observed.

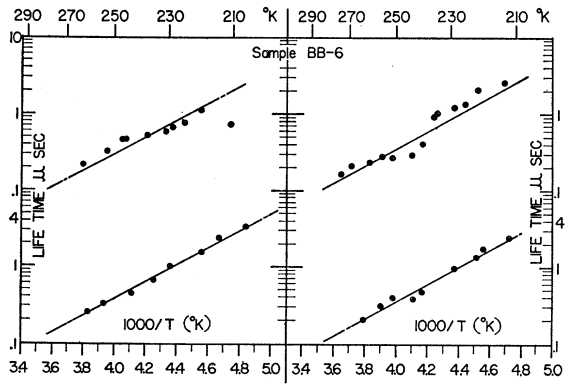

FIG. 5. Electron lifetime as a function of temperature for the high-resistivity p-type nickel-doped germanium sample for which resistivity and Hall coefficient data are shown in Fig. 4.

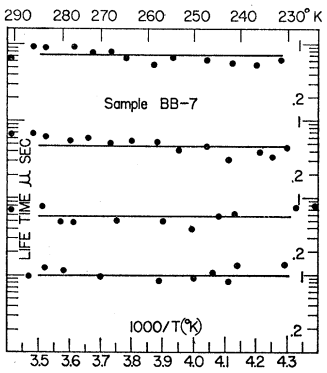

FIG. 6. Electron lifetime as a function of temperature for a low-resistivity p-type nickel-doped germanium sample.

For sufficiently p-type samples in which the lifetime is equal to $1/C_n$, the lifetime becomes independent of carrier concentration. It can be seen from the work of Burton *et al.*[4] that a sample with a room temperature hole concentration of 4.5×10^{15} cm^{-3} is sufficiently p-type for this to be true. Consequently, for such a sample τ_n equals $1/C_n$. Plots of lifetime *vs* reciprocal temperature after nickel doping are shown for a sample of this carrier concentration in Fig. 6. It will be seen that within the accuracy of the data, C_n, is temperature-independent. Inasmuch as there is no Coulombic repulsion between the uncharged nickel atoms and the recombining electrons, this is the result to be expected in the absence of other effects which would selectively favor the recombination of electrons of certain energies. Presumably, in this instance, the recombination is going through the lower nickel level.

B. *n*-Type Samples

Some additional measurements of lifetime *vs* temperature have been made on *n*-type samples similar to the one for which Hall coefficient and resistivity data are shown in Fig. 1. Representative lifetime data on a number of samples are shown in Fig. 7. It will be noticed that the lifetime decreases exponentially as the temperature increases. The hole lifetime in a *n*-type sample whose recombination is dominated by a single energy level is given by[2]

$$\tau_p=\frac{(1/C_n)(p_0+p_1)+(1/C_p)[n_0+n_1+N_t(1+n_0/n_1)^{-1}]}{n_0+p_0+N_t(1+n_0/n_1)^{-1}(1+n_1/n_0)^{-1}}. \quad (2)$$

Hall coefficient and resistivity measurements taken as a function of temperature show that the dominant term in the denominator, over the temperature range of interest, is $N_t(1+n_0/n_1)^{-1}(1+n_1/n_0)^{-1}$. If it is assumed that the first term dominates the numerator of (2) and the known temperature dependences of the various factors are used, it would be expected that τ_p would show a strong exponential increase with increasing temperature. This is the behavior exhibited by most germanium samples.[6] Since this is not what is observed in this instance, it must be assumed that the second term in the numerator is dominant. Then, it is expected that $\tau_p \simeq (1/C_p)(1+n_1/n_0)$. In the temperature range of interest, $(1+n_1/n_0)$ is only weakly temperature-dependent. Consequently, the temperature dependence of τ_p gives the temperature dependence of $1/C_p$. The suggestion is again advanced that C_p increases exponentially with increasing temperature because only holes of energy less than a certain critical value can enter the recombination traps. The critical energy as obtained from the slopes of the lifetime *vs* reciprocal temperature curves shows appreciable differences on samples which are presumed to be similar and even on different regions of the same sample. The values range from 0.18 to 0.28 ev with a probable error of about 0.03 ev. The source of these discrepancies is not understood. It is clear that no Coulombic barrier will exist for holes approaching negatively charged nickel atoms. It is possible that only holes from the branch in the valence band derived from atomic $p^{\frac{1}{2}}$ states are entering the nickel levels. From the analysis of infrared absorption data in *p*-type samples, Kahn[7] concludes that this branch lies a minimum distance of approximately 0.30 ev below the top of the valence band.

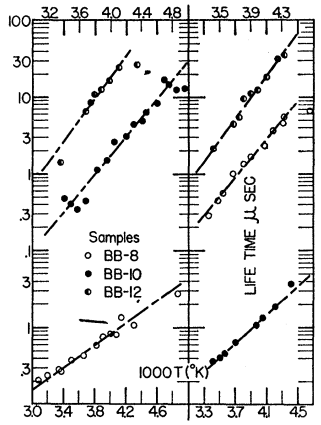

FIG. 7. Hole lifetime as a function of temperature for high-resistivity *n*-type nickel-doped germanium samples similar to the sample for which resistivity and Hall coefficient data are shown in Fig. 1.

TABLE II. Electron and hole capture constants.

Sample	Nickel atom concentration (cm^{-3})	c_{n0} ($cm^3\ sec^{-1}$)	c_{p0} ($cm^3\ sec^{-1}$)	c_n ($cm^3\ sec^{-1}$)
BB– 3	9.8×10^{14}	4.2×10^{-5}		
BB– 6	1.1×10^{15}	6.5×10^{-5}		
BB– 7	1.8×10^{14} [a]			9.2×10^{-9}
BB– 8	3.0×10^{14}		2.6×10^{-2}	
BB–10	4.4×10^{14}		2.4×10^{-2}	
BB–12	3.7×10^{13}		1.7×10^{-2}	
Copper-doped[b]		6.4×10^{-6}		

[a] Obtained from reference 5.
[b] See reference 1.

The experimental data indicates that the temperature dependence of the electron capture probability for high-resistivity *p*-type samples can be approximately represented by $C_n=N_t c_{n0}\exp(-E_1/kT)$, with $E_1=0.23$ ev. Similarly, the temperature dependence of the hole capture probability for high-resistivity *n*-type samples can be represented by $C_p=N_t c_{p0}\exp(-E_2/kT)$, with E_2 usually appearing to be about 0.28 ev. Values of c_{n0} and c_{p0} together with the temperature-independent value of the electron capture probability, $c_n\equiv C_n/N_t$, obtained for the low resistivity *p*-type sample, are shown in Table II. The value of c_{n0} obtained for the high-resistivity copper-doped sample[1] is included for comparison.

ACKNOWLEDGMENTS

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[6] See, for instance, Fig. 1 of reference 1; also R. N. Hall, Phys. Rev. **87**, 387 (1952), and P. Ransom and F. W. G. Rose, Proc. Phys. Soc. (London) **B67**, 646 (1954).

[7] A. H. Kahn, Phys. Rev. **97**, 1647 (1955).