PHYSICAL REVIEW B VOLUME 3, NUMBER 2 15 JANUARY 1971

Annealing of Electron-Irradiated *n*-Type Silicon. I. Donor Concentration Dependence

L. C. Kimerling, H. M. DeAngelis, and C. P. Carnes
Air Force Cambridge Research Laboratories (AFSC), Bedford, Massachusetts 01730

(Received 27 July 1970)

The annealing behavior of electron-irradiated phosphorus-doped silicon of low oxygen content (float zoned and Lopex) was studied by monitoring changes in the carrier concentration with Hall-effect measurements. In isochronal anneals, the *E*-center annealing stage was observed to shift to higher temperatures as the donor concentration was increased. This behavior was found to be consistent with a charge-state influence on the stability of the *E* center. Analysis of the experimental data with respect to a charge-state model suggests an activation energy for recovery of the neutrally charged *E* center of 0.9–1.2 eV. This value is in good agreement with previous annealing studies of Watkins and Corbett and Hirata *et al.*

I. INTRODUCTION

The primary defects produced in silicon by 1-MeV electron irradiation are isolated lattice vacancies and interstitials. However, at room temperature, these primary defects are, apparently, not stable and are observed only in association with other lattice imperfections. In phosphorus-doped silicon of low oxygen content, the predominant defect observed after room temperature irradiation is the *E* center.[1] The defect is an associate of a lattice vacancy with a substitutional phosphorus atom, which introduces an acceptor level about 0.4 eV below the conduction band. When the Fermi level is above this energy, the defect possesses a net single negative charge corresponding to the compensation of two electrons from the conduction band and the positive charge of the phosphorus donor.

The *E* center has been observed to anneal out at about 150 °C using electron-paramagnetic-resonance (EPR),[2] Hall-effect,[3] and minority-carrier-lifetime[4] techniques. Isothermal-annealing data have indicated a first-order process with an apparent activation energy of 0.94 eV, which has been associated with the migration of these centers to sinks.[4,5]

Carnes *et al.*[6] have reported much more complex annealing behavior over a broad range of phosphorus-dopant concentrations. Activation energies appear high in comparison, about 1.7 eV; frequency factors are unreasonable, about 10^{18} sec^{-1} (as compared to the lattice vibration frequency of $\sim 10^{13}$ sec^{-1}); and, the kinetics are not uniquely first order. Recently DeAngelis *et al.*[7] have reported that the temperature of the *E*-center isochronal-annealing stage tends to increase with increasing donor concentration. A possible charge-state influence was suggested. Watkins and Corbett,[2] and Hirata *et al.*[8] have also mentioned parenthetically that defect charge state might be an important consideration.

The importance of the charge state on the stability of the primary vacancy-interstitial pairs was first proposed by Wertheim[9] for silicon and Klontz and MacKay[10] for germanium, and has apparently been verified by Stein and Vook[11] in the case of silicon. It seems, therefore, constructive to explore the role of charge state in defect stability in order to reconcile the apparent anomalies in the annealing data.

The *E*-center concentration was monitored using Hall-effect measurements at 275 °K. At this temperature, levels below E_c, 0.3 eV are detected. While there is no microscopic assurance that the *E* center is the only deep level being monitored, the divacancy (being the only other deep level which has been consistently found) is estimated to be present in concentrations less than 10% of the *E*-center concentration and does not anneal out until about 300 °C.[12]

II. RECOVERY MECHANISMS

The variety of paths that have been proposed and are possible for the recovery of the *E* center serves as a warning to the experimenter who attempts to derive an isolated mechanism from observed annealing data. Two main mechanisms are generally considered: (i) migration of the defect as an entity to a sink, e.g., an interstitial atom, which could annihilate the vacancy component of the pair; and (ii) break up of the defect followed by migration of the isolated vacancy to another impurity or annihilation site.

The migration process has been suggested by Hirata and co-workers[4,5,13] to explain an observed activation energy of 0.94 eV which corresponds closely to the migration energy predicted by Watkins and Corbett[2] from the stress-induced realignment of the *E* center. The experiments of Hirata and coworkers were performed using both Hall-effect and minority-carrier-lifetime techniques on silicon of resistivity greater than about 50 Ω cm. The recovery rates, however, suggest a sink concentration in the order of 10^{18} cm^{-3}.[7] In float-zoned silicon, no imperfection is generally known to be present in such a concentration, although the behavior of carbon is not yet well characterized.

The break up of defect pairs has been well documented in the work of Reiss *et al.*[14] characterizing ion-pairing processes in silicon and germanium. Break up occurs when the thermal energy of the lattice locally exceeds the attractive forces between the two components of the pair. The process may be retarded by the back reaction or recapture of the mobile species. The EPR description indicates that the phosphorus-vacancy nearest-neighbor bonding forces are more nearly covalent than ionic. At larger separations, however, Coulombic forces are expected to dominate. Using this approach, Watkins and Corbett have estimated the binding energy of the defect to be 1.2–1.4 eV.[2]

Recent work of Stein and Vook[15] indicates a higher divacancy concentration in float-zoned material than in crucible grown material following the E center anneal. If, initially, all divacancies are produced as primary defects (and, thus, in equal concentrations in the two materials), these results suggest that additional divacancies are formed indirectly during the E-center anneal. Similarly, DeAngelis *et al.*[7] have noted an increase in the unannealed deep-state concentration following E-center recovery with increasing E-center concentration. These findings provide strong evidence for a breakup mechanism and for the interaction of the resulting isolated vacancies to form divacancies.

In annealing studies one can observe changes in defect concentration, but there is no way, at present, to determine how many simultaneous processes have contributed to the recovery. The longer times (lower-frequency factor) expected for a migration process together with the higher activation energy of dissociation point to the distinct possibility that both processes could occur at the same time.

This paper suggests an additional complication in that the parameters of the aforementioned mechanisms may be further modified by the charge state of the defect. However, whereas it has proven extremely difficult to isolate a particular process of recovery, it is possible in rather fundamental ways to investigate a charge-state influence through changes in the Fermi level. This work reports such an examination employing a variation in donor concentration. Subsequent reports, to be published, will deal with the effects of illumination and radiation fluence.

III. EXPERIMENTAL

The single crystals employed were obtained mainly from Texas Instruments Corp. However, some samples were derived from material received from General Diode and Sandia Laboratories for the purpose of comparison. There were quantitative differences in character and behavior, but all samples followed the same general trends. The oxygen concentration in all crystals was below that detectable by room-temperature measurements of the 9-μ ir absorption band ($\leq 3\times10^{-16}$ cm^{-3}). The dislocation density, as estimated by etch pit counts, was $\sim10^5$ cm^{-2} for float-zoned material and $\leq 10^2$ cm^{-2} for Lopex grown material.

Bridge-type samples having dimensions of 1.4 ×0.15 (exclusive of contact arms)×0.025 cm thick were used for Hall-effect measurements. Electrical contacts were made using a gold-antimony alloy. Hall voltages were measured using dc techniques with a Vidar 510 integrating digital voltmeter. A magnetic field strength of 2250 G was employed.

The carrier concentration n was calculated from the Hall coefficient R_H according to the equation

$$n = r/R_H e.$$

Since all measurements were taken at the same temperature (275 °K), the Hall factor r ($\simeq 1$) was constant and assumed to be unity.

A 1.5-MeV Dynamitron was used as a source of electrons. The electron beam (~2 cm in diameter) from the accelerator was passed through a 1-mil aluminum foil, a beam cropper, rough collimators, and a 2-ft drift tube to obtain a uniform beam. The beam then passed through a defining slit fabricated from 40-mil platinum before entering the irradiation apparatus. Electrons passing through and around the sample with its broad face normal to the incident electron beam were collected in a Faraday cup and monitored with a current integrator. The samples were irradiated in vacuum at room temperatures with 1.0-MeV electrons; the average flux was $\sim 3\times10^{12} e^- \text{cm}^{-2}\,\text{sec}^{-1}$.

Isochronal and isothermal anneals, were performed in a silicone-oil bath; the annealing temperature range of 80–220 °C was controlled to within ±0.5 °C and isochronal annealing periods were 10 min with temperature intervals of 10 °C.

IV. RESULTS

Isochronal-annealing studies were performed on n-type silicon of varying donor concentrations and growth types. The samples were irradiated to a fluence which resulted in approximately 25% compensation of the initial carrier concentration. Figures 1 and 2 show the results for float-zone and Lopex grown material, respectively. The trend of increasing annealing temperature with increasing dopant concentration reported by DeAngelis *et al.*[7] is generally followed in both materials. Also apparent is a general increase in the fraction of carriers unrecovered with increasing donor concentration. As mentioned earlier this behavior correlates with an increasing probability for the indirect formation

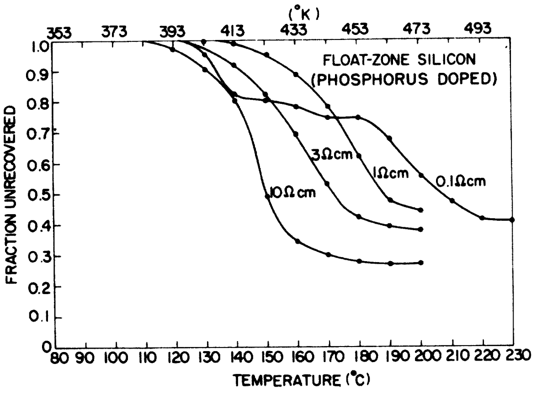

FIG. 1. Isochronal annealing curves for 1-MeV electron-irradiated float-zoned silicon of varying phosphorous-dopant concentrations.

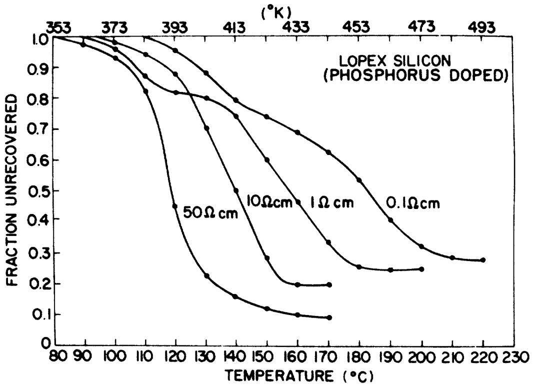

FIG. 2. Isochronal annealing curves for 1-MeV electron-irradiated Lopex silicon of varying phosphorous-dopant concentrations.

of divacancies during the E-center anneal.[16]

We can propose no explanation at this time for the two-stage behavior exhibited by the lower-resistivity materials, even though the subject has been investigated somewhat extensively.[17] However, if the displacement of the annealing stage with increasing dobant concentration is to be followed throughout, one must conclude that it is the second stage which represents a recovery of the E center. Hirata *et al.*[8] have arrived at a similar conclusion based on recent isothermal data.

Figure 3 shows the Fermi-level positions during anneal based on the preanneal and postanneal carrier concentrations and the temperature of anneal. It is interesting to note that, in all cases but the 0.1-Ωcm material, the E-center annealing stage occurs at a temperature where the Fermi level is within 2 kT of the E-center energy level, a region in which the charge state of the defect is a strong function of temperature. This behavior suggests that the charge state may play a determining role in the displacement of the isochronal-annealing stage.

In contrast to the 0.1-Ωcm material in which all of the E centers are negatively charged during anneal, the E centers in the 50-Ωcm material ($n \simeq 10^{14}$ cm^{-3}) are almost all in the neutral charge state during anneal. This comparison together with the nearly continuous variation for intermediate resistivities suggests that the activation energy for anneal may be higher for the negative charge state than the neutral charge state. From a Coulombic standpoint this indication is attractive because the ionic binding energy of a defect ($\Delta H = -q_1 q_2/\epsilon r$) is directly proportional to the charges on its components.[18]

It should be mentioned here that all of the previous quantitative studies of the annealing of the E center concern only the neutral charge state. Only the neutral defect has an unpaired electron for EPR observation. The studies of Hirata and coworkers[4,5,13] were made, for the most part, on material of resistivity > 50 Ωcm, in which the Fermi level is below the E-center level at the annealing temperatures employed.

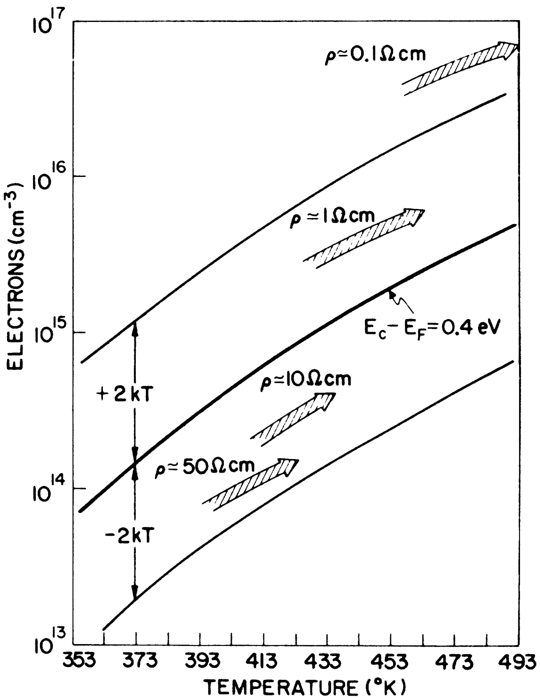

FIG. 3. Fermi-level position during anneal relative to the E-center acceptor-level position. The solid curves represent lines of constant Fermi energy according to the relation $E_F = kT \ln(N_c/n)$. The broad arrows show the approximate paths of isochronal anneal for material of several different resistivities.

If the E center anneals in a single-activated process with a constant activation energy, then the rate of change of the concentration of the defect can be expressed by the chemical rate equation

$$\begin{aligned}\frac{dN_E}{dt} &= -k_E N_E^\gamma \\ &= -\nu \exp(-E_a/kT) N_E^\gamma, \qquad (1)\end{aligned}$$

where N_E is the concentration of E centers and k_E is the reaction rate constant, which consists of a frequency factor ν and an activation energy E_a. γ is the reaction order which is assumed to be unity.[19]

Equation (1), though general, is fairly restrictive in its application.[20] If two single-activated processes occur simultaneously, the results can be described by a relation in the same general form of Eq. (1), but the activation energy becomes an additional variable. At low temperatures, however, the activation energy approaches a constant value equal to the lower E_a of the two processes. This case is treated in detail in the Appendix.

If the charge state of the E center is a determining annealing parameter, then Eq. (1) must be appropriately modified. As a first approximation, based on the discussion above, it is assumed that the anneal of the neutral center is the rate limiting step. Thus, the concentration of centers N_E eligible for anneal becomes $N_E(1-F)$, where F is the Fermi function. Equation (1) takes the form

$$\begin{aligned}\frac{dN_E}{dt} &= -\nu \exp\left(-\frac{E_a^0}{kT}\right) N_E(1-F) \\ &= -\nu \exp\left(-\frac{E_a^0}{kT}\right) \frac{N_E}{1+\exp[(E_E - E_F)/kT]}, \qquad (2)\end{aligned}$$

where E_F is the Fermi level at the annealing temperature T; E_E is the location of the E-center acceptor level with respect to the conduction band; and E_a^0 is the activation energy for the anneal of the neutral defect. It should be noted that the normal convention of positive electron energies has been reversed in order to conform with the Arrhenius convention of negative activation energies.

Figure 4 depicts a simplified energy-level structure for the irradiated material at room temperature prior to anneal. Under these conditions, in which the isochronal anneal essentially begins, the constraint $E_E - E_F \gg kT$ holds and the Fermi function can be approximated by a simple exponential,

$$\begin{aligned}\frac{dN_E}{dt} &\approx -\nu \exp\left(-\frac{E_a^0}{kT}\right) \frac{N_E}{\exp(E_E - E_F)/kT}, \\ &\qquad E_E - E_F \gg kT \\ &\approx -\nu \exp[-(E_a^0 + E_E - E_F)/kT] N_E . \qquad (3)\end{aligned}$$

As the temperature is increased, the Fermi level is driven toward the center of the gap. More energy becomes available to overcome the activation barrier to annealing, but the probability of an E center being in the favorable neutral charge state is also increased. In effect, the activation energy acquires a temperature dependence. This result is notable in a comparison of Eq. (3) with Eq. (1). The activation energy E_a is replaced by the term $(E_a^0 + E_E - E_F)$ in which E_F contains the temperature dependence.

Further simplification is possible when one considers that $E_F - E_{G/2} \gg kT$ so that n is a constant ($\simeq n_0$), provided a significant concentration of E centers do not anneal. Since $n = N_c \exp(E_F/kT)$, Eq. (3) takes the form

$$\frac{dN_E}{dt} = -\nu \frac{N_c}{n} \exp\left(-\frac{E_a^0 + E_E}{kT}\right) N_E , \qquad (4)$$

where N_c is the density of states in the conduction band and n is the density of electrons in the conduction band prior to anneal.

By comparing the form of Eq. (4) with Eq. (1), one can qualitatively account for some of the anomalies in the data[6] reported earlier. An apparent activation energy of 1.7 eV could represent an E_a^0 of 1.3 eV (reasonable for a dissociation mechanism) and an E_E of 0.4 eV (the E-center ionization level). The reported frequency factor of $\sim 10^{18}$ sec^{-1} might consist of the term N_c/n, $\approx 10^5$ for 1–10-Ω cm silicon, multiplied by a real ν of 10^{13} sec^{-1} (the lattice vibration frequency). In addition, since n changes during the course of the anneal, a unique reaction order should not be evident.

In order to apply this approach to the data of Figs. 1 and 2, we examine the very early times of anneal during which $n \simeq n_0$. Integrating Eq. (4),

$$\ln \frac{n_{E_0}}{n_E} = +\nu \frac{N_c}{n_0} \exp\left(-\frac{E_a^0 + E_E}{kT}\right) \Delta t , \qquad (5)$$

where Δt is the isochronal time interval (10 min) during which the E-center concentration anneals from n_{E_0} to n_E at a temperature T. Applying limits at the 10% annealing point (90% unannealed) and rearranging, we obtain

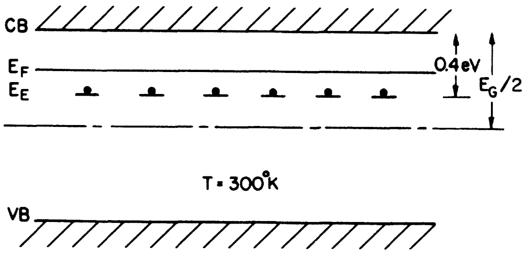

FIG. 4. Schematic representation of the relative E-center energy-level position in irradiated n-type silicon ($\rho < 1000$ Ω cm) at room temperature.

$$n_0=\frac{\nu N_c \Delta t}{\ln 1.1}\exp\left(-\frac{E_a^0+E_E}{kT_{0.9}}\right), \tag{6}$$

which relates the temperature $T_{0.9}$ required to anneal 10% of the E centers during a time interval Δt in a material with a carrier concentration of n_0.

Neglecting the temperature dependence (which is relatively small) of the density-of-states function N_c, the "activation energy" $(E_a^0+E_E)$ may be obtained from a series of isochronal anneals on material of varying electron concentrations according to

$$\frac{d\ln n_0}{d(1/T_{0.9})}\simeq-\frac{E_a^0+E_E}{k}\ . \tag{7}$$

Figures 5 and 6 show the fit of this relation to the data of Figs. 1 and 2. The second stage of the two-stage curves is assumed to be the E-center anneal. The surprisingly good fit of the experimental points to a straight line must be considered partly fortuitous when one considers the multiprocess complications discussed earlier and the fact that some of the approximations made in deriving this analysis break down in the case of high-resistivity materials (>10 Ωcm). It does show, however, that the observed displacement of the isochronal annealing stage is generally consistent with a charge-state effect.

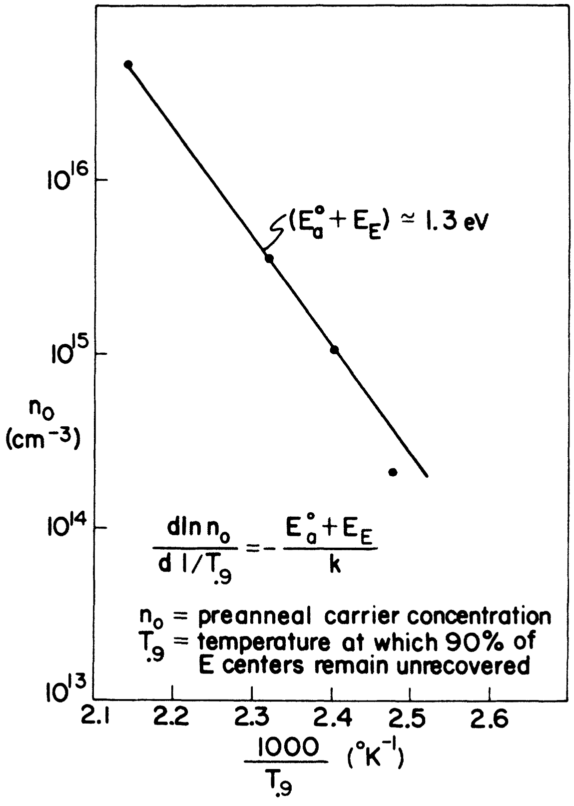

FIG. 5. Isochronal anneal of float-zoned silicon from Fig. 1 (see text).

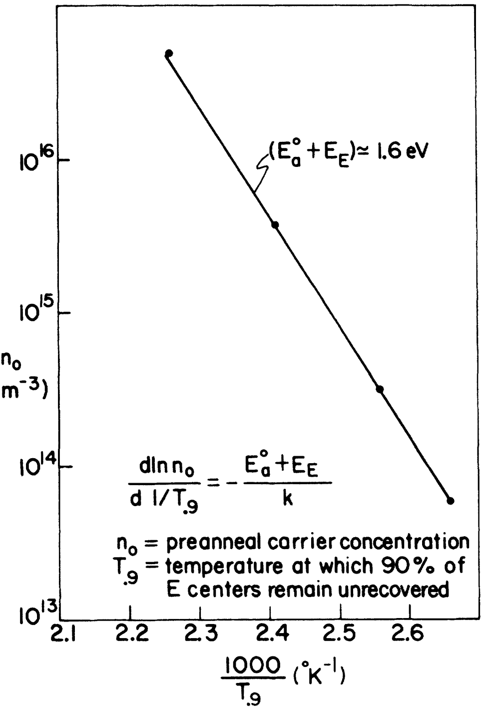

FIG. 6. Isochronal anneal of Lopex silicon from Fig. 2 (see text).

Based on a location of the E-center acceptor level at E_c, 0.4 eV, the slope of the lines indicate an activation energy of anneal for the neutral center of 0.9–1.2 eV. The value can, of course, accommodate either or both of the migration or dissociation mechanisms discussed. The fact that the 0.1-Ωcm material also falls on the line suggests that the anneal of the negative center requires an activation energy of 1.3–1.6 eV.

V. SUMMARY AND CONCLUSIONS

A generalized model of the charge-state effect on the stability of the donor-vacancy associate in silicon can be constructed from the analysis presented in this paper. In order to anneal via either the dissociation or the migration mechanisms, the E center must undergo at least partial break up. As described by Watkins and Corbett,[2] partial break up involves separation of the donor and vacancy to third-nearest-neighbor positions. An energy barrier of ~0.94 eV has been proposed for this process, which corresponds to the overcoming of the short-range covalent forces. At the third-nearest-neighbor site a binding energy of about 0.3 eV remains (probably electrostatic). It is too early to describe accurately the manner in which these forces are modified by the addition of an electron to the E center. Covalent forces, in general, increase as electrons are added to unsatisfied orbitals. Electrostatic forces, being directly proportional to the charge product of the two components, would be expected to double as the vacancy acquires a double-negative charge. Both of these tendencies follow the increase in activation energy with electron acceptance reported in this paper.

In summary, the variation of the E-center annealing behavior with carrier concentration has been shown to be consistent with a charge-state dependence of the activation energy of anneal. In a first approximation approach, the activation energy was estimated to increase about 0.4 eV with the addition of a second electron to the defect. The exact correlation of this value with the ionization energy for the electron suggests that the E center cannot anneal in the negative charge state. Further substantiation of these results are apparent in experiments presently being conducted in this laboratory which indicate that the annealing activation energy can be lowered by the presence of ionizing radiation (white light).

APPENDIX

This section treats the reaction-rate analysis of one species n annealing through two different but concurrent processes, both of which are first order [e.g., migration (process 1) and dissociation (process 2)].

A first-order rate equation has the general form

$$\frac{dn}{dt} = -k_n n, \tag{A1}$$

where k_n is the rate constant for the process. In the multiprocess case,

$$\begin{aligned} k_n &= k_1 + k_2 \\ &= \nu_1 \exp\left(-\frac{E_1}{kT}\right) + \nu_2 \exp\left(-\frac{E_2}{kT}\right), \end{aligned} \tag{A2}$$

where ν_1, E_1 and ν_2, E_2 are respective frequency factors and activation energies for processes 1 and 2.

The apparent activation energy E_a' for the over-all reaction is represented by the temperature dependence of the rate constant k_n:

$$\frac{d \ln k_n}{d(1/T)} = \frac{E_a'}{k} \quad . \tag{A3}$$

Thus, we have

$$E_a' = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2} \quad . \tag{A4}$$

Since k_1 and k_2 contain temperature-dependent terms, E_a' will vary with temperature. In the limit $E_1 < E_2$ and $\nu_1 > \nu_2$, reaction 2 is not important and $E_a' = E_1$ at all temperatures. When $E_2 > E_1$ and $\nu_2 > \nu_1$ (as might be expected for a migration process 1 and a dissociation process 2), E_a' approaches E_1 at low temperatures and varies continuously to a value of $(\nu_1 E_1 + \nu_2 E_2)/(\nu_1 + \nu_2)$ at high temperatures. Thus, E_a' and ν_a' range between E_1 and E_2, and ν_1 and ν_2, respectively, where ν_a' is the frequency factor associated with E_a'.

---

[1] G. D. Watkins, J. W. Corbett, and R. M. Walker, J. Appl. Phys. 30, 1198 (1959).

[2] G. D. Watkins and J. W. Corbett, Phys. Rev. 134, A1359 (1964).

[3] E. Sonder and L. C. Templeton, J. Appl. Phys. 34, 3295 (1963).

[4] M. Hirata, M. Hirata, and H. Saito, J. Appl. Phys. 37, 1867 (1966).

[5] H. Saito and M. Hirata, Japan. J. Appl. Phys. 2, 678 (1963).

[6] C. P. Carnes, P. J. Drevinsky, and H. M. DeAngelis, Bull. Am. Phys. Soc. 14, 845 (1969).

[7] H. M. DeAngelis, C. P. Carnes, and L. C. Kimerling, Bull. Am. Phys. Soc. 15, 397 (1970).

[8] M. Hirata, M. Hirata, and H. Saito, J. Phys. Soc. Japan 27, 405 (1969).

[9] G. K. Wertheim, Phys. Rev. 115, 568 (1959).

[10] E. E. Klontz and J. W. MacKay, J. Phys. Soc. Japan Suppl. 18, 216 (1963); J. Appl. Phys. 30, 1269 (1959).

[11] H. J. Stein and F. L. Vook, in *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum , New York, 1968), p. 115–123.

[12] J. W. Corbett and G. D. Watkins, Phys. Rev. 138, A555 (1965).

[13] M. Hirata, M. Hirata, H. Saito, and J. H. Crawford, Jr., J. Appl. Phys. 38, 2433 (1967).

[14] H. Reiss, C. S. Fuller, and F. J. Morin, Bell Syst. Tech. J. 35, 535 (1956).

[15] H. J. Stein and F. L. Vook, Phys. Rev. 163, 790 (1967).

[16] The probability of divacancy formation should be proportional to the square of the vacancy concentration. If some E centers anneal out by dissociation, then the vacancy concentration present during the anneal is a direct function of the E-center concentration.

[17] R. E. Penczer, P. J. Drevinsky, C. P. Carnes, and H. M. DeAngelis, Bull. Am. Phys. Soc. 13, 1476 (1968); 13, 710 (1968); 13, 380 (1968).

[18] This approach is based on the assumption that the added electron acts to increase the effective charge on the vacancy to -2. Whereas it is an oversimplication to describe the E center solely in terms of ionic bonding, the acceptor level at E_c, 0.4 eV might be expected to be more "vacancylike" than "phosphorouslike" because the approach of two oppositely charge defects (V^-, P^+) tends to drive their respective energy levels toward the band from which they originated. Thus, the phosphorous donor level might be pushed into the conduction band and the acceptor level for a second vacancy electron would

move to a deeper position, i.e., from near the conduction band toward the valence band.

[19]All of the proposed mechanisms, should, generally, lead to first-order kinetics.

[20]C. P. Carnes, P. J. Drevinsky, and H. M. DeAngelis, AFCRL Technical Report No. 70-0423, 1970 (unpublished).

PHYSICAL REVIEW B VOLUME 3, NUMBER 2 15 JANUARY 1971

Calculation of the Exchange Energy for Excitons in the Two-Body Model*

Peter G. Rohner†

II. Institut für Theoretische Physik, Technische Universität Berlin, 1 Berlin 12, Germany

and Department of Physics, University of Dayton, Dayton, Ohio 45409

(Received 11 August 1969; revised manuscript received 7 May 1970)

The exchange energy for the Wannier exciton is calculated by solving a previously derived two-body Hamiltonian $H^{(2)}$. The solution of the eigenvalue problem of $H^{(2)}$ in the effective-mass approximation is performed with a numerical diagonalization method. The values obtained for the exchange energy in several II-VI compounds are between 10 and 20% of the binding energy of the pure hydrogenlike exciton. The comparison with experimental results shows a satisfactory agreement.

I. INTRODUCTION

The influence of the electron-hole exchange interaction on the energy spectrum of the Wannier exciton is generally said to be small for large exciton radii.[1] Therefore, this exchange interaction is normally neglected in deriving a two-particle equation for the exciton from the N-electron Hamiltonian.[2-4] In a previous paper,[5] we presented a two-body operator for the exciton which was also derived from the N-electron Hamiltonian, but which included an exchange term in the two-body picture. With this term it became possible to handle the exchange energy of the exciton in the two-particle formalism. We did this in the above-mentioned paper with a perturbation calculation and our results were comparable to those of Makarov.[6]

It is, however, not necessary to use a perturbation method to compute the exchange energy of the exciton. We will show that the calculation of the exchange interaction can be performed on the same footing as the calculation of the Coulomb interaction. We obtain the exchange energy for the Wannier exciton in the effective-mass approximation (EMA) without fitting parameters. The physical restrictions to the validity of the calculated values are caused by the approximations used in deriving the exciton Hamiltonian. The derivation of a two-body Hamiltonian is only possible with the assumption of one-particle excitations in the N-electron picture. This assumption and the EMA have to be discussed in order to decide to which crystals the obtained results may be applicable.

In Sec. II, we shall first consider the main points in formulating the eigenvalue problem for $H^{(2)}$. We shall see that there are two possible methods for obtaining the eigenvalue spectrum of $H^{(2)}$ in the EMA. Only the diagonalization method will be described in detail. Then, in Sec. III, we shall solve the eigenvalue problem of $H^{(2)}$ and, in Sec. IV, the results will be discussed. In Sec. V, finally, we shall compare the calculated energy spectra for several substances with experiment.

II. EIGENVALUE PROBLEM FOR EXCITON HAMILTONIAN

In order to calculate the exchange energy of the exciton, we solve the eigenvalue problem of the exciton Hamiltonian $H^{(2)}$ which includes an exchange term. This Hamiltonian has the form[5]

$$H^{(2)}=E_0+h(\vec{r}_1)-h^*(\vec{r}_2)-\frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}+\delta(\vec{r}_1-\vec{r}_2)\,\delta_{\sigma_1\sigma_2}\sum_{\sigma_1'\sigma_2'}\delta_{\sigma_1'\sigma_2'}\int_\Omega\frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_1{}'|}\,\delta(\vec{r}_1{}'-\vec{r}_2{}')\cdots d\tau_1'd\tau_2'\,, \tag{1}$$

where E_0 is the ground-state energy of the whole crystal in the Hartree-Fock method[7] and is here a constant, and $h(\vec{r}_1)$ and $-h(\vec{r}_2)$ are the self-consistent one-particle Fock operators,[7]

$$h(\vec{r}_i)=-\frac{\hbar^2}{2m}\nabla_i^2+V(\vec{r}_i)+\sum_v\sum_\sigma\int_\Omega\frac{e^2}{|\vec{r}-\vec{r}_i|}\,|\varphi_v(\vec{r},\sigma)|^2d\tau-\sum_v\delta_{s_is_v}\,\varphi_v(\vec{r}_i,\sigma_i)\sum_\sigma\int_\Omega\frac{e^2}{|\vec{r}-\vec{r}_i|}\,\varphi_v^*(\vec{r},\sigma)\cdots d\tau_1\,, \tag{2}$$