

Diffusion in Diamond¹

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INTRODUCTION

With the development of semiconducting diamonds, the diffusion of vacancies and impurities in diamond has become of great interest. The main purpose of this investigation is to study diffusion in diamond and, in particular, to determine under what conditions it might be possible to diffuse impurities into insulating diamonds to produce semiconducting diamonds.

There are several different kinds of diffusion of atoms in solids—the vacancy, interstitial, direct interchange modes, the ring mechanism, the interstitialcy mode, and combinations of these. There are even more complicated modes. Vacancy diffusion assumes the presence or the formation of vacant lattice sites into which a diffusing atom moves, leaving a vacancy into which another atom may move. In interstitial diffusion an atom in an interstitial position moves to another interstitial position. Either a small diffusing atom or a relatively open lattice structure is required to obtain sufficiently large interstitial positions. In direct interchange, two atoms which are adjacent change places simultaneously. No vacancy is required. The ring mechanism is an extension of the idea of direct interchange. A number of atoms are involved this time, not just two. The diffusing atoms are located on a "ring", that is, a circle may be drawn intersecting all the diffusing atoms. All the atoms move at the same time and in the same direction around the ring. In the interstitialcy mechanism an atom in an interstitial position displaces an atom in a normal lattice position, and the atom in the normal lattice position is displaced into an interstitial position. The pattern can be repeated so that the interstitial distortion moves through the lattice.

The diamond lattice is a relatively open structure. It has large interstitial sites, their size being on the order of that of a lattice site. It is believed, however, that the predominant mode of diffusion in the diamond lattice is the vacancy method. In germanium and silicon, experimental evidence seems to indicate a vacancy method for nearly every diffusing impurity (Swalin, 1960).

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DIFFUSION THEORY FOR DIAMOND TYPE LATTICE

Swalin (1958) worked out a model for diffusion in the diamond lattice structure that seems to agree fairly well with experiment, at least in the cases of germanium and silicon. The basic assumption is that substitutional impurity diffusion and self-diffusion both occur by a vacancy mechanism. Self-diffusion will be considered first.

Fick's first law of diffusion is

$$J = -D\Delta C \quad (1)$$

where J is the diffusion current (of the diffusing substance) with the dimensions, amount per unit area per unit time. D is the diffusion coefficient with dimensions of area per unit time, and C is the concentration of the diffusing substance. In general, D is a tensor, but in an isotropic material it is a scalar independent of the orientation of the concentration gradient.

With certain reasonable approximations it can be shown (Swalin, 1960) that

$$D = D_0 \exp [-Q/RT]$$

where $D_0 = (1/16)a^2 \nu \exp [(\Delta S_v + \Delta S_1)/k]$

$$Q = (\Delta H_v + \Delta H_1)N$$

R = the gas constant.

a = lattice parameter of the crystal.

ν = frequency of oscillation of the diffusing particle about its equilibrium position.

ΔS_v = change in entropy upon formation of a lattice vacancy

ΔS_1 = change in entropy when the diffusing particle goes from its equilibrium position to the top of the potential barrier which it must surmount in order to diffuse.

N = Avogadro's number.

k = Boltzmann constant.

ΔH_v = change in enthalpy upon formation of a lattice vacancy.

ΔH_1 = change in enthalpy when the diffusing particle goes from its equilibrium position to the top of the potential barrier which it must surmount in order to diffuse.

Solute, or impurity, diffusion differs from self-diffusion because one is no longer looking at similar atoms. The diffusing atom in impurity diffusion differs in size and possibly valency from the solute atoms.

If vacancies act as electron acceptors then the concentration of charged vacancies will depend on the position of the Fermi level, which is influenced by the addition of impurities. Since to a first approximation the number of neutral vacancies remains constant at a given temperature, the total number of vacancies will be changed depending on the level of doping (Swalin, 1958; Longini and Green, 1956; Valenta and Ramasastry, 1957). A second effect to be taken into account is the coulomb interaction between the charged vacancies and the charged impurity ions. Positively charged impurity ions will be attracted to the negative vacancies and negative ions will be repulsed. A third factor is that impurity ions which have an ionic size considerably different from the solvent ions will introduce considerable strain energy into the structure. Part of the strain energy will be reduced if vacancies preferentially situate themselves next to the wrong-sized impurity ions. All of these factors will have to be taken into account in deriving equations for solute diffusion.

In the case of impurity diffusion the equation for D becomes

$$D = D_0 \exp [-Q/RT]$$

with D_0 being the same expression as before (not the same value) and with

$$\exp [-Q/RT] = \exp [-(\Delta H_v + \Delta H_1 + \Delta H_c)/kT] \\ [1 + 2 \exp (E_p - E_v - \Delta H_c)/kT]$$

The new terms appearing in this expression are:

ΔH_s = the energy difference between ΔH_v , the energy of formation of a vacancy next to solvent atoms, and ΔH_i , the energy of formation of a vacancy next to a wrong-sized impurity ion.

E_F = Fermi energy.

E_v = vacancy acceptor energy level.

When $(E_F - E_v - \Delta H_c) \ll kT$, then $Q = [\Delta H_v + \Delta H_i + \Delta H_s]N$

This condition could be possible in insulating diamonds.

Friedel (1954) derived equations for the strain-energy contribution to the heat of solution of a wrong-sized impurity ion. From the equations one can get an estimate of ΔH_s .

$$\Delta H_s \cong \frac{6\pi(r_s - r'_s)r'_s}{z(1 + \alpha)X'} \\ \alpha = (1 + \rho)Xr'_s/2(1 - 2\rho)X'r_s$$

where

r'_s is the ionic radius of the solute atoms, r_s is the ionic radius of the solvent atoms, X is the solvent compressibility, X' is the solute compressibility, and ρ is Poisson's ratio for the solvent.

The coulomb interaction energy can be estimated from

$$\Delta H_c = \pm q_v q_i / Kd$$

where q_v is the charge of the vacancy, q_i is the charge of the impurity, K is the dielectric constant, and d is the nearest-neighbor distance.

CALCULATED VALUES FOR DIFFUSION CONSTANT AND

ACTIVATION ENERGY

The differing values for D_0 for the cases of self-diffusion and impurity diffusion arise because of differences of ν and ΔS , for the two cases. The difference in ν of the solute and solvent ions will be neglected. If the difference between ΔS , for the solute diffusion and self-diffusion is also neglected, then D_0 will be the same for solute diffusion and for self-diffusion. This is a gross assumption, but according to germanium and silicon data (Swalin, 1960), this approximation does seem to give at least the order of magnitude of D_0 .

Swalin (1960) obtained a value of 11.6 cm²/sec for D_0 for self-diffusion and also computed Q for self-diffusion in diamond using a Morse function for determining the enthalpy terms.

CALCULATION OF ACTIVATION ENERGY

In the present paper Q is calculated by a different method. The method follows that used by Dienes (1952) for calculation of diffusion in graphite.

Although diamond does not have the same crystal structure as graphite, the bonds are still carbon-carbon bonds, and for this reason the following procedure was used to calculate Q . Data from Pauling (1960) were used in making Table 1. If a graph is made of the log of bond energies, B , versus bond length, r_c , it is seen that for the longer bonds (C - C and C = C) this is essentially a straight line whose equation is $\log_{10} B = -1.180r_c + 3.741$. In the following development the above equation is used to compute bond energies instead of the Morse function which Swalin used. With a diamond bond length of 1.542 Å, then $B = 83.5$ Kcal/mole. To calculate ΔH_v , when an atom is removed from lattice site, four bonds are broken requiring an expenditure of $4(83.5) = 334$ Kcal/mole. When the atom is placed on the surface two bonds are formed

yielding $2(83.5) = 167$ Kcal/mole. So, $\Delta H_v = 334 - 167 = 167$ Kcal/mole. Next ΔH_i is computed. When the atom is at the saddle point there will be six bonds, each of a greater length than before. Upon examination of the geometry of the configuration it is found that the new length is 1.94 Å. The corresponding bond energy is found to be 28.3 Kcal/mole, but because there are six bonds this becomes $6(28.3) = 169.8$ Kcal/mole. When the atom was at the lattice site there were three bonds of length 1.542 Å for

TABLE 1. CARBON-CARBON BOND ENERGIES

Bond	Interatomic Distance	Bond Energies
C - C	1.544 Å	83.1 Kcal/mole
C = C	1.334 Å	147 Kcal/mole
C \equiv C	1.206 Å	194 Kcal/mole

an energy of $3(83.5) = 250.5$ Kcal/mole. Therefore a preliminary value for the energy to move a vacancy is $250.5 - 169.8 = 80.7$ Kcal/mole. This value, however, has to be corrected for bond angle distortion. When the atom is at the saddle point, six bond angles have been distorted; three of these have each been distorted 22° . Following Dienes (1952) the energy of bond angle distortion is 1.5 Kcal/mole per 10° distortion which gives in this case $(1.5)(2.2) = 3.3$ Kcal/mole. There are three of these distortions, so, $3(3.3) = 9.9$ Kcal/mole. The other three bonds have been distorted 28.55° giving an energy of 12.84 Kcal/mole. The total energy due to bond angle distortion is $9.9 + 12.84 = 22.74$ Kcal/mole. Hence, $\Delta H_i = 80.7 + 22.74 = 103.44$ Kcal/mole and so, $Q = 167 + 103.44 = 11.74$ ev.

In a similar way, the activation energy for diffusion of aluminum in diamond was computed using the approximation that $Q = [\Delta H_v + \Delta H_i + \Delta H_j]N$. The calculated results are 11.7 ev for Q (self) and 14.7 ev for Q (impurity). The values computed by Swalin using the Morse function are Q (self) = 6.18 ev and Q (impurity) = 9.12 ev.

EXPERIMENTAL RESULTS

Experimental studies were carried out to determine if aluminum, boron, or beryllium could be diffused into insulating diamonds in a reasonable time under conditions similar to those for diffusion in germanium and silicon, that is, without going to high pressures. A diffusion temperature of 900°C was chosen, at which the rate of change of diamond to graphite is negligible. A moderate vacuum environment was used in each case. Diffusion times were up to one week. The impurity was in contact with the diamond in each case although various methods were used to obtain the contact. The boron was in the form of a powder and was merely placed in contact with the diamond in the crucible. The beryllium was deposited as a vapor onto the surface of the diamond. The aluminum was either deposited as a vapor or, in some cases, was placed in contact as a relatively large molten mass surrounding the diamond.

Two methods were used to detect diffusion, change in resistivity and optical transmission. Resistivity measurements were made with a vibrating-reed electrometer. Both volume and surface resistivity were measured. Guarded electrodes, shielding, and a dark environment were found necessary. Measurements made after each diffusion run showed no changes in the resistivities.

Optical transmission measurements were made both before and after the diffusion runs from 0.285 microns to 14 microns, but no change in the transmission was noted. The prominent 3.5 micron band associated with semiconducting diamond was absent in all cases. The concentration of nitrogen as an impurity has been connected with the 8-micron absorption

band by Kaiser and Bond (1959), but in this case the magnitude of the absorption did not change. If the absorption band had decreased, this would have indicated possible out-diffusion of nitrogen.

CONCLUSIONS

The computed values of the activation energies for vacancy and impurity diffusion are so high that significant diffusion should not occur below 1000C, the temperature above which the rate of change of diamond to graphite becomes significant. The experimental results are in agreement with this. The possibility of diffusion by some other mechanism such as diffusion along dislocation edges does exist, but this was not evident from the experimental results.

LITERATURE CITED

- Dienes, G. J. 1952. Mechanism for self-diffusion in graphite. *J. Appl. Phys.* 23: 1194.
- Friedal, J. 1954. Electronic structure of primary solid solutions in metals. *Advances in Phys.* 3: 446.
- Kaiser, W. and Bond, W. L. 1959. Nitrogen, a major impurity in common type I diamonds. *Phys. Rev.* 115: 857.
- Longini, R. L. and Greene, R. F. 1956. Ionization interaction between impurities in semiconductors and insulators. *Phys. Rev.* 102: 992.
- Pauling, L. 1960. *The Nature of the Chemical Bond*. 3rd ed. Cornell University Press, Ithaca, New York.
- Swalin, R. A. 1960. The theory of diffusion in semiconductors, ASTIA - AD-243, 429, University of Minnesota.
- Swalin, R. A. 1958. Model for solute diffusion in crystals with the diamond structure. *J. Appl. Phys.* 29: 670.
- Valenta, M. W. and Ramasastry, C. 1957. Effect of heavy doping on the self-diffusion of germanium. *Phys. Rev.* 106: 73.
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