STUDY OF DIFFUSION IN DIAMOND

By

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INTRODUCTION

Objective

The phenomenon of diffusion has been observed in germanium and silicon which have the diamond structure. The objective of this work is the determination of the existance of observable diffusion in diamond under conditions similar to those for germanium and silicon.

Classification of Diamonds

Diamonds in the past were grouped into three separate classes, type I, type IIa, and type IIb. This classification system was started in 1934 by Robertson, Fox, and Martin (1). They divided diamonds into the two groups, type I and type II, on the basis of optical absorption. Type I diamonds transmit light in the ultraviolet region down to a wavelength of 0.3 microns and have an absorption band in the infrared at 8 microns. Type II diamonds transmit light in the ultraviolet region down to 0.225 microns and do not have the 8 micron absorption band. In 1952, Custers (2) reported finding an unusual phosphorescence in some diamonds. These diamonds were also found to conduct electricity more readily than other diamonds, which are insulators. He proposed the subdivision of type II into type IIa and type IIb, denoting the conducting diamonds as type IIb. Type I and type IIa have a resistivity of at least

10^{14} ohm-cm (3). Type IIb diamonds have a room temperature resistivity in the range 25 ohm-cm (3). Type IIb, unlike type IIa, shows a strong phosphorescence when irradiated by short ultraviolet in the region of 2500 Å (3). Also, Raman (4) states that type I diamonds fluoresce in the near ultraviolet region while type II diamonds do not. Leivo and Smoluchowski (5) showed that the type IIb diamonds behave as impurity activated semiconductors.

Concerning the relative abundances of the different types of diamonds, it has been stated that 95% of all diamonds are of type I (6). Of the remaining two types, type IIb is considered to be the rarer; in fact, it is very rare (3).

The above classification system, although recognized in the past, has been found to be unsatisfactory in some respects.

Diamond Research

The present project is part of a larger program of research on semiconducting diamonds that is being carried out in this laboratory under the direction of W. J. Leivo. A brief indication of this work follows. Stein (7) (8) studied the optical transmission from the fundamental cutoff in the ultraviolet near 0.23 microns to 13 microns. Bell (9) (10) investigated rectification, photoconductivity, and the photovoltaic effect. Young (11) studied the Hall effect. He found the diamonds he studied have p-type conductivity. The slope of $k \ln R_H T^{3/2}$ versus 1/T is 0.35 ev where R_H is the Hall constant, T the Kelvin temperature, and k is the Boltzmann constant. Johnson (12) (13) investigated photoconductivity as a function of intensity of illumination, spectral distribution, electric field strength, temperature, and crystal orientation.

Wayland (14) (15) studied carrier lifetimes in semiconducting diamond, and Krumme (16) studied various types of luminescence in semiconducting diamond.

Impurity Semiconduction in Germanium and Silicon

Germanium and silicon have the same crystal structure as diamond. The lattice may be considered as being formed from two interpenetrating face-centered cubic lattices (see Fig. 1).

Silicon and germanium are semiconductors at room temperature, even when absolutely pure; this is called intrinsic conductivity. The conductivity arises from thermal excitation of electrons from the valence band to the conduction band. However, the resistivity of both can be decreased by the judicious insertion of certain well chosen impurity atoms, in low concentrations, into the lattice. The reduction of resistivity is due to various energy levels being introduced into the forbidden energy gap. Germanium and silicon are in group IV of the periodic table and each has four valence electrons. If an element from group III, such as B, Al, Ga, or In, is introduced substitutionally into the lattice, there will be one unoccupied electron state. That is, the four nearest neighbors of the impurity atom each share one of their valence electrons with the impurity atom, and the impurity atom shares its three valence electrons with the nearest neighbor atoms. A new energy level called an acceptor state is formed which lies a little above the valence band. If an atom from group V such as P, As, or Sb is introduced substitutionally, then there will be an extra electron associated with the impurity atom. A new energy level is formed which is called a donor state, and it lies just below the conduction band. At any temperature above $0^{o}K$, the

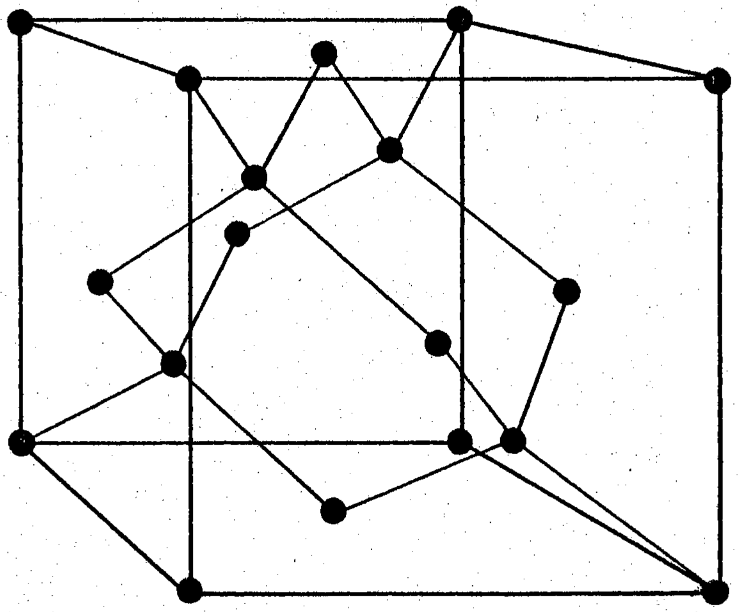

Fig. 1. Diamond Lattice

acceptor states will be partially filled by electrons thermally excited from the valence band, leaving a hole in the valence band, and, for the second case, the donor states will be partially empty because of the electrons being thermally excited to the conduction band. Either condition gives rise to increased conductivity.

In germanium, the energy gap is about 0.72 ev, and in silicon it is 1.1 ev. Because of the relatively small energy gaps they both show an intrinsic conductivity without going to high temperatures. In diamond, however, the energy gap is about 5.6 ev. This means that at room temperature diamond would have a negligible intrinsic conductivity. One would then expect that the conducting properties of type IIb diamond would be due to impurities or other crystal imperfections.

Observed Impurities in Diamond

There are few references in the literature on the impurity content of diamonds. One of the first of significance is that of Chesley (17) which appeared in 1942. By a cursory examination of 138 diamonds from 15 different localities, Chesley selected 33 stones, an average of two stones from each locality, upon which to run an emission spectrographic analysis. Thirty elements were analyzed for, and thirteen, of the thirty, were found. Elements found to be present were Al, Si, Ca, Mg, Cu, Ba, Fe, Sr, Na, Ag, Ti, Cr, and Pb. Elements sought for but not found were Sb, As, Be, Bi, Co, Ge, Au, Li, Mn, Ni, K, Rb, Sc, Sn, W, Zn, and Zr. Due to the method used, it is not possible to state either the presence or absence of B, O, N, P, and S. This work is semi-quantitative in nature, no attempt having been made to determine the absolute concentration of impurities present in the diamonds (see the following three pages for

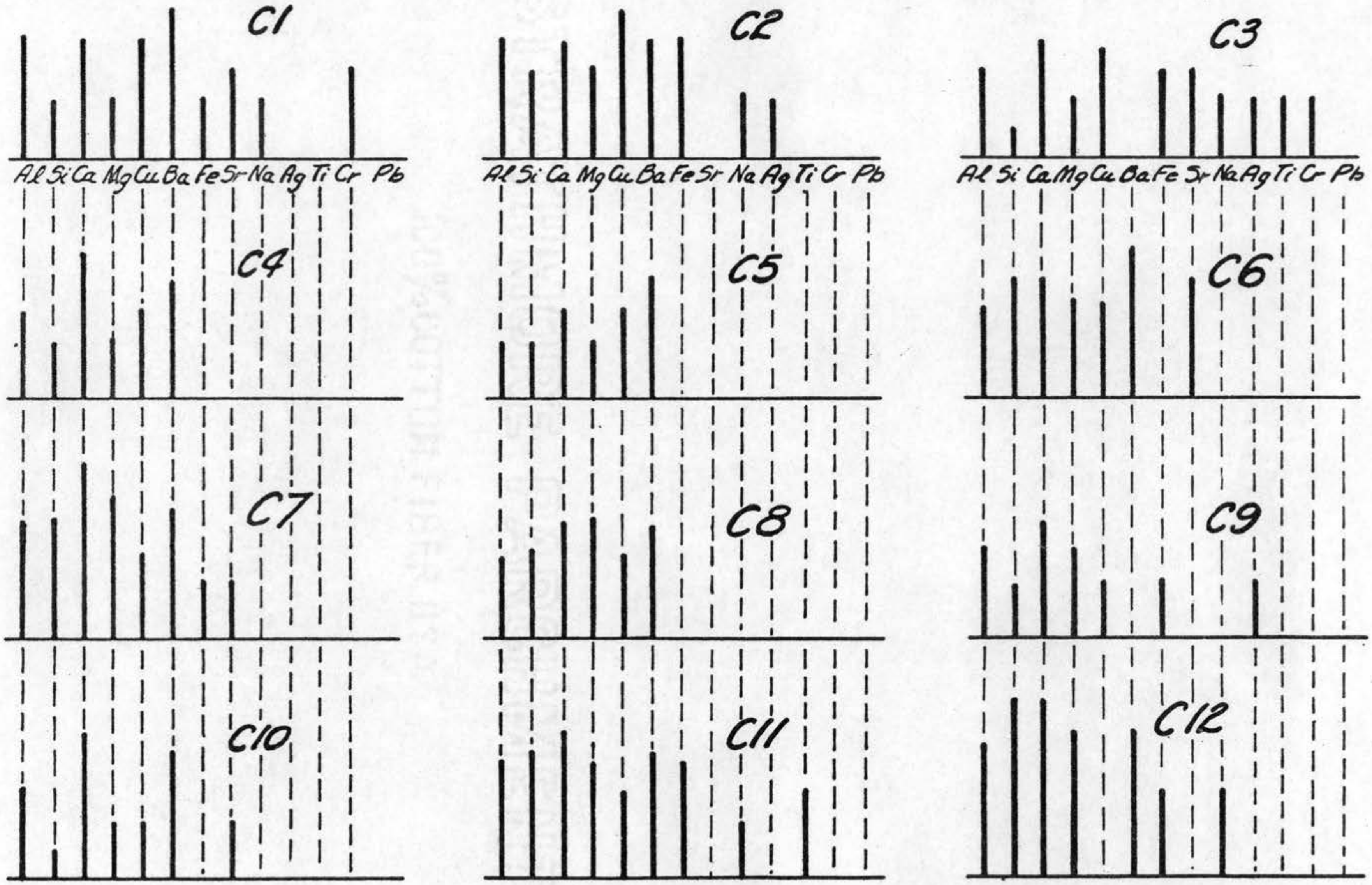

FIGURE 2a. RELATIVE AMOUNTS OF IMPURITIES IN CHESELY'S DIAMONDS C1 to C12

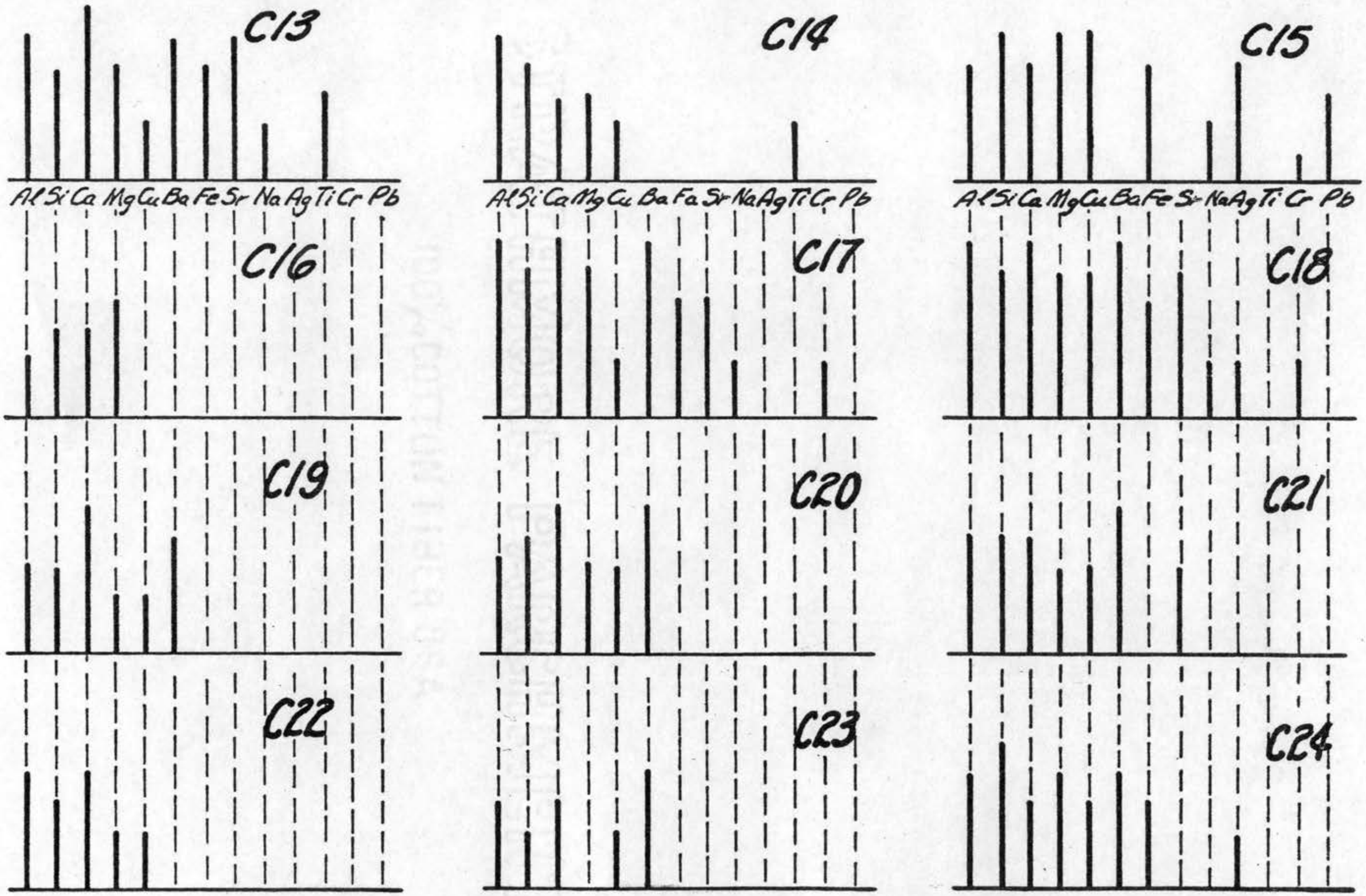

FIGURE 2b. RELATIVE AMOUNTS OF IMPURITIES IN CHESELY'S DIAMONDS C13 TO C24

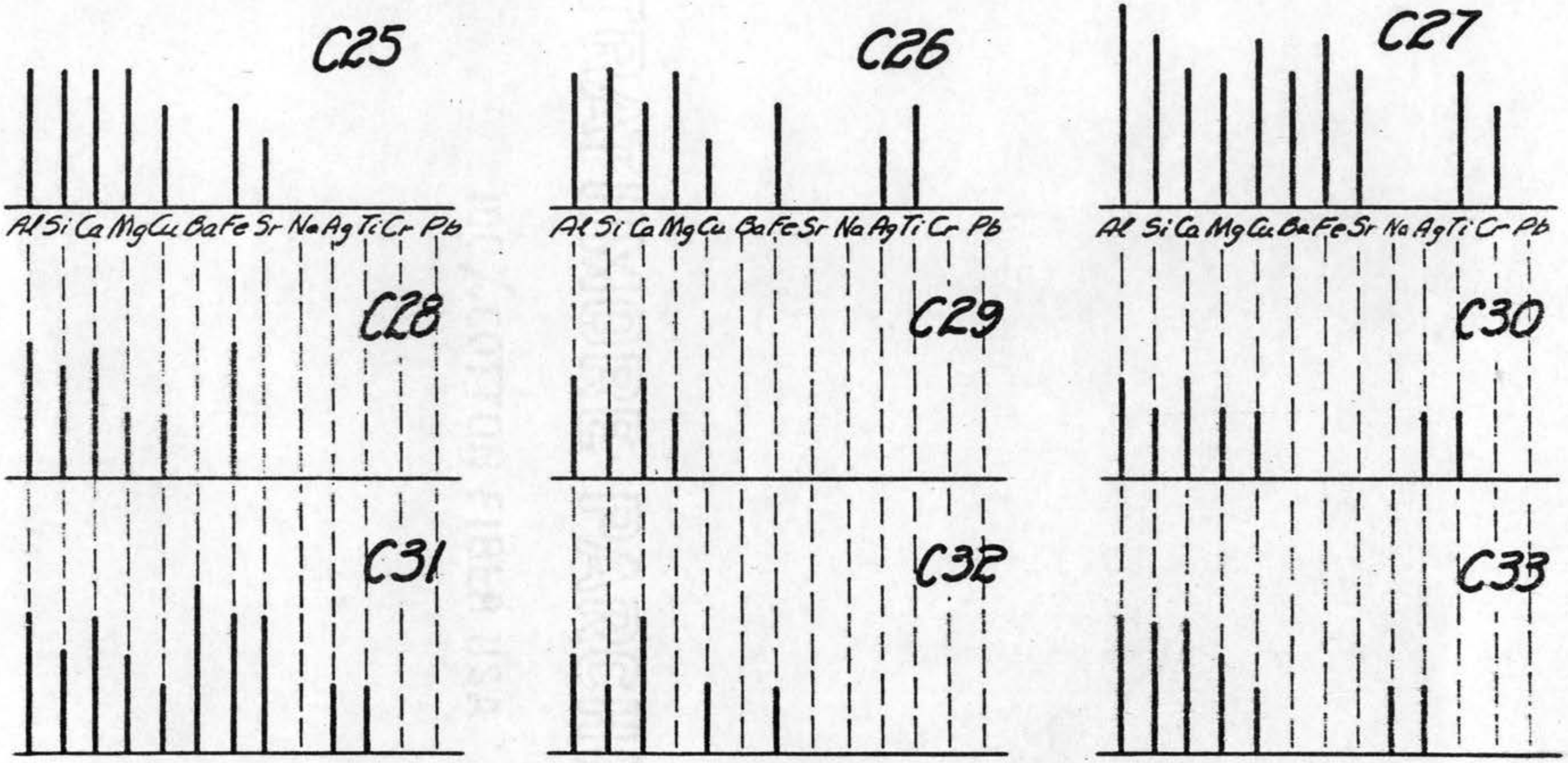

FIGURE 2c. RELATIVE AMOUNTS OF IMPURITIES IN CHESELY'S DIAMONDS C25 TO C33

graphs adapted from Chesley's table).

It will be noted from the graphs that Al, Si, and Ca were present in all 33 of the diamonds. Also, Al and Si seem to exhibit a relationship--if the amount of one is large, then the amount of the other is large, and if the amount of one is small, then the amount of the other is small. Of the remaining elements, Mg was found in 31 stones, Cu in 30, Ba in 20, Fe in 18, Sr in 12, Na in 10, Ag in 10, Ti in 8, Cr in 6, and Pb in 1. There seem to be no other relative abundance trends than the one of Al and Si.

Chesley examined the ultraviolet absorption curves of some of the diamonds in order to locate the ultraviolet transmission cutoff and to so determine whether the diamonds are type I or type II. This was done for six of the diamonds, the other 27 stones not allowing sufficient light through because of their non-parallel faces. Five of the diamonds did not transmit past 0.3 microns and therefore were labeled type I. The other stone transmitted down to 0.25 microns and so was labeled type II. The stone labeled type II was more pure than those called type I. In the type II, only four elements were found, these being traces of Si and Mg and small amounts of Al and Ca.

In 1951, Straumanis and Aka (18) reported on their work on diamonds. They also did a semiquantitative analysis by emission spectra. They examined three stones, one of gray bort and two of gem quality, all from the Belgian Congo (see Fig. 3 for graphs). Fifteen elements were found: Al, B, Ca, Co, Hf, Fe, Pb, Mg, Mn, Pt, Si, Ag, Sn, Ti, and Zn. B, Hf, Pb, Mn, and Ag were each found in two diamonds and Co, Pt, Sn, and Zn were each found in one diamond only. The diamond in which the Pt was found, however, had been treated with hydrofluoric acid for twelve hours in a

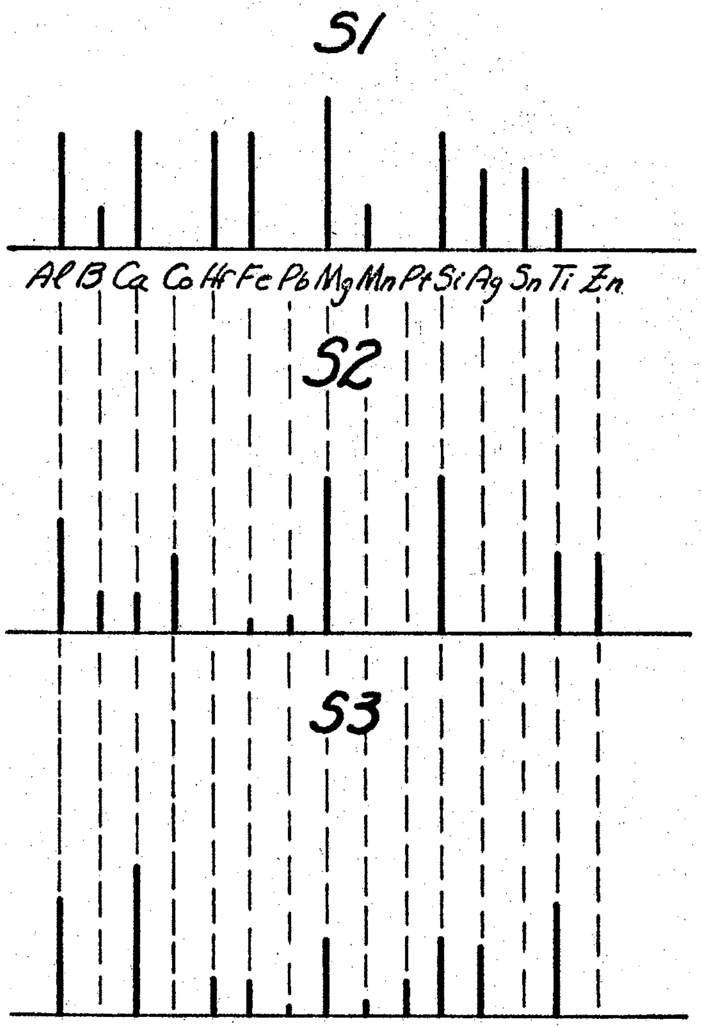

Fig. 3. Relative Amounts of Impurities in Straumanis's and Aka's Diamonds.

Pt crucible. This possibly was the reason for the presence of the Pt.

Few conclusions can actually be drawn from only three such samples. However, the Al and Si do show the same relationship as in Chesley's data. Although Mg also shows such a relative variation, considering that only three samples were used, it is seen that this can also be considered to be in agreement with Chesley.

The possibility of gold as an impurity in diamond was reported in 1952 by Freedman (19). He irradiated a light-yellow colored diamond with neutrons from a pile for eight hours. Subsequent to the irradiation, low intensity radioactivity was observed. The decay of the activity was followed, and a single 2.7 day half-life was found. It was decided, by measurements of the absorption in aluminum, that the radiation was 1 mev beta-particle radiation. It was stated that the only activity fitting these data is that of Au^{198}. Freedman thought it likely that one or two micrograms of gold in the one-tenth gram diamond would account for the observed intensity and possibly also for the initial yellow coloration. Gold as a surface contaminant of this magnitude was not considered likely because the diamond had never been mounted.

In 1957, Raal (20) carried out a quantitative spectrographic analysis of diamond. Twenty-five diamonds from at least four different sources were studied. There were fifteen type I stones, four type IIa stones, and six type IIb stones. Of the fourteen elements looked for, Si, Ca, Mg, Al, Fe, Ti, Cu, and Cr made their appearance, while Ag, Ni, Pb, Na, Ba, and Sr were absent in all cases. Cobalt could not be looked for because it was used as the internal standard. The Cr was listed as only a trace in one of the diamonds.

The failure to detect the above six elements mentioned does not, however, preclude their presence. The limits of detection of some of these elements, notably Pb and Ba, are of the order of anything up to 10 parts per million, and they might be present to an extent such that the most persistent lines are not detectable. Quantitative spectrographic analysis is never an easy procedure, and with diamond in particular it proves to be even more difficult due to the nature of the material and the fact that the trace constituents are present to the extent of only a few parts per million (20) (see Figs. 4a and 4b for graphs).

The main impurities seem to be Si, Ca, Mg, Al, Fe, and Cu with the aluminum predominant in most cases. The total impurity content of any one diamond seems to be roughly 10 to 60 parts per million. From the graph it may be seen that the type I stones are, in general, more impure than the type II. The type IIa and type IIb appear to differ very little as regards impurity content. In the type II diamonds, the main impurities are, almost exclusively, Si, Mg, and Al with the latter predominant in most cases. The relation between Al and Si is not as marked as in Chesley's data. The dominant group, for Raal's data, for all types of diamond is apparently Al, Si, and Mg with a great preponderance of Fe in type I diamonds. It may be noted that some of the impurities found by Chesley were not found by Raal.

In 1958, Bunting and Van Valkenburg (21) reported on their semi-quantitative spectrographic analysis of diamond. They examined six stones. Three were type I, and three were type II. Of the elements tested for, 36 were not found. No test was made for Cs, Li, K, Rb, or the rare earth elements. The elements found were Al, B, Ca, Cu, Fe, Mg, Na, and Si (see Fig. 5).

They found no noticeable difference between the two types of diamond

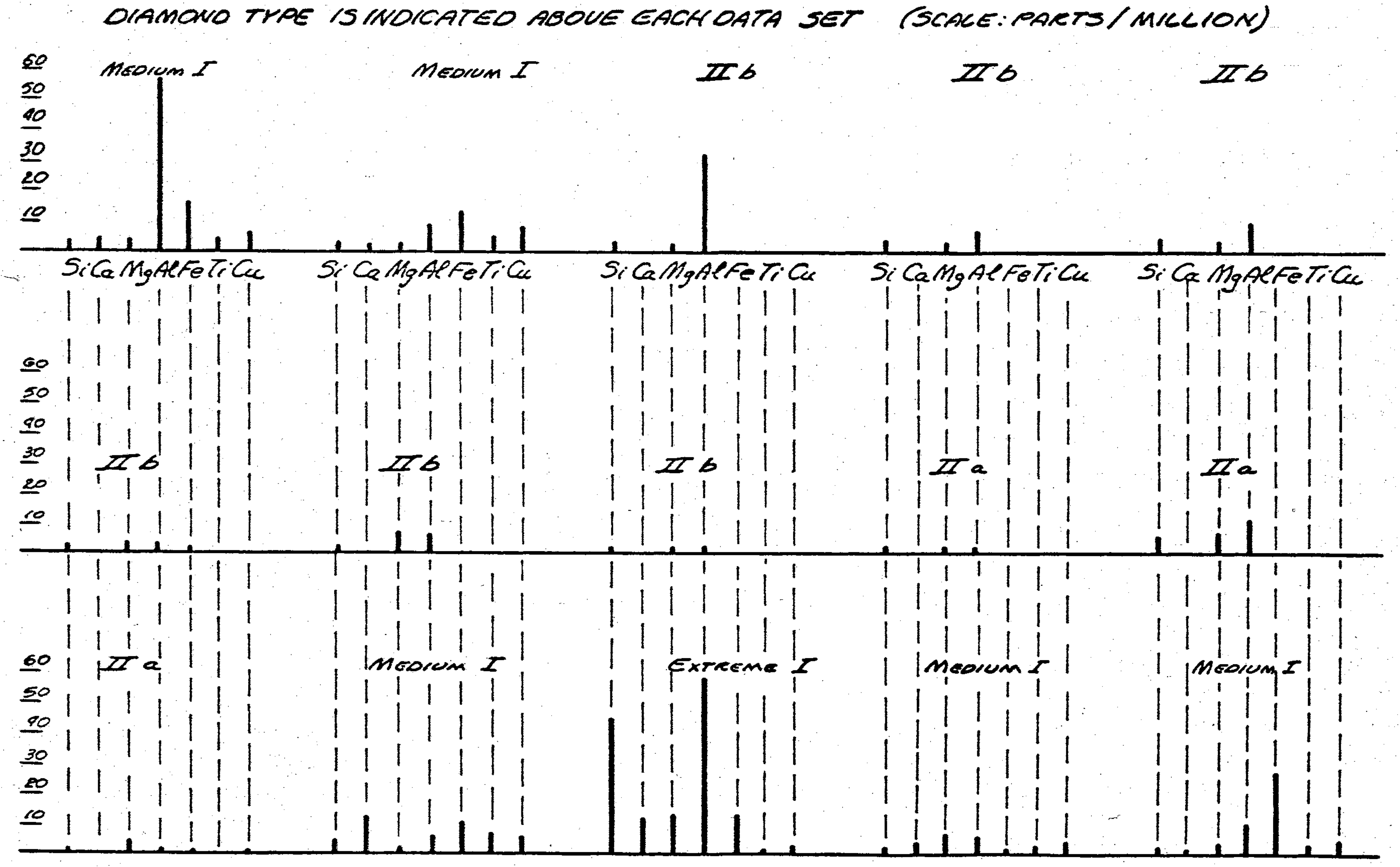

Fig. 4a. Amounts of Impurities in Raal's Diamonds R1 to R15.

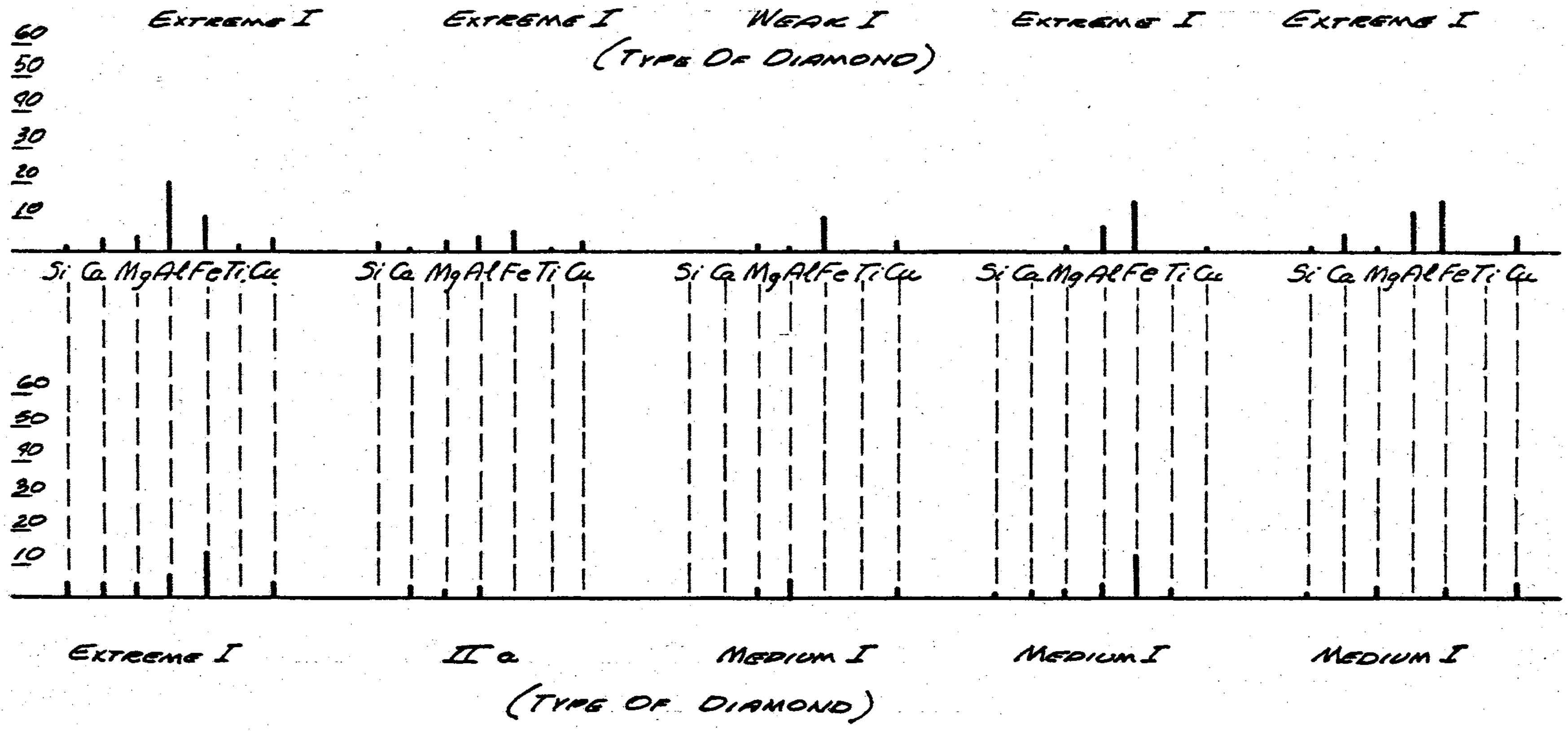

Fig. 4b. Amounts of Impurities in Raal's Diamonds R16 to R25.

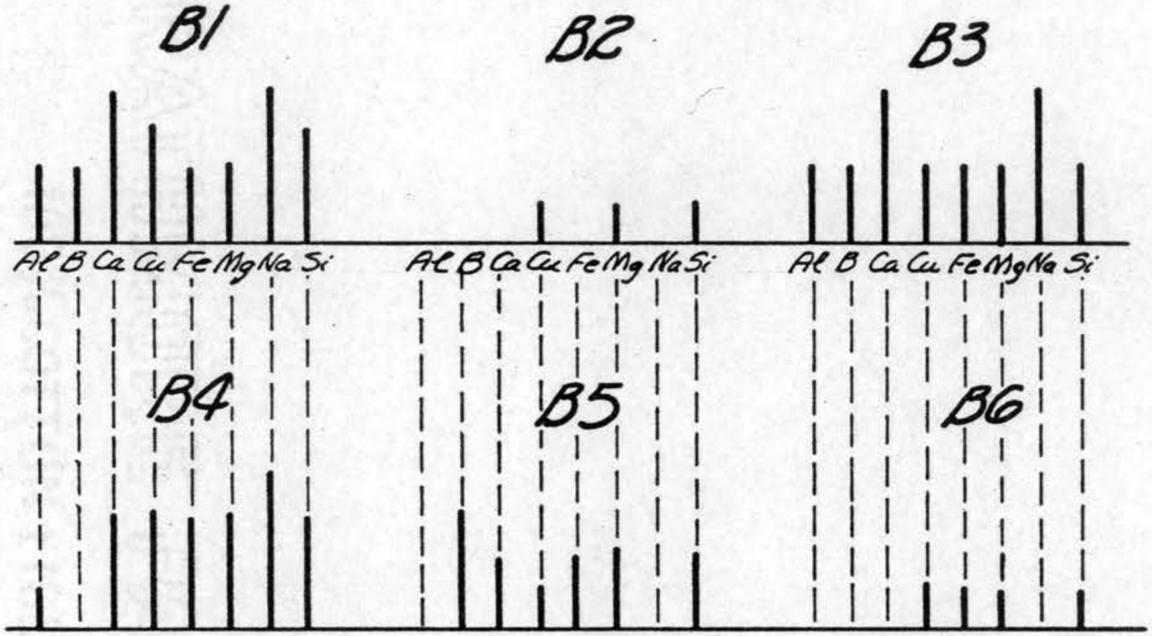

Fig. 5. Relative Amounts of Impurities in Bunting's and Van Valkenburg's Diamonds

as regards impurity content. Aluminum was not found in one of the type I stones and was not found in two of the type II stones. Boron was not found in one of the type I stones and in two of the type II. Five additional diamonds, all of type II, were analyzed, and most were found to have as much impurity content as any of the type I diamonds in the first group. It should be noted that the paper of Bunting and Van Valkenburg rather refutes the earlier work in regards to the relative quantity of impurities in type I and type II diamonds.

In 1958, Raal (22) reported some further work on diamond. All the stones examined were either pink or mauve. A spectographic analysis of the diamonds revealed the presence of Mn besides the impurities Si, Mg, Ca, and Al normally found in diamond. The most persistent lines of Mn were found to be more intense the deeper the color of the diamond. Some of the pale pink stones analyzed did not show Mn as an impurity. Since the minimum concentration of Mn which can be detected is about ten parts per million, it is probably due to Mn being present in a concentration such that its presence cannot be established spectrographically.

In 1959, Kaiser and Bond (6) reported on the gas content of diamonds. The speciments were heated to 2000° C in a carbon crucible in a system normally used for vacuum fusion gas analysis. The gas content freed during the graphitization of the diamond was analyzed for Co, H_2, and residual gases. In several cases, the gas evolved was investigated by means of a mass spectrometer. The residual gas was found to be nitrogen. The quantities of nitrogen found were large compared to the small quantities of CO and H_2 found. The nitrogen content of the diamonds varied from about 0.001 percent concentration to 0.23 percent concentration. The 0.23 percent concentration corresponds to an atom concentration of 4 times 10^{20} atoms per cubic cm. All of these measurements were on type I diamond.

Effects of These Impurities

Chesley (17) noted that there seemed to be a tendency for the diamonds he examined to be colored when the elements Fe and Ti occurred, either together or separately. In regards to crystal habit, he noted that the diamonds of cubic habit revealed the presence of Ag and Ti, whereas these elements were not detected together in the octahedral diamonds.

In 1957, Raal (20) stated that although it was apparent that impurities in diamond have an effect on the color, it was by no means an established fact that they constitute the main contributing factors for the anomalous light absorption of diamond in the ultraviolet and infrared regions, or for the semiconductivity in type IIb diamonds. He thought that possibly it was the impurities in conjunction with defects inherent in the diamond which were responsible for the observed phenomena.

In 1958, Raal (22) reported finding a new absorption band in diamond at approximately 0.55 microns. The band could not be resolved into component lines even at liquid oxygen temperatures. The band was found in all pink and mauve diamonds examined by Raal and also in some brown stones in which the pink or mauve color could have been masked. The strength of the band varies considerably and is correlated with the intensity of the coloration of the diamond. The fact that the band is not temperature dependent and is not typical of those known to be associated with structural defects in diamond suggests that the absorption center is a foreign impurity atom rather than a simple vacancy or other crystal imperfection. As mentioned previously, the Mn content of the diamonds varied with the intensity of the coloration of the diamonds, having a higher Mn concentration with a deeper coloration. Since the strength of the band is dependent on the depth of the color, it was therefore inferred that the new absorption is correlated with the Mn concentration.

Raal states further that since the characteristic band produced by the Mn is probably associated with a transition in an incompleted shell, one would expect the wavelength of the band to be roughly the same for Mn in diamond and in glass; in glass, the band is at 0.5 microns.

In 1952, Willardson and Danielson (23) reported finding a new absorption band at 20.8 microns in type I diamonds. It was present in all the type I diamonds they examined.

In 1959, Kaiser and Bond (6) also found that in type I diamonds, the absorption bands around 8 microns and the ultraviolet absorption below 0.4 microns can be quantitatively correlated with the nitrogen content of the diamond. They report that the absorption bands between 2 and 6 microns are true lattice bands which are independent of the nitrogen content of the crystal. They suggest that the 7.8, 8.3, 9.1, and 20.8 micron bands are C-N bond vibrations.

Raal (20) in 1957, stated that a current theory is that aluminum, by virtue of its being an electron-acceptor is, at least in part, responsible for the semiconducting properties of type IIb diamonds. If this is the case, the aluminum in type IIb diamonds may be accommodated differently in type IIb diamonds than in type IIa diamonds, since the amounts of aluminum are virtually the same in the two types. Alternatively, an excess of donor levels in type IIa diamonds may quench the p-type conductivity.

Brophy (24) suggests that aluminum would result in lowlying accepter levels, while calcium and magnesium would be expected to generate two levels near the middle of the gap as in the case of zinc in germanium. Gold also generates two deep accepter levels. Substitutional silicon would give rise to no impurity levels, but interstitially, it could lead to a donor level in the middle of the gap.

The type IIb diamonds act as normal p-type impurity semiconductors (5). Leivo and Smoluchowski (5) found that the slope of the curve of k lnR plotted against 1/T at low temperatures is about 0.35 ev. The hydrogen atom approximation of an impurity, using a dielectric constant of 5.7, yields a value of 0.4 ev.

CHAPTER II

DIFFUSION

Introduction to Diffusion

The term diffusion is used to describe any motion of, or changes in the relative positions of, atoms or molecules in a medium which is stationary. In other words, the intermingling of atoms with respect to a stationary coordinate system.

At some time almost everyone has observed the gross effects of diffusion in some system or another. The diffusion of a gas in a gas, for instance, as an odor in air; or the diffusion of a liquid in a liquid, as ink in water, are fairly obvious, at least as an effect. However, the diffusion of solids in solids is less easily observed even though it too surrounds one with its effects.

As in other fields, the art preceded the science. People have used solid state diffusion for centuries even though they have not understood the process, nor even that they were using it. Ancient smiths in the iron age welded metals together and made steel from iron by diffusing carbon into iron (25).

It was not until only a little over a century ago that scientific observation of diffusion was reported. Parrot in 1815 observed qualitatively that gases tend to intermingle no matter how carefully mechanical agitation and convection are avoided. Further observations of diffusion phenomena in gases and in liquids were reported by Graham in the decade 1860-1870. In 1870 Loschmidt first performed experiments on gaseous diffusion in such a way as to permit mathematical treatment of the data (26). The theoretical work of Adolf Fick published in 1855 precedes any quantitative experimental work and is still regarded as the phenomenological or descriptive bases of diffusion theory (26). It was not until 1896, when Roberts-Austen measured the rate of diffusion of gold in lead, that the first quantitative study of the subject of solid state diffusion was made for its intrinsic interest (27). Since this modest beginning, much work has been done on diffusion in the solid state, most of it, until recent times, being on metals or metal alloys. Recently, however, interest has been aroused concerning diffusion in ionic crystals and covalent crystals.

As a matter of fact, a significant body of diffusion data has now been collected for semiconducting materials. Most of this work to date has been performed on elemental semiconductors although, increasingly, work is being performed on compound semiconductors such as the group III-V compounds (28).

With regard to elemental semiconductors, self-diffusion measurements have been performed on graphite, white phosphorus, and germanium, and extensive solute diffusion measurements have been performed in germanium and silicon (28).

References in the literature on diffusion are very great in number. Some of the better known collections of such information are: Jost (29), Le Claire (27) (30), Barrer (31), Crank (32), Seitz (33), Bardeen and Heering (34), Zener (35). Jost (29) has a rather extensive bibliography on diffusion up to 1959.

The two elemental semiconductors which have been intensively examined, germanium and silicon, have the same lattice structure as diamond. Some of the many impurities that have been diffused into germanium and silicon are Al, Ga, In, B, P, Bi, Sb, and As. The choice of the impurity deciding the fate of the germanium or silicon as regards p-type or n-type conductivity (28).

Impurity diffusion work in Ge or Si has usually been performed in a vacuum or in an inert gas. The diffusing impurity can be placed in contact with the Ge or Si, or if the impurity has a large enough vapor pressure at the working temperature, the Ge or Si sample may be placed in the impurity vapor, the diffusion following deposition from the vapor phase. Table I is a collection of pertinent data for Al, B, and Be diffusing in Ge and Si. The diffusion constant D_o, the activation energy Q, and the diffusion coefficient D will be discussed later.

There are several different modes of diffusion in solids; vacancy, interstitial, direct interchange, ring mechanism, the interstitialcy mode, and combinations of these. There are even further complicated modes.

Vacancy diffusion assumes the presence or the formation of vacant lattice sites, the diffusing atoms moving into the vacancy, leaving a vacancy into which another atom may move.

In interstitial diffusion, an atom in an interstitial position moves to another interstitial position. Either small diffusing atoms or a relatively open lattice structure is required to obtain large enough interstitial positions.

In direct interchange, two atoms that are adjacent change places simultaneously. No vacancy is required.

The ring mechanism is an extension of the idea of direct interchange.

TABLE I

DIFFUSION DATA FOR Ge AND Si

Impurity/Solvent	D_o(cm^2/sec)	Q (ev)	T (^{o}C)	Time (sec)	D (cm^2/sec)	Depth (cm)	Reference
Al/Si	8.0	3.47	1130	$2.3x10^{5}$	$1.4x10^{-12}$	$0.95x10^{-3}$	36
B/Si	10.5	3.69	950	$17.3x10^{5}$	$8.7x10^{-15}$	$8x10^{-4}$	36
B/Ge			890	$4.1x10^{5}$	$12x10^{-13}$	$32x10^{-4}$	37
Be/Ge	0.5	2.5	900		$1.5x10^{-11}$		38

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 all in the same direction around the ring.

In the interstitialcy mechanism, an atom in an interstial position, displaces an atom in a normal lattice position. This atom in the normal lattice position is displaced into an interstial position. This pattern can be repeated so that the interstial distortion moves through the lattice.

The diamond lattice is a relatively open structure. It has large interstitial sites, the size being on the order of that of a lattice site (28). 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 (28).

Diffusion Theory for Diamond Type Lattice

Swalin (28) (39) has 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 looked at first and some of the results applied to impurity diffusion.

Written in vector notation, Fick's first law of diffusion is

$$J = -D \nabla C$$

where J is the diffusion current (of the diffusing substance) whose dimensions are, 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 scaler, independent of the orientation of the concentration gradient. The diamond structure is cubic and is therefore isotropic.

Since the total number of atoms is constant during diffusion, then

$$\nabla \cdot J = - \frac{\partial C}{\partial t} \quad .$$

If Fick's first law is used to substitute for J, one obtains Fick's second law which is

$$\frac{\partial C}{\partial t} = \nabla \cdot D \nabla C \quad .$$

If D is assumed independent of both concentration and position, then the above may be written

$$\frac{\partial C}{\partial t} = D \nabla^2 C \quad .$$

In one dimension, this becomes

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

A solution of this equation is

$$C = \frac{s}{\sqrt{4 \pi D t}} \exp \left[-x^2/4Dt \right]$$

where s is the total amount of diffusing material present in a cylinder of unit cross-sectional area and infinite length (29).

Let Pdx be the probability of a particle being in an elemental volume of the infinite cylinder, the elemental volume having a unit cross-sectional area and a thickness dx. Since the concentration in the cylinder is sP, then from the above equation the probability density of a particle being in the region dx at x is seen to be

$$P = \frac{1}{\sqrt{4\pi Dt}} \exp\left[-x^2/4Dt\right] \quad .$$

So, denoting the average value of x^2 as $\langle x^2 \rangle$, then

$$\langle x^2 \rangle = \frac{\int_{-\infty}^{\infty} x^2 P \; dx}{\int_{-\infty}^{\infty} P \; dx} \quad .$$

Upon substitution for P in the above equation and after performing the integration, one finds that

$$\langle x^2 \rangle = 2Dt \quad .$$

In a similar manner, one finds for the average values of y^2 and z^2

$$\langle y^2 \rangle = 2Dt \qquad \qquad \langle z^2 \rangle = 2Dt \quad .$$

Considering that $r^2 = x^2 + y^2 + z^2$, then

$$\langle r^2 \rangle = 6Dt \quad .$$

If the jump distance of an atom is d, the nearest neighbor distance, then $1/t$ is f, the frequency of jumping. Substituting for $\langle r^2 \rangle$ and t, the above equation becomes

$$D = (1/6)d^2 f \quad .$$

From geometrical considerations, it can be shown that the nearest neighbor distance in the diamond lattice is $\frac{1}{4}\sqrt{3}$ a where a is the lattice parameter (39).

The above equation is the usual relation for D based on random-walk theory in cubic crystals, disregarding a correlation factor (40). This correlation factor arises in the following manner. In the vacancy mechanism of diffusion, an atom exchanges position with a neighboring vacancy. The atom, on its next jump, has a greater than random probability of returning to its original site, which is now the vacancy site, and there is a correlation between the directions of successive jumps taken by a given atom. In the absence of a driving force, correlation effects can be taken into account by introducing a correlation factor,

f_c, on the right-hand side of the equation for the diffusion coefficient (40). This equation now becomes

$$D = (1/6)f_c d^2 f \quad . \qquad \text{(Eq. 1)}$$

The value for f_c will vary for different lattice structures. In the diamond lattice, $f_c = 0.5$ (41).

In equation 1, the frequence of jumping, f, still needs to be evaluated. The following derivation for f follows that of Zener (35) and Wert (42), which is based on the theory of absolute reaction rates as developed by Eyring (43).

For the diffusing atom to move from its position to the neighboring vacancy, it must cross an energy barrier that exists between the two sites. The height of this barrier depends on the type of crystal, the nature of the migrating atom, the diffusion mechanism, the interatomic forces, etc. . . The energy to overcome the barrier must be provided by thermal vibrations. This is one of the reasons why atomic diffusion requires an energy of activation, the other is that the equilibrium concentration of defects also depends on the temperature (44). The height of the potential energy barrier, of course, influences the jump frequency.

The rate at which a particle crosses an energy barrier equals the probability density of the particle being at the top of the barrier times the average positive velocity of the particle, that is, the rate $= P\bar{v}$ where $\bar{v}$ is the average velocity, and P is the probability density at the top of the barrier. The explanation of probability density is: If (P dx) is the probability of an atom being in the length dx at the top of the barrier, then P is the probability density at the top of the barrier.

The assumption is made that the site, to which an atom is diffusing, is vacant. Let x be the coordinate along a line connecting the site of the atom with the vacant site. The coordinate of the rest position of the atom is x_o, and that of an adjacent site is x_1. Let x' be the position of the top of the potential barrier over which the atom must pass. Let N equal the number of atoms in the site about x_o plus the atoms at x'. Let n equal the linear density of atoms at x'. The symbol $\bar{v}$ is the average velocity of all atoms at x' crossing the barrier from x_o to x_1.

Using these definitions, the probability density of an atom at the top of the potential barrier is n/N. So, the rate at which the atoms pass x' is given by $n\bar{v}/N$. This is the frequency with which the atoms leave a site x_o along one path. Now, if n' equals the number of equivalent paths of diffusion from a given lattice site, then the frequency with which the atoms leave a site x_o is $n'n\bar{v}/N$. This is also the jump frequency mentioned earlier. So, the jump frequency is

$$f = n'n\bar{v}/N \quad . \qquad \text{(Eq. 2)}$$

Consider two states that respectively contain the number of particles A and B. Let their partition functions be F_A and F_B. Then

$$A/B = F_A/F_B \quad .$$

Let the top of the barrier be a small flat region of length Δx. Then $n\Delta x = A$ where A is the number of particles within the flat region at x'. If it is assumed that A is small compared to the total number of particles N, then $B \approx N$. So,

$$(1/\Delta x)\ (A/B) = (1/\Delta x)\ (F_A/F_B)$$

which becomes

$$n/N = (1/\Delta x)\ (F_A)/F_B \quad .$$

The partition function is assumed to be

$$F = h^{-L}\iint\cdots\int_{-\infty}^{\infty} \exp\left[-H(p_i,q_i)/kT\right] dp_1 \cdots dp_L\, dq_1 \cdots dq_L$$

so,

$$(1/\Delta x)(F_A) = (1/\Delta x)h^{-L}\iint\cdots\int_{-\infty}^{\infty} \exp\left[-H_1(p_i,q_i)/kT\right] dp_1 \cdots dp_L\, dq_1 \cdots dq_L$$

where H_1 is the Hamiltonian of the diffusing atom and adjacent atoms when the diffusing atom is in the region Δx at x'. Now, within the region Δx, the Hamiltonian H_1 does not depend on the coordinate x since the potential does not change with respect to x. This means the dq_1 integration may be carried out, yielding a value of Δx. The above equation then becomes

$$(1/\Delta x)(F_A) = h^{-L}\iint\cdots\int_{-\infty}^{\infty} \exp\left[-H_1(p_i,q_i)/kT\right] dp_1 \cdots dp_L\, dq_2 \cdots dq_L$$

and so,

$$\frac{n}{N} = \frac{h^{-L}\iint\cdots\int_{-\infty}^{\infty} \exp\left[-H_1(p_i,q_i)/kT\right] dp_1 \cdots dp_L\, dq_2 \cdots dq_L}{h^{-L}\iint\cdots\int_{-\infty}^{\infty} \exp\left[-H_2(p_i,q_i)/kT\right] dp_1 \cdots dp_L\, dq_1 \cdots dq_L}$$

where H_2 is the Hamiltonian of the system when the atom is at x. If the cartesian coordinate system is used for the N-point particles making up a system, and if the potential energy depends on the coordinates only, the Hamiltonian contains the momenta only as the sum of 3N terms of the type $p^2/2m_i$, in which m_i is the mass of particle i (45). So, separating the Hamiltonians, the above equation can now be written as

$$\frac{n}{N} = \frac{h^{-L}\iint\cdots\int_{-\infty}^{\infty} \exp\left[-p_i^{\,2}/2m_i kT\right] dp_1 \cdots dp_L \iint\cdots\int_{-\infty}^{\infty} \exp\left[-\phi_{x'}/kT\right] dy\,dz\,dq_4 \cdots dq_L}{h^{-L}\iint\cdots\int_{-\infty}^{\infty} \exp\left[-p_i^{\,2}/2m_i kT\right] dp_1 \cdots dp_L \iint\cdots\int_{-\infty}^{\infty} \exp\left[-\phi_x/kT\right] dx\,dy\,dz\,dq_4 \cdots dq_L}$$

where $\phi_{x'}$ is the potential energy of the system when the diffusing atom is at x' and ϕ_x is the general potential energy of the system. The momentum of an atom is p_i and its mass is m_i.

Now, an integral of the form

$$\int_{-\infty}^{\infty} \exp\left[-p^2/2m_i kT\right] dp$$

can be evaluated and will be found to be $(2\pi m_i kT)^{\frac{1}{2}}$. There will be L integrals of this form, one for each degree of freedom. Since the masses of the diffusing particles are the same, then these momentum integrals, yielding the above L factors, will cancel out of the above probability density equation. The equation for the probability density is now

$$\frac{n}{N} = \frac{\iint\cdots\int_{-\infty}^{\infty} \exp\left[-\phi_{x'}/kT\right] dydzdq_4 \text{---} dq_L}{\iint\cdots\int_{-\infty}^{\infty} \exp\left[-\phi_x/kT\right] dxdydzdq_4 \text{---} dq_L} \quad . \qquad \text{(Eq. 3)}$$

Now to find an expression for $\bar{v}$, the average velocity in the positive-x direction. Since $\bar{v} = \overline{(p_x/M)}$ where p_x is the momentum of the diffusing atom and M is its mass, then according to maxwell-boltzman statistics,

$$\bar{v} = \overline{\left(\frac{Px}{M}\right)} = \frac{\int_0^{\infty}(p_x/M)\exp\left[-p_x{}^2/2MkT\right] dp_x}{\int_{-\infty}^{\infty} \exp\left[-p_x{}^2/2MkT\right] dp_x} \quad . \qquad \text{(Eq. 4)}$$

Substituting equation 3 and equation 4 into equation 2, the jump frequency is now

$$f = n' \, \frac{\iint\cdots\int_{-\infty}^{\infty} \exp\left[-\phi_{x'}/kT\right] dydzdq_4 \text{---} dq_L}{\iint\cdots\int_{-\infty}^{\infty} \exp\left[-\phi_x/kT\right] dxdydzdq_4 \text{---} dq_L} \cdot \frac{\int_0^{\infty}(p_x/M)\exp\left[-p_x{}^2/2MkT\right] dp_x}{\int_{-\infty}^{\infty} \exp\left[-p_x{}^2/2MkT\right] dp_x} \quad .$$

Since ϕ is unknown away from x_o, this expression cannot be evaluated in general. However, if the height of the barrier is large compared to kT, not much error is introduced by replacing in the denominator of the above equation, the function ϕ_x, [which is $\phi(x,y,z,q_i)$], by $[\phi(x_o, y,z,q_i) + \frac{1}{2}Kx^2]$, where K is the force constant for a small region about x_o equal 0 (42). Using this approximation, the above equation can be written as,

$$f = n' \frac{\iint \cdots \int_{-\infty}^{\infty} \exp \left[-\phi_{x'}/kT \right] dydzdq_4 --- dq_L}{\iint \cdots \int_{-\infty}^{\infty} \exp -\phi(x_0,y,z,q_i)/kT \; dydzdq_4 --- dq_L} \cdot$$

$$\frac{\int_0^{\infty} (p_x/M) \exp \left[-p_x^2/2MkT \right] dp_x}{\iint_{-\infty}^{\infty} \exp \left[-p_x^2/2MkT \right] \exp \left[-Kx^2/2kT \right] dp_x dx} \cdot$$

The second factor can be evaluated and will be found to be $(1/2\pi) \cdot \sqrt{K/M}$ which is the frequency ν of small oscillations about x_0. The first fraction represents the ratio of two partition functions; the numerator that for the system with the particle moving in the y-z plane at x', the denominator that for the system with the particle moving in the y-z plane at x_0 (42). So, denoting these partition functions by F, the equation for f is now

$$f = n' \nu \frac{F'}{F_0} \; .$$

Kittel (46) gives a relation between the Helmholtz Free Energy, H_f, and the partition function F. This is

$$F = \exp \left[-H_f/kT \right] .$$

So, considering two states, A and B, each accessible from the other, then

$$\frac{F_1}{F_2} = \exp \left[-(H_{f_1} - H_{f_2})/kT \right] = \exp \left[-\Delta H_f/kT \right] \; .$$

The Helmholtz free energy of a body has the property that the work done on the body in a reversible process at constant temperature is the change of its Helmholtz free energy (46).

For condensed systems, that is, liquids or solids, the difference between the Helmholtz free energy and the Gibbs free energy is usually taken as negligible. So, using Gibbs free energy instead of Helmholtz free energy, the jump frequency is

$$f = n'\nu \exp\left[-\Delta G_j/kT\right] \qquad \text{(eq. 5)}$$

where ΔG_j is the isothermal work expended in moving an atom from an equilibrium position to the top of the potential barrier.

Now, n' is the number of equivalent diffusion paths available to an atom. So, n' equals zC_v where z is the coordination number, that is, the number of closest neighbor sites, and C_v is the probability of a vacancy being at one of these closest neighbor sites. According to maxwell-boltzman statistics (29),

$$C_v = \exp\left[-\Delta G_v/kT\right]$$

where ΔG_v is the free energy of formation of a vacancy. The coordination number of the diamond lattice is four. So, substituting for n' in equation 5 and then substituting for f in equation 1, the equation for the diffusion coefficient becomes

$$D = (1/16)a^2\nu \exp\left[-(\Delta G_v + \Delta G_j)/kT\right] \quad .$$

Since, for an isothermal process, $\Delta G = \Delta H - T\Delta S$, where ΔH is the enthalpy change and ΔS is the entropy change, then D may be written as

$$D = (1/16)\ a^2\nu \exp\left[(\Delta S_v + \Delta S_j)/k\right] \exp\left[-(\Delta H_v + \Delta H_j)/kT\right] \qquad \text{(Eq. 6)}$$

Now, Zener (35) says, aside from a few exceptions, the diffusion coefficient is found to vary with temperature in the manner

$$D = D_o \exp\left[-Q/RT\right] \qquad \text{(Eq. 7)}$$

through the temperature range of the experiments, where R is the gas constant, and Q is the enthalpy of activation, commonly called the heat of activation, or the energy of activation.

So correlating equation 6 with equation 7, it is seen that

$$D_o = (1/16)a^2\nu \exp\left[(\Delta S_v + \Delta S_j)/k\right] \qquad \text{(Eq. 8)}$$

and

$$Q = (\Delta H_v + \Delta H_j)\ N \qquad \text{(Eq. 9)}$$

where N is avogadro's number.

The temperature variation of $a, \nu, \Delta S_v$, and ΔS_j can be neglected (39).

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 perhaps valency from the solute atoms.

Several different points are taken into account by Swalin (39). Swalin states that vacancies, at least in germanium and silicon, have been demonstrated to act as electron acceptors. This has been shown for germanium and silicon by Cleland, Crawford, and Holmes (47) and by Wertheim (48).

If vacancies act as electron acceptors, then the concentration of charged vacancies will depend on the position of the fermi level, the fermi level being 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 (39). These statements are also discussed by Longini and Greene (49), and by Valenta and Ramasastry (50).

A second effect to take into account is a coulombic 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.

The third factor is: 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 (39).

All of these factors will have to be taken into account in deriving equations for solute diffusion.

The concentration of charged vacancies in a crystal is

$$[V^-] = \frac{[V]}{1+\frac{1}{2}\exp[(E_V-E_F)/kT]} \qquad \text{(Eq. 10)}$$

where $[V]$ is the total concentration of vacancies (number per mole), E_F is the fermi energy, and E_V is the vacancy acceptor level (49) (50). Letting V^o be the concentration of neutral vacancies, then

$$[V] = [V^o] + [V^-] \ .$$

Substituting this for $[V]$ in equation 10, it becomes

$$[V^-] = [V^o]2\exp[(E_F - E_V)/kT] \ . \qquad \text{(Eq. 11)}$$

If $P_V^{\ o}$ is the probability that an impurity ion is in a nearest neighbor position to a neutral vacancy, and $P_V^{\ -}$ is the probability that the impurity ion is in a nearest neighbor position to a charged vacancy, then the total probability that the ion is in a nearest neighbor position to a vacancy is $(p_V^{\ o} + p_V^{\ -})$.

To write an equation for $p_V^{\ o}$, it must be realized that the energy of formation of a vacancy will depend on whether the vacancy is formed in the perfect lattice portion or next to a wrong-sized impurity atom. Letting ΔH_s represent the energy difference between ΔH_V, the energy of formation of a vacancy next to solvent atoms, and $\Delta H_V'$, the energy of formation of a vacancy next to a wrong-sized impurity ion, then

$$p_V^{\ o} = z\ [V^o]\ \exp[-\Delta H_s/kT] \qquad \text{(Eq. 12)}$$

where z is the number of nearest neighbor sites. The small entropy change between the two states has been neglected. Assuming all impurity atoms are ionized, then in a similar manner to the above, one obtains

$$p_V^- = z\,[V^-]\exp[-\Delta H_s/kT]\exp[-\Delta H_c/kT]$$

where ΔH_c is the coulombic interaction energy between the charged vacancy and the ion. Substituting for $[V^-]$ in the above equation, one obtains

$$p_V^- = z\,[V^o]2\exp[(E_F - E_V - \Delta H_s - \Delta H_c)/kT]\ . \qquad \text{(Eq. 13)}$$

Since the concentration of neutral vacancies is dependent on temperature only, the dependence can be given by the following,

$$[V^o] = \exp[-\Delta G_v/kT] = \exp[\Delta S_v/k]\exp[-\Delta H_v/kT]\ .$$

By substituting this into equations 12 and 13, one can obtain

$$(p_v^o + p_v^-) = z\exp[\Delta S_v/k]\exp[-(\Delta H_v + \Delta H_s)/kT]\left(1+2\exp[(E_F - E_V - \Delta H_c)/kT]\right)\ .$$

Substituting $(p_v^o + p_v^-)$ for n' in equation 5, one gets

$$f = z\exp[\Delta S_v/k]\exp[-(\Delta H_v + \Delta H_s)/kT]\left(1+2\exp[(E_F - E_v - \Delta H_c)/kT]\right)\nu\exp[-\Delta G_j/kT]\ .$$

Substituting this into equation 1, we have

$$D = (1/16)a^2\nu\exp[(\Delta S_v + \Delta S_j)/k]\exp[-(\Delta H_v + \Delta H_j + \Delta H_s)/kT]\ .\left(1+2\exp[(E_F - E_v - \Delta H_c)/kT]\right)\ . \qquad \text{(Eq. 14)}$$

As stated before, the small entropy terms ΔS_s and ΔS_c have been neglected. The difference in vibrational frequency between solute and solvent ions will also be neglected (39).

Comparing equation 14 with equation 7, one obtains

$$D_o = (1/16)a^2\nu\exp[(\Delta S_v + \Delta S_j)/k] \qquad \text{(Eq. 15)}$$

and

$$\exp[-Q/RT] = \exp[-(\Delta H_v + \Delta H_j + \Delta H_s)/kT]\left(1+2\exp[(E_F - E_V - \Delta H_c)/kT]\right)\ .$$

Swalin assumes the temperature dependence of $(E_F - E_V)$ and the other energy terms to be small. For the case where $(E_F - E_v - \Delta H_c) \gg kT$, then

$$Q = [\Delta H_v + \Delta H_j + \Delta H_s + \Delta H_c - (E_F - E_v)] N - RT \ln 2 \quad \text{(Eq. 16)}$$

and when $(E_F - E_V - \Delta H_c) \ll kT$, then

$$Q = [\Delta H_v + \Delta H_j + \Delta H_s] N \quad \text{(Eq. 17)}$$

where N is again Avogadro's number.

Friedel (51) derived some equations for the strain-energy contribution to the heat of solution of a wrong-sized impurity ion. From his equations, one can get an estimate of ΔH_s.

$$\Delta H_s \cong \frac{6\pi (r_s - r_s')^2 r_s'}{z\,(1 + \alpha)\, X'} \quad \text{(Eq. 18)}$$

where

$$\alpha = \frac{(1 + \rho)\, X\, r_s'}{2\,(1 - 2\rho)\, X'\, r_s}$$

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 coulombic interaction energy can be estimated to be

$$\Delta H_c = \pm \frac{(q_v)\,(q_i)}{K\,d} \quad \text{(Eq. 19)}$$

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

It is seen that equations 8 and 15 are the same. The differing values for D_o for the cases of self-diffusion and impurity diffusion arise because of differences of ν and ΔS_j for the two cases. It has already been stated that the difference in ν of the solute and solvent ions will be neglected. If the difference between ΔS_j for solute diffusion and self-diffusion is also neglected, then D_o will be the same for solute diffusion and for self-diffusion. This is rather a gross assumption, but according to germanium and silicon data in the article by Swalin (28), this approximation does seem to give at least the order of magnitude of D_o.

Swalin (28), gives for D_o, in the case of self-diffusion in diamond, 11.6 cm^2/sec. This was calculated from equation 8. Swalin (28) states the contributions to the entropy terms will consist of a vibrational term, and a configurational term resulting from the availability of positions for the high energy covalent bonds about the vacancy. The latter contribution ΔS_c can be readily evaluated using the expression $\Delta S_c = k \ln W$ where W represents the number of ways of distributing bonds. Swalin found that the configurational contribution to ΔS_v is equal to $2k \ln 3 = 4.4$ entropy units. He says the vibrational contribution seems to be small, and therefore we can approximate ΔS_v by the configurational contribution. Similar reasoning for the configurational contribution to ΔS_j yields $W = 180$. Subtracting the configurational term of the atom in its equilibrium site just calculated above indicates the configuration contribution to ΔS_j to be 5.9 entropy units. Comparison with germanium diffusion data indicates that the vibrational term is about the same as the configurational term. So, we will assume that the value of D_o as given (11.6 $cm^2/sec.$) is at least an indication of the order of magnitude.

Now for a value for the activation energy Q. Swalin (28) gives for self-diffusion in diamond, $Q = 6.18$ ev. Since Q for self-diffusion will enter into the equation for Q for impurity diffusion, it will be advantageous to look at some approximations for Q.

It is well known that for metals, the following experimental relation holds true Q_s/T_M = constant where Q_s is the activation energy for self-diffusion and T_M is the melting point of the metal in degrees-Kelvin (39). Evaluating the constant from germanium data, where $Q_s = 68.5$ Kcal./mole, and $T_M = 1232^\circ K$, then the constant equals 0.0556 (Kcal./mole) /°K. Now, for diamond, using this constant and a T_M of 4000°K, one finds that $Q_s = 222.4$ Kcal./mole = 9.67 ev. Of course, the difficulty with this approximation is that neither germanium nor diamond is a metal, and also the melting point of diamond is not known; in fact, diamond is not the stable form of carbon at atmospheric pressure. Graphite is the stable form, but even graphite does not melt at atmospheric pressure, but sublimes. So this value of Q_s should not be trusted.

Swalin (28) has computed a value for Q for self-diffusion in diamond. He used equation 9 and got a value of 6.18 ev. He took advantage of the following two facts: (a) the bonding forces between atoms in semiconductors can be conveniently thought of in terms of classical covalent bonds. For purposes of treatment, it is assumed that the enthalpy expended in changing a bond from length d_o to d is given by the Morse function

$$\Delta H = H_d \left\{ 1 + \exp\left[-2\gamma(d - d_o)\right] - 2\exp\left[-\gamma(d - d_o)\right] \right\}$$

where H_d is the enthalpy of bond disruption and γ is related to the second derivation of ΔH versus d. (b) the diamond lattice is not dilated by an atom moving through the saddle point to a vacancy. Swalin assumed that $\Delta H_v = \Delta H_1 + \Delta H_2 + \Delta H_3$ where ΔH_1 is the enthalpy of breaking z bonds and forming z/2 bonds, ΔH_2 is the enthalpy of lattice relaxation, and ΔH_3 is the enthalpy gain due to the 4 dangling bonds forming 2 covalent bonds.

For the value of ΔH_j, Swalin calculated the change in bond lengths when the atom is at the saddle point and used the morse function. So, for germanium, $\Delta H_j = 0.95$ ev. and for diamond, $\Delta H_j = 2.02$ ev. So, since equation 9 is $Q = \Delta H_v + \Delta H_j$, then the calculated Q for germanium is 3.02 ev. which compares with the experimental Q of 2.98 ev., and the calculated Q for diamond is 6.18 ev. As is seen, this is at variance with the Q from $Q_s/T_M = \text{const.}$

The author has computed a value for Q by a little different method. The method used for the calculation follows that of Dienes (53). 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 (54) was used in making Table II.

TABLE II

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 ≡ C	1.206 Å	194 Kcal./mole

If a graph is made of the log of bond energies, B, versus bond length, r_o, it is seen that for the longer bonds (C - C and C = C), this is essentially a straight line whose equation is $\log_{10} B = -1.180 r_o + 3.741$. In the following development, the above equation is used to compute bond energies instead of the Morse function as Swalin did. Assuming a diamond bond length of 1.542 Å, (46), then B = 83.5 Kcal./mole. To calculate ΔH_v, when an atom is removed from a 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, ΔH_v = 334-167= 167Kcal./mole. Now to compute ΔH_j. When the atom is at the saddle point, there will be six bonds, each a greater length than before. By an 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. So, because there are six bonds, 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 an energy of 3(83.5) = 250.5 Kcal./mole. So, 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°. According to Dienes (53), the energy of bond angle distortion is 1.5 Kcal./mole per 10° distortion. So, 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°. So, energy is (2.855) (1.5) = 4.28 Kcal./mole and for the three angles is 3(4.28) = 12.84 Kcal./mole. The total energy due to bond angle distortion is 9.9 + 12.84 = 22.74 Kcal./mole. So, ΔH_j = 80.7+22.74 = 103.44 Kcal./mole. and so, Q = 167 + 103.44 $\cong$ 11.74 ev. which is much higher than the previously calculated values.

Consider aluminum as an impurity which, in substitutional diffusion, is an acceptor impurity. Type I diamond is an insulator, so the fermi level is assumed to be in the center region of the band gap. The band gap is 5.5 ev so the fermi level is assumed to be at 2.75 ev (7). At 900°C, which is the diffusion temperature, kT becomes approximately 0.1 ev. Using equation 19 to find a value for ΔH_c and assuming a dielectric constant K of 5.7, a d of 1.54 Å, the electrical charge as 4.8×10^{-10} e.s.u., and the impurity atom as singly ionized, then $\Delta H_c = 1.64$ ev.

Now, we wish to know if the following condition is true in the present case:

$$(E_F - E_v - \Delta H_c) \ll kT$$

Or,

$$(2.75 - E_v - 1.64) \ll kT$$

which means that

$$E_v \gg 1.01 \text{ ev.}$$

Billington and Crawford (55) drew a conclusion in their paper that the 0.3-0.4 ev absorption is due to impurity atoms and since other absorption is at 1.5-2.5 or 2.8-3.0 ev, then the condition is satisfied:

$$E_v \gg 1.01 \text{ ev.}$$

which means that

$$(E_F - E_v - \Delta H_c) \ll kT$$

which, in turn, means that equation 17 applies to aluminum diffusion in diamond.

$(\Delta H_v + \Delta H_j)$ is Q_{self} for diamond and ΔH_s is found from equation 18. Swalin (39) states that for singly ionized aluminum, Al^-, r_s' equals 1.74 Å. The coordination number z is four. McSkimin and Bond (56) say that the elastic stiffness constants, C_{11} and C_{12}, for diamond are, respectively, 10.76×10^{12} dynes/cm^2 and 1.25×10^{12} dynes/cm^2. Kittel (57) gives for aluminum, C_{11} equals 1.08×10^{12} dynes/cm^2 and C_{12} equals 0.62×10^{12} dynes/cm^2. Using these values for C_{11} and C_{12}, one can find, through the usual relations, that X equals 2.26×10^{-13} cm^2/dyne,

ρ equals 0.104, and X' equals 1.29×10^{-12} $\mathrm{cm}^2/\mathrm{dyne}$. From these values it is found that $\Delta H_s = 2.94$ ev. Calculated values for Q for aluminum diffusion are listed in Table III.

TABLE III

COMPUTED ACTIVATION ENERGIES

	Q/T Data	Swalin	Author
Q_{self}	9.67 ev	6.18 ev	11.74 ev
$Q_{impurity}$	12.61 ev	9.12 ev	14.68 ev

These are remarkably high activation energies. One would think that at the relatively moderate temperatures used in this work, diffusion would not be observable in any convenient time period due to these high activation energies. The lowest value (9.12 ev), if it is true, might admit some slight observable diffusion.

CHAPTER III

EXPERIMENTAL PROCEDURE AND RESULTS

Sample Description

The diamond designated as D-12 was chosen for this study because no experimental work had yet been done on this particular stone and also because its shape would facilitate resistivity measurements. Although the diamond is a spinel twin, its overall appearance is that of a triangular prism. The three altitudes of the triangular faces are 4mm, 4mm, and 4.8mm in length. Two corners of the diamond are chipped, which is the reason for the unequal altitudes. The distance between the triangular faces is 1.78mm. The diamond is colorless, but there are such a large number of trigons on all surfaces that the diamond appears to be translucent. Trigons are small triangular shaped depressions which apparently are a growth feature of the diamond surface. Several small carbon inclusions which appear to be near the surfaces, are also present.

Optical transmission measurements were made on diamond D-12 from 0.25 microns in the ultraviolet to 14 microns in the infrared. The ultraviolet and visible transmission measurements to 2.95 microns were obtained by using a Beckman DK-1 spectrophotometer. The infrared transmission measurements from 2.5 microns to 14 microns were obtained by using a Beckman IR-7 spectrophotometer with sodium chloride optics.

These transmission measurements showed that the 8 micron absorption band is present, and the ultraviolet cutoff occurs at approximately 0.293 microns, which indicates that diamond D-12 is a type I.

Resistivity Measurements

If the diffused impurities are electrically active, then resistivity measurements should provide an accurate and sensitive means whereby diffusion may be observed. Volume resistivity and surface resistivity measurements were made both before and after a diffusion run. Resistivity measurements were made by placing a known difference in potential across the diamond, measuring the resulting current, and using Ohm's law to determine the resistance. To measure the current, a vibrating-reed electrometer, model 31, from the Applied Physics Corporation, was used.

The electrometer was designed to be used primarily with an ionization chamber. It has a mounting bracket and a spring-loaded contact for an input electrode. This configuration required an accomodating design of a diamond mount which would fit the input. Figure 6 is a diagram of the diamond mount. The mount is a 4-inch brass cylinder with Teflon insulation. The large Teflon input insulator in the diamond mount had to be kept quite clean. Periodic swabbings with methyl alcohol was found to keep the insulator clean enough so that the leakage current across the insulator appeared negligible. The diamond was mounted with copper probes between the two screw terminals. The Teflon insulated terminal through the side of the mount made contact with the guard electrode on the diamond by means of a thin copper wire.

The usual procedure used in cleaning the diamond, which will be referred to later as the normal cleaning procedure, was a succession of

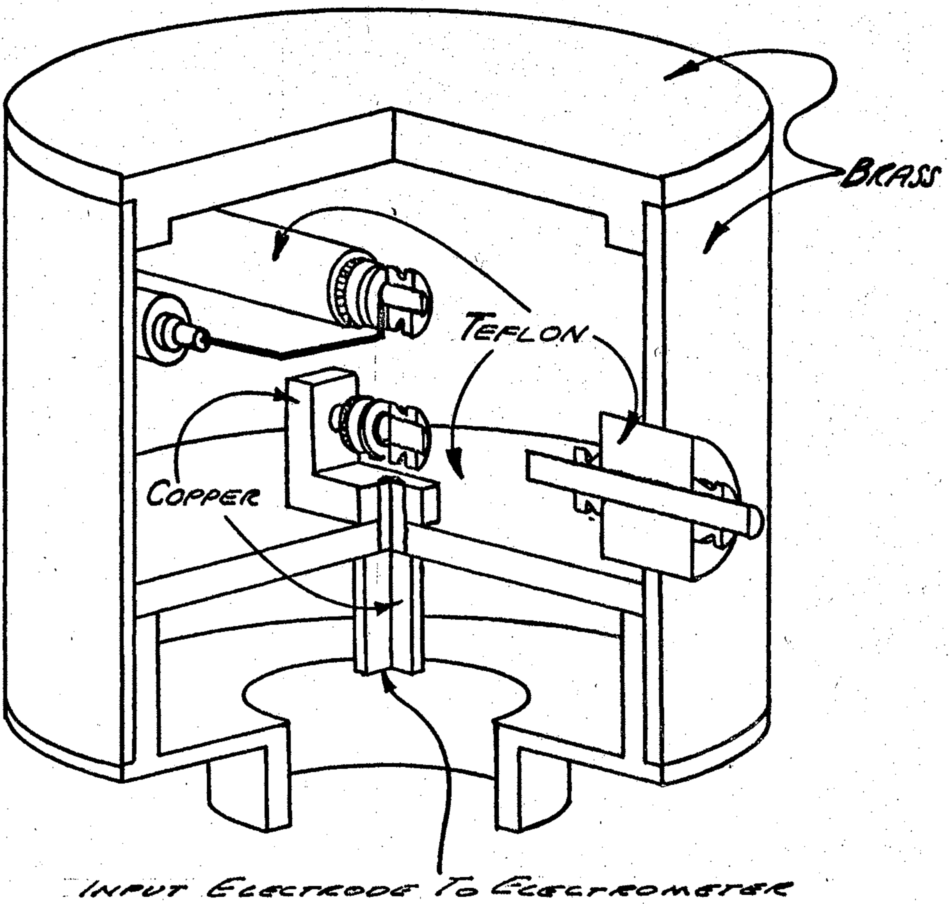

Fig. 6. Mount for Diamond Resistivity Measurements

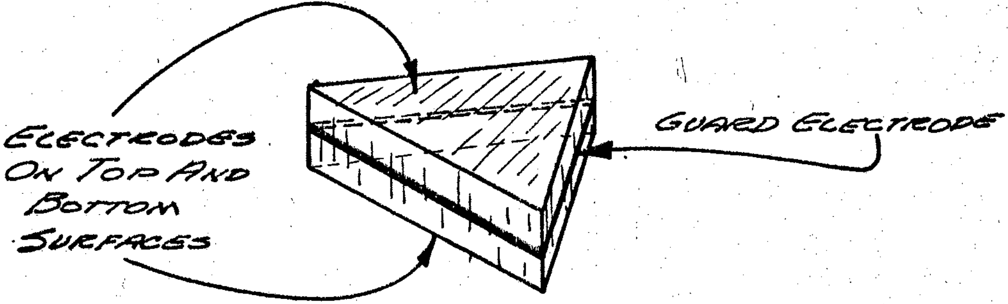

Fig. 7. Electrode Configuration on the Diamond

baths: acetone, nitric acid, distilled water, and methyl alcohol. Sulfuric, hydrochloric, and hydrofluoric acids were used on occasion. The normal cleaning procedure was used each time before electrical contacts were made to the diamond.

Electrical contacts were made using a Dupont silver paint number 4817. Three electrodes were used and were painted on the diamond in the manner of Fig. 7. The guard electrode was a thin band painted around the diamond. The guard electrode was found necessary for bulk resistivity measurements because of the surface leakage of the diamond.

The circuit used for bulk resistivity measurements is shown in Fig. 8. It is drawn schematically in Fig. 9. The volume resistance of the diamond is R_1, and R_2 and R_3 are the surface resistances between the guard electrode and the end electrodes. The voltage source was obtained by connecting in series anywhere from one to four 300 volt, type U200 Burgess batteries. The entire circuit was shielded, and the shield grounded. The batteries were in a grounded aluminum box and insulated from the box with Lucite. Connections from the battery box to the diamond mount were made with coaxial cable to maintain shielding. Surface resistances were measured as indicated in Fig. 10, and the corresponding schematics are shown in Fig. 11. The resistance R_1 is fairly large compared to R_2 and R_3 so little error is introduced when measuring R_2 or R_3 in parallel with R_1.

The electrometer can be used two different ways in measuring current magnitude. A high value resistor contained in the electrometer can be switched into the circuit, the measured voltage drop across it indicating the current in the circuit. The other method measures the voltage across a capacitor, the rate of change of voltage, or the rate of charging of

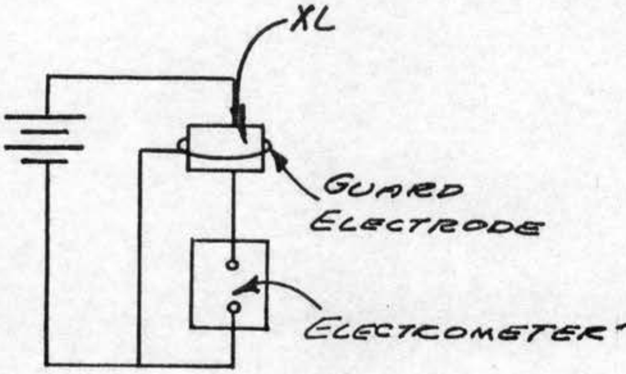

Fig. 8. Method for Measuring Volume Resistivity

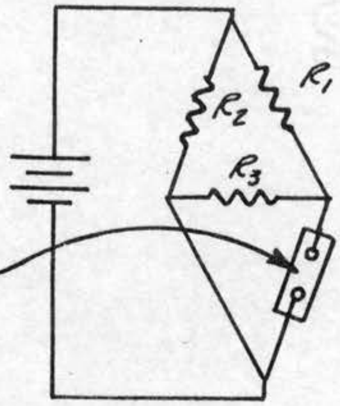

Fig. 9. Schematic Diagram of Fig. 8

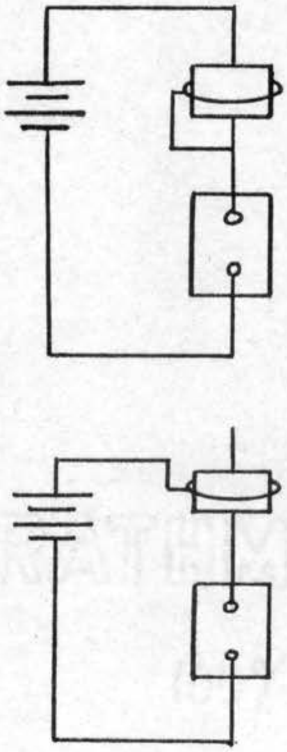

Fig. 10. Methods for Measuring Surface Resistivity

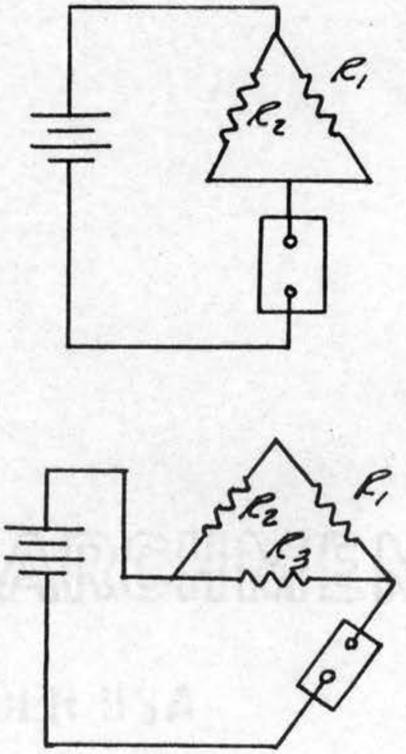

Fig. 11. Schematic Diagram of Fig. 10

the capacitor, indicating the current in the circuit. The rate-of-charge method is used for measuring smaller currents than the voltage drop method.

Bulk resistivity, ρ, was computed from the equation $\rho = (A/L)R$ where R is the measured bulk resistance, A is the area of one of the contacts, and L is the distance between the contacts which is the thickness of the crystal. It was tried to make the area, A, the same in each case so that A/L would have the same value for all the measurements. Current constriction effects due to the guard electrode are neglected.

Surface resistivity σ, was computed from $\sigma = (P/g)R$ where R is the resistance of the surface, P is the perimeter of the electrode, and g is the distance between the electrodes (58). For circular electrodes, P is approximately equal to πD_0 where D_o is the diameter of the median circle between the electrodes.

A polarization was noted in the diamond, requiring the voltage source to be connected to the circuit for a time on the order of 30 minutes in order to obtain constant current through the diamond. Using the above procedure, bulk resistivity of D-12 is approximately 10^{17} ohm-cm. and surface resistivity is approximately 10^{16} ohms.

Photoconductivity was noted which required resistivity measurements to be made with the diamond in the dark. The diamond mount was judged to be sufficiently light-tight. The diamond was usually left in the dark for 3 to 5 hours before resistivity measurements were made.

The above outlined procedure for resistivity measurements was the one used, somewhat rough measurements being considered unavoidable because of differing electrode areas, and a fringe effect due to the guard electrode.

It was decided to examine the influence of electrode configuration on resistivity determinations. Electrodes were painted on the diamond as shown in Fig. 12. Let g be the width of the gap between electrodes 1 and 2. Let D_1 be the diameter of electrode 1 and D_2 be the inner diameter of electrode 2. So, letting t be the thickness of the diamond, then the effective area of the guarded electrode is

$$A = \pi (D_1/2 + g/2 - \delta)^2$$

where

$$\delta = t \left[\frac{2}{\pi} \ln \cosh \left(\frac{\pi g}{4t} \right) \right] .$$

These equations are taken from the A.S.T.M. Standards (58). Measurements of the size of the electrodes were made with a traveling microscope and it was found that $D_1 = 0.75$ mm and $D_2 = 1.65$ mm which means that $g = 0.045$ cm. Putting these values in the above equations, the area of the guarded electrode is $A = 0.014$ cm^2. The circuit in Fig. 13 was used with a source voltage of 290 volts. The bulk resistance was measured as $R = 1.32 \times 10^{18}$ ohms. Using the values of A and t given above, the bulk resistivity is found to be $\rho = 0.8 \times 10^{17}$ ohm-cm. Normally the contacts are made as in Fig. 7 with an A/t approximately equal to 0.35 cm. The measured resistance, with a source voltage of 570 volts, is in the neighborhood of 8×10^{17} ohms, so the resistivity is usually measured as approximately 2.8×10^{17} ohm-cm. This shows that one can get fair agreement without extreme care in making the contacts. The second method of making contacts will be used hereafter. Absolute values of ρ are not necessary, only consistency is needed since a change in ρ is what is wanted. Many resistivity measurements have been made at various times on D-12; the source voltage differing nearly every time but the bulk resistivity has been in every case on the order of 10^{17} ohm-cm. This indicates

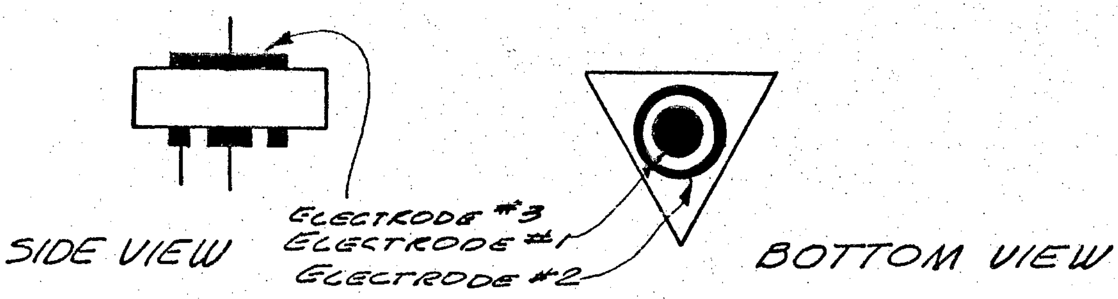

Fig. 12. Alternate Electrode Configuration on Diamond.

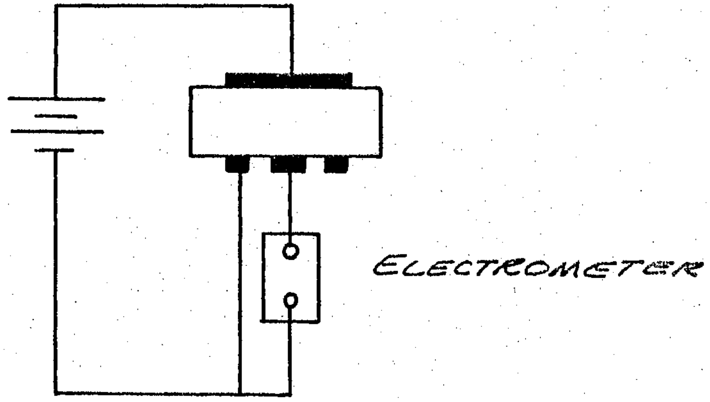

Fig. 13. Method for Measuring Resistivities for Alternate Electrode Configuration.

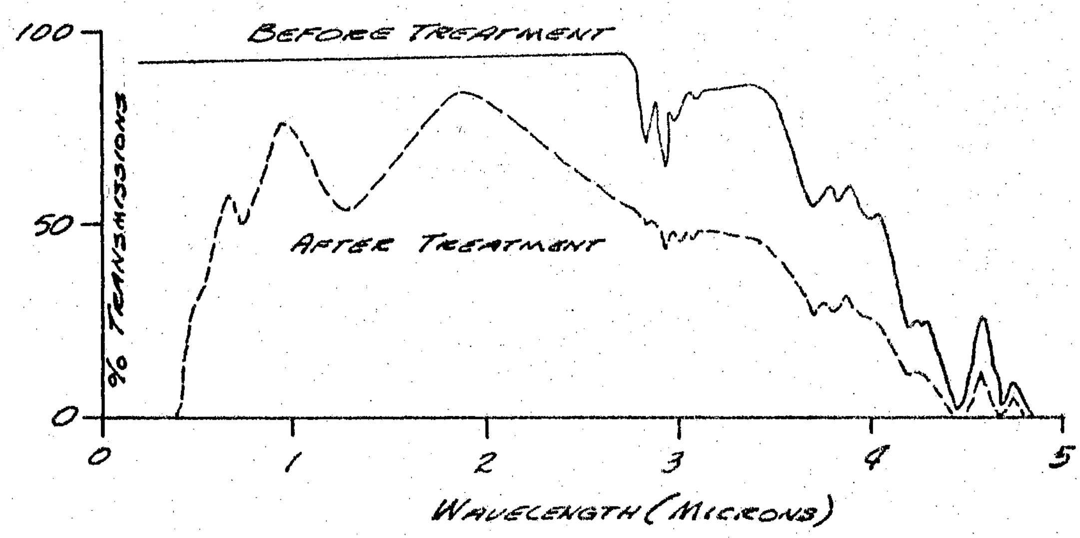

Fig. 14. Optical Transmission of Quartz Window.

that battery voltage is known with sufficient accuracy.

Both bulk and surface resistivity measurements were judged necessary because if the depth of diffusion is large, the bulk measurements would be of interest, whereas if the depth is small, which would be the case for a high activation energy situation, the region of lowered conductivity would be very thin, and the conduction would be through this shallow layer in a manner akin to surface conduction.

As stated earlier, the surface conductivity, σ, is $\sigma = (P/g)R$. Assuming the usual electrode configuration as in Fig. 7, P/g can be roughly approximated to be 12. Absolute values of surface conductivity have not been determined by this author. As it is stated in the A.S.T.M. Standards (58), very little is known at present of the variation of surface resistivity with potential gradient or current density. There is some evidence, however, that such variations are significant. However, once again only a change is being looked for. If the same type of electrodes is used and their spacing kept constant in each measurement, then any appreciable variation in R should signal a true corresponding change in σ.

The surface resistivity is of the order of 10^{16} ohms. The surface resistivity seems to be increased by nearly a factor of 10, that is, to a value of $\sigma = 10^{17}$ ohms when in an atmosphere dried with a desiccant.

Diffusion Technique

Two different furnaces were used in carrying out the diffusion work. A diffusion temperature of 900°C was employed in all cases. The first furnace used is a resistance wound muffle furnace. A Leeds and Northrup, series 60, temperature controller with a chromel-alumel thermocouple was used to control the temperature of both furnaces.

Diamond, if heated to moderate temperatures in an oxygen atmosphere, will form CO and CO_2. Aluminum, which was chosen as the first diffusing impurity with which to work, also cannot be satisfactorily heated in oxygen because of the extreme chemical activity of aluminum, which results in rapid oxide formation. This means diffusion work with aluminum or diamond must be carried out in an inert atmosphere or a vacuum. It was decided to use a vacuum in this work.

The aluminum used has the Baker and Adamson trademark, and was obtained from the General Chemical Division of the Allied Chemical Corporation. The listed impurities of the aluminum are 0.10% of silicon, 0.001% of nitrogen compounds, 0.02% of copper, 0.10% of iron, 0.002% of manganese, and 0.03% of titanium.

For the first several diffusion runs, the diamond was placed with a small amount of aluminum in a quartz ampoule that had been evacuated and sealed; the ampoule was placed in the furnace and the diffusion run begun. This procedure was not found to be satisfactory because the aluminum would diffuse through and react vigorously with the quartz ampoule. Both alumina and platinum crucibles were placed within the quartz ampoule to contain the melt, but they were not found to be sufficiently inert to molten aluminum. A silicon carbide crucible was obtained from Norton Company and was found to be satisfactory in practice, neither reacting with the diamond, the aluminum, nor with the quartz. The quartz ampoule, after being degreased, was rinsed in hydrofluoric acid and then in distilled water to remove surface contaminants.

For a time, difficulty was encountered with the vacuum because of outgassing of the crucible and of the quartz. This problem was overcome by having the ampoule, together with the diamond and the aluminum, undergo a regular Pyrex-glass annealing cycle. This consisted of evacuating the ampoule with an oil diffusion pump while the temperature of the ampoule was raised to 565°C, held there for two hours, and then had an 8 hour cooling period. Later when the ampoule was sealed, the pressure was 2×10^{-6}mm of Hg. Prior to this type of procedure, the aluminum would react with residual and outgassed oxygen to form a thick oxide layer. The molten aluminum was contained within the oxide layer and would not come into contact with the diamond. However, the above annealing-outgassing cycle overcame this problem.

The above procedure was followed for two diffusion runs. The total time, for both runs, the diamond was in contact with the molten aluminum at the diffusion temperature was 37 hours. On the first diffusion run no crucible was used, and the aluminum diffused through a small pore in the ampoule. Microscopic yellow crystals were found on the diamond. These will be discussed later.

The diamond, after being cleaned in hot hydrochloric acid or aqua-fortis ($2/3\ H_2SO_4 + 1/3\ HNO_3$) for times up to 5 hours, would show no decrease of either bulk resistivity ρ, or surface resistivity σ .

Due to the apparent reaction between aluminum and diamond, it was not thought desirable to heat the diamond for a longer time in the molten aluminum. Therefore a layer of aluminum was vapor deposited on one surface of the diamond from a tungsten filament. The diamond was then placed in the evacuated ampoule, sealed, and placed in the furnace for the diffusion run in the usual manner. The temperature was kept at 900°C for 168 hours. After cleaning the diamond in hot aqua-fortis, resistivities were the same as before the diffusion run. In other words, the diamond has been kept at 900°C in contact with aluminum for a total time of 205 hours with no apparent diffusion. Optical transmission measurements from approximately 0.225 microns to 14 microns were made on the diamond after the diffusion run but no change in the transmission was noticed.

The next impurity to be tried was beryllium. A tube furnace was used, the furnace again being controlled by the Leeds and Northrup temperature controller. A vacuum environment was maintained by employing a Vycor-brand glass tube, sealed at one end, the sealed end being placed in the tube furnace. A roughing pump was connected to the tube to evacuate it, and also to maintain the vacuum during the diffusion run. The diffusion temperature was again 900°C. The beryllium was obtained from A. D. Mackay, Inc. The beryllium was vacuum deposited onto the diamond from a tantalum foil boat source. The diamond was then placed in the silicon carbide crucible, both placed in the Vycor tube, and the diffusion run begun. The furnace maintained a temperature of 900°C for 25 hours. Hot aqua-fortis was used to clean the diamond for resistivity measurements. When the resistivity measurements were made, they showed that neither surface resistivity nor bulk resistivity had changed.

The next material to be tried as a diffusing impurity was boron. A quantity of amorphous boron, 95 to 97% pure, was obtained from A. D. Mackay, Inc. This is in the form of a fine powder and was placed in the bottom of a silicon carbide crucible. The diamond was placed on top of the boron and the furnace in the same manner as the beryllium diffusion run. The vacuum roughing pump was again used to maintain a vacuum. The temperature was held at 900°C for 170 hours. After the diamond was removed from the furnace, it was cleaned in hot aqua-fortis and resistivity measurements made. Bulk resistivity and surface resistivity had not changed.

Another diffusion run with boron was tried. The boron was placed in the bottom of the SiC crucible as before with the diamond on top. The loaded crucible was placed in a quartz ampoule, the ampoule evacuated, outgassed, and sealed. At the time of sealing, the vacuum was better than 1×10^{-5} mm of Hg. The ampoule was placed in the muffle furnace and the temperature maintained at 900°C for 170 hours.

After the diffusion run the diamond was cleaned in hot aqua fortis and electrical contacts were made. Resistivity measurements showed no change in surface or volume resistivity.

Optical transmission measurements were made on the diamond from 0.285 microns to 14 microns but no change was noted in the transmission.

The possibility of nitrogen diffusion was also kept in mind. The diamond used in this study is a type I. This means, according to the work of Kaiser and Bond (6), the diamond has an appreciable nitrogen content. The magnitude of the 8 micron absorption band is determined by the amount of nitrogen present. It was thought that outdiffusion of nitrogen might be possible. Ignoring for the moment all diffusion runs in the muffle furnace and looking only at the tube furnace results, the diamond was held at 900°C in a fore-pump vacuum for 200 hours. Transmission measurements were made, but no change in the 8 micron absorption band was found that could not be explained by the overall lowered transmission due to the etched surface of the diamond (see Figs. 15 and 16).

Observations of Other Phenomena

As it was stated before, diamond is not the stable form of carbon at atmospheric pressures. The stable form is graphite. This means diamond

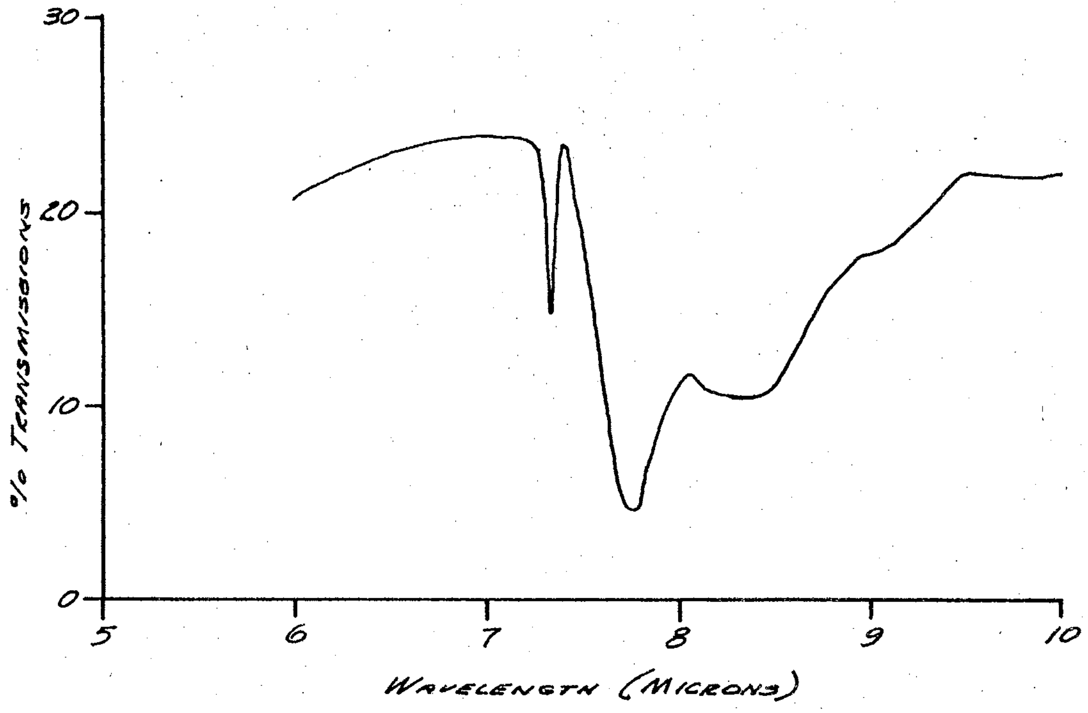

Fig. 15. Eight Micron Optical Absorption of Diamond D12 Prior to all Heat Treatments.

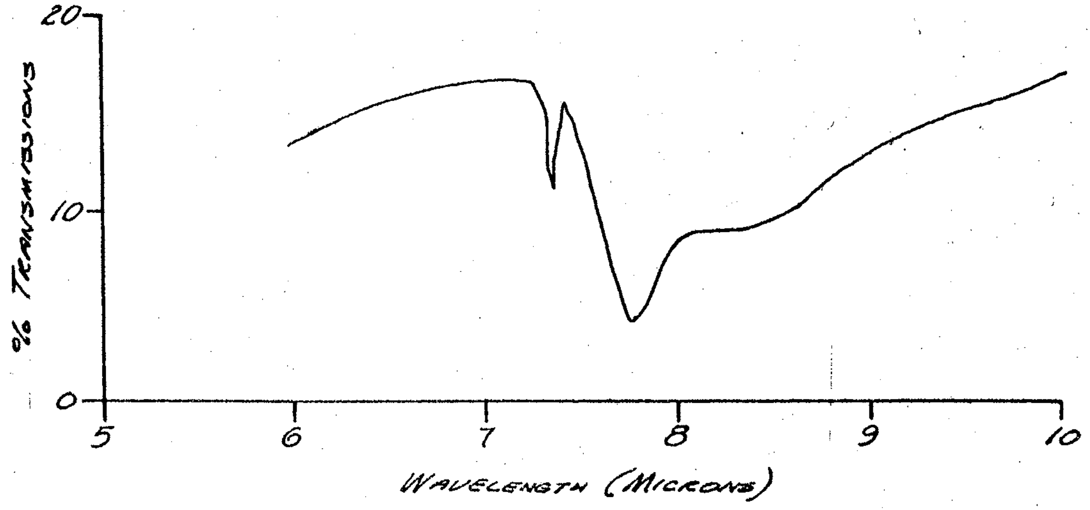

Fig. 16. Eight Micron Optical Absorption of Diamond D12 Following all Heat Treatments.

has a tendency to turn to graphite. Although at room temperatures, this rate is immeasurably small, as the temperature increases, this rate increases (59). It has been reported by Seal (59) that graphitization does not seem to occur below 1200°C, at least for periods of 15 to 30 minutes, in a vacuum of 10^{-4} mm of Hg. Since our diffusion runs were to be of some duration, and also because of the temperature tolerences of the furnaces used, it was decided to use a temperature of 900°C for the diffusion work.

Mutch and Raal (60) reported observing a decrease in resistivity of a semiconducting diamond after heat treatment. They state that the change could be brought about by heating the diamond at 850°C for 70 hours in a vacuum of better than 10^{-5} mm of Hg. The same effect could be noted in an argon atmosphere as well as a vacuum. The diamond they reported on was a rectangular slab with two regions, a blue and a white. They give a table listing the change.

TABLE IV

RAAL'S CHANGE OF DIAMOND RESISTIVITY

	ρ of blue portion	ρ of white portion
unheated	97.8 ohm-cm	20,500 ohm-cm
heated	56.5 ohm-cm	313 ohm-cm

Mutch and Raal attempt to account for the resistivity decrease by saying the acceptor concentration is constant throughout the diamond and the donor concentration, being less in the blue portion, allows this region to be bluer and more conducting than the white portion, in which the donor concentration is higher. Mutch and Raal state that an unpublished thesis by Wedepohl establishes that displaced atoms in the diamond lattice give rise to donor centers. Mutch and Raal think the heat treatment causes annealing of the displaced atoms with the existing vacancies. They state there are more donors in the white portion so there is more annealing which means a greater decrease in resistivity. According to their theory, insulating diamonds have the same number of donors as acceptors, therefore a heat treatment such as they describe should change the resistivity drastically due to the apparently large number of donor sites.

Before the diamond D-12 was made to undergo any type of heat treatment, it was decided to see if it could be annealed as the conclusions of Mutch and Raal indicated.

The diamond was cleaned in the normal manner and placed in the quartz ampoule. The ampoule was then evacuated, flushed with helium, evacuated and sealed. No crucible was used. The ampoule was maintained at a temperature of 900°C for 20 hours, after which the temperature was decreased at the rate of 200°/hour. The diamond, when removed, appeared somewhat darker than usual. The normal cleaning procedure was used and electrical contacts made. Surface resistivity seemed to be on the order of 2×10^6 ohms. The dark color of the diamond was not changed by the normal cleaning procedure. The source voltage was 550 volts. A green electroluminescence was noticed. The current being in the range of a milliamp or larger. Such an electroluminescent effect has been observed in type I diamond before by Logie and Urlau (61). This was after a collodial suspension of graphite had been painted on the diamond and annealed. They reported the diamonds returning to their normal conducting state after they were cleaned.

Bulk resistivity of D-12 was measured at 10^{14} ohm-cm, but this could be due to low surface resistivity. After being cleaned in hot aqua fortis the surface resistivity was measured at 10^{10} ohms and the bulk resistivity measured at 10^{17} ohm-cm. Another annealing cycle was performed with a better vacuum. The vacuum was obtained with an oil diffusion pump with a liquid nitrogen trap. The ampoule was heated to approximately 800°C with a torch to outgass. Pressure at time of sealing was 10^{-5} mm of Hg. The temperature of the furnace was again maintained at 900°C for 20 hours and then decreased at the rate of 200°/hour. The diamond again appeared darker. The normal cleaning procedure was used and electrical contacts made. Surface resistivity seemed to be of the order of 10^4 ohms. After cleaning in hot aqua fortis for several hours, the surface resistivity was measured as approximately 10^{10} ohms and the bulk resistivity measured at approximately 10^{16} ohm-cm.

In the light of the work reported by Logie and Urlau, it would appear that possibly a layer of graphite had formed on the surface of the diamond. The reason for this effective graphitization is not known. It is possible that this is the normal phase change to the stable graphite form. It is also possible that outgassed material from the quartz ampoule reacts with the diamond, the reaction products undergoing pyrolytic dissociation, the carbon forming graphite since diamond is an unstable phase. Such a process might be the origin of the observed effect reported by Mutch and Raal. It should also be mentioned that silicon monoxide might be formed by the reduction of quartz by carbon, the diamond being in contact with the quartz.

It was thought that if silicon monoxide was being formed, as the temperature was brought down there would be some temperature where the silicon monoxide would be deposited and not decomposed. So the diamond was made to undergo another annealing period of 20 hours at 900°C. Transmission measurements were made with the intention of looking for the reported absorption of silicon monoxide. Howarth and Spitzer (62) reported silicon monoxide absorption bands in the infrared region at 10 microns, 13.6 microns, and 16.3 microns. The infrared transmission of the diamond was examined only out to 14 microns. The 10 microns band of silicon monoxide is prominent in the Howarth and Spitzer data but it was not found in the transmission curve of the diamond. In fact, the transmission curve of the diamond appears to be completely normal.

Photoconductivity was observed in the normal clean diamond. This required all resistivity measurements to be made in the dark. The diamond mount was believed to be satisfactorily light tight. With just the room fluorescent lights illuminating the diamond, the measured bulk resistivity decreases to 3×10^{12} ohm-cm. The decay time constant of the photocurrent is 10 seconds.

As it was mentioned in the previous section, on one of the earlier diffusion runs with aluminum small microscopic yellow crystals were found on the diamond after the diffusion run. These crystals were on a dark substrate which in turn was on the diamond. Since aluminum carbide (Al_4C_3) crystals are yellow, it was thought possibly the crystals might be aluminum carbide. With this in mind, J. Hayden of this laboratory took a powder X-ray diffraction picture of the crystals and substrate. However, at the time the picture was taken, the crystals were either very pale yellow or white. Comparing the interplanar spacings with published values, it was seen that aluminum was present, a small amount of silicon present, Al_2O_3 possibly present and some lines unaccounted for, graphite apparently was not present. Comparing these unaccounted lines to values for aluminum carbide published in the ASTM X-ray powder index file, it is seen that they also are not due to aluminum carbide. Possibly the sample had decomposed due to the water vapor in the atmosphere.

After the diffusion runs with boron, etch pits were found on the diamond. Etching action had taken place with the other diffusion runs but not the formation of etch pits. Figs. 17 and 18 are microphotographs of the same region on the diamond. The magnification of Fig. 17 is 50X and that of Fig. 18 is 170X. The large triangles seen in both figures with their apices down are trigons. The small triangles seen in Fig. 18 oriented oppositely to the trigons are etch pits.

As it was mentioned earlier, aluminum reacts with quartz forming a dense, hard, dark material. J. Hayden obtained an X-ray powder diffraction picture of this material. Comparing its d-spacings to published d-spacings of various materials, it appears that the material is composed of alpha-Al_2O_3, silicon, and aluminum in relatively large crystals. Apparently all that happened was reduction of the quartz to silicon by the aluminum.

It was noticed earlier that when aluminum was melted in a quartz ampoule, the area inside the ampoule above the molten aluminum region was tinted an amber color with very faint alternating red and green bands. These bands might be interference colors due to a thin film. It was decided to examine this phenomenon further. A quartz ampoule was prepared with 4 small quartz projections on the inside in such a manner that when the ampoule had been sealed and suspended in the muffle furnace, a quartz window could be supported by the projections, above the molten aluminum and parallel to the aluminum surface. The system was carefully cleaned, evacuated, and sealed. The ampoule was outgassed by the Pyrex-

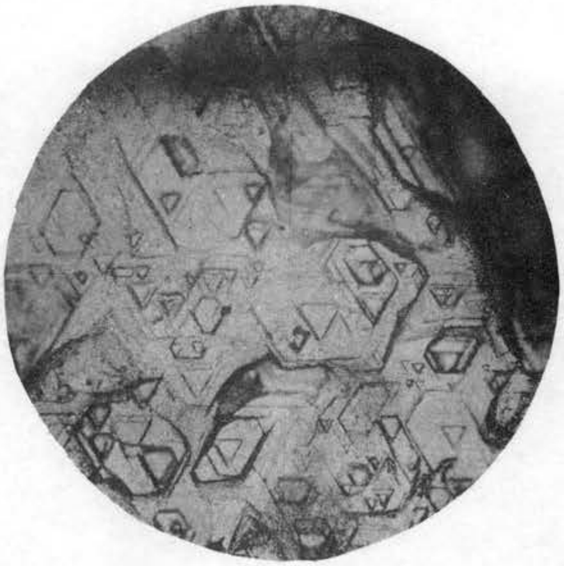

Fig. 17. Microphotograph of Diamond Surface--50X.

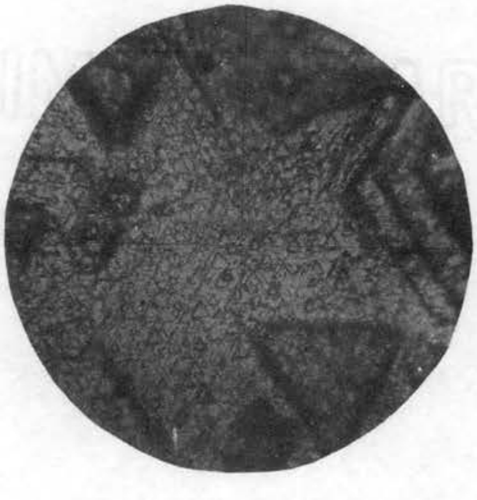

Fig. 18. Microphotograph of Diamond Surface--170X.

glass annealing cycle already mentioned, and sealed at a pressure of 2×10^{-6} mm of Hg. The ampoule was held at a temperature of 900°C for 12 hours. Upon removal from the furnace, one side of the quartz window had a faint red hue and the other side had a faint green hue. It is not known which side of the window faced the aluminum. The overall color is a dark amber. Transmission measurements in the ultraviolet, visible, and infrared regions were made on the window both before and after the heat cycle. The transmission measurements extended from 0.22 microns to 4.8 microns. The window before the heat treatment did not transmit in the infrared beyond 4.8 microns. After the heat cycle, the window did not transmit in the ultraviolet beyond about 0.4 microns. Also, there is now a slight absorption band at approximately 0.6 microns, an absorption band at 0.78 microns, and a broad band at 1.25 microns. From about 1.9 microns on into the infrared, there are no new absorption bands, but the transmission tails off gradually (see Fig. 14). Nitric, hydrochloric, and sulfuric acids seemed to have no effect on the transmission. A small portion of the ampoule, which also had the amber coloration and the pale red and green bands, was placed in hydrofluoric acid for one hour. Etch pits were formed, it appeared as if the surface was a film, the acid penetrating the film in weak spots and attacking the quartz underneath. The film retained the amber coloration but the quartz underneath was clear. The film also seemed to be attacked by the acid but at a much slower rate than the quartz.

Summary and Conclusions

This study was concerned with the possibility of obtaining impurity diffusion in diamond for similar conditions of pressure and temperature as those under which the diffusion work on germanium and silicon had been carried out.

Assuming a vacancy mechanism of diffusion, values for the diffusion constant D_o and the activation energy Q were calculated for the case of aluminum diffusing in diamond. The resulting value for the diffusion coefficient D is very small compared to diffusion coefficients of impurities in Ge and Si. This means the diffusion depth would be small compared to diffusion depths in Ge and Si for similar temperatures and times. The theory used to compute the D_o and Q values for diamond, seems to account for the experimental diffusion results in Ge and Si. Of course, one does not know if the same theory holds true in the case of diamond.

The diffusion work was carried out at a temperature of 900^{o}C in a moderate vacuum. Aluminum, beryllium, and boron were separately tried as the diffusing impurity. Diffusion times were on the order of 10^2 hours.

Since the chosen impurities are electrically active in Ge and Si, it is assumed that they will also be electrically active in demand. Therefore, resistivity measurements were used to determine if diffusion had occurred. No change in either surface or volume resistivity was found, indicating no appreciable diffusion took place.

Nitrogen diffusion was looked for by observation of the 8 micron absorption band but no change in the absorption band indicates no diffusion occurred.

The reason for not observing impurity diffusion is of course, not known, but several plausible explanations can be advanced. The first is the magnitude of the activation energy. It is conceivable the activation energy is large enough so that the diffusion depth, for a time on the order of 10^2 hours and a temperature of 900°C, is so small that essentially no diffusion occurs. Using Swalin's value for Q of 9.12 ev and a value for D_o of 11.6 cm^2/sec, letting $T = 900°C$ which means that $kT = 0.1$ ev, substituting into the equation $d^2 = 6Dt$ where $D = D_o\exp(-Q/kT)$ and letting $t = 200$ hours $= 7.2 \times 10^5$ sec, then the diffusion depth d is 6.9×10^{-18} cm. This is much less than one lattice spacing.

The second possible reason for not observing diffusion is concerned with the phase diagram of carbon. It seems possible that the impurity at the surface of the diamond chemically reacts with the diamond to form a carbide. This carbide then undergoing pyrolytic decomposition to the impurity atom and carbon. Since graphite is the stable phase of carbon at atmospheric pressure, the carbon does not deposit in the form of diamond but instead in the form of amorphous carbon or graphite, and is subsequently removed by the cleaning process. However, since the Gibb's free energy of formation of the carbides has a large negative value, indicating good stability, a fairly large amount of the carbides cannot have undergone pyrolytic decomposition. The carbides Al_4C_3 and Be_2C are decomposed by acids and might then have been removed during cleaning. However, B_4C is reported as inert to acids and would not then be removed. It seems therefore that at least B_4C was not formed. However etching action did occur with all the impurities. Although dissolution of the diamond was noticed after each diffusion run, etch pits were not found until after the boron run. Due to the insoluable nature of B_4C, if the etch pits are due to the formation of B_4C, then one would think this material would still be on the diamond surface. Crystalline B_4C has been reported as a dark grey, semiconducting material (63). After cleaning, the diamond did not appear discolored or dark and its resistivity was normal. One can only conclude that B_4C was not formed. It is possible that a small amount of oxygen outgassed from the porous crucible and etched the diamond.

It is always advantageous in diffusion work to employ as high a diffusion temperature as possible. The difficulty with diamond in this respect is the phase change. It would be desirable to increase the pressure until one is operating in the diamond stable region of the carbon phase diagram. If this were done, the temperature could be increased to a large value with a resulting increase in diffusion depth for the same diffusion times.

Just recently, it has been reported by General Electric that they have diffused impurities into diamond (64). They stated they have made semiconducting diamonds by diffusing boron and aluminum into man-made or natural diamonds at high pressures and temperatures. No other information was given as to the pressures, temperatures, diffusion times, diffusion depths, activation energies, or diffusion coefficients. Quantitative work of this nature would be interesting. The effect of pressure would, of course, have to be taken into account. Hydrostatic pressures seem to usually cause a considerable decrease in the diffusion rate, the diffusion coefficient decreasing exponentially with increasing pressure (65).

Synthetic diamonds have of course been grown, General Electric being the first organization to do this beyond a reasonable doubt (66). The synthetic diamonds are grown at pressures up to 100,000 atmospheres and temperatures up to $3000^{\circ}K$ (67). General Electric has also reported growing semiconducting diamonds by adding impurities such as boron, beryllium, or aluminum to the mixture of graphite and catalyst from which diamonds are made (64). Donor, or n-type, diamond crystals do not occur in nature and have not yet been grown synthetically. General Electric also states that the semiconducting diamonds prepared with boron are blue, in shades ranging from a pale blue-white to a deep blue-black, depending on how much boron is present in the crystal (64).

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