

Diffusion of Antimony Out of Germanium and Some Properties of the Antimony-Germanium System

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In a recent paper, a rate limitation at the surface for impurity diffusion into semiconductors was discussed. The rate limitation leads to a radiation-type boundary condition for the diffusion differential equation. Experiments on the diffusion of radioactive antimony out of germanium have shown that the solution to the diffusion differential equation appropriate to this boundary condition does indeed agree with the experimental data. The constant which describes the rate limitation has been measured as a function of temperature and has an activation energy close to that of the diffusion constant of antimony in germanium. The diffusion constants found in this work are in agreement with those found in other experiments in which antimony was diffused into germanium. By a proper choice of the diffusion-system geometry, an increased rate limitation was produced which provided data from which sticking coefficients and partition coefficients were calculated for the system gaseous antimony-solid germanium. These data have also been used to estimate the binding energy of an antimony atom in the germanium lattice.

INTRODUCTION

THE boundary condition for the transport of impurities across a solid-ambient interface has been discussed in a recent paper.¹ Evidence was given that for some systems there was a significant measurable rate limitation at a solid-gaseous interface. This rate limitation can be pictured as a potential barrier at the surface which the impurity atom must surmount to leave the solid.

The research reported in this paper is concerned with quantitative experiments on the diffusion of antimony out of germanium and it is shown that the experimental antimony distributions are consistent with the picture of a rate limitation, or potential barrier, at the germanium-ambient interface. In addition, external rate limitations have been purposely introduced to provide data from which one can calculate partition coefficients and sticking coefficients for the antimony-germanium system. These data have also been used to estimate the binding energy of antimony in germanium.

DIFFUSANT DISTRIBUTIONS

The material presented in this section has been discussed in detail elsewhere.¹ A brief treatment of the appropriate expressions will be given here for the outward diffusion of impurities from a homogeneously doped crystal.

For the diffusion of an impurity out of a solid in a perfect vacuum, the rate limitation at the solid-ambient interface results in a flow of diffusant atoms out of the solid whose rate is proportional to the concentration of the diffusant in the solid at the surface, $N(0,t)$. Thus, the boundary condition becomes

$$D \left[\frac{\partial N(x,t)}{\partial x} \right]_{x=0} = KN(0,t), \quad (1)$$

¹ F. M. Smits and R. C. Miller, *Phys. Rev.* **104**, 1242 (1956).

where D is the diffusivity and $N(x,t)$ is the concentration of the diffusant in the solid at a depth x from the surface at time t . The rate constant K has the dimensions of velocity and is termed the interfacial conductance.

When the experimental conditions are such that the impurity which diffuses out of the solid is not immediately removed from the diffusion system, $N(0,t)$ decreases more slowly with time than when the ambient is a perfect vacuum. Thus, the effect is that of an additional rate limitation which is termed "external rate limitation." For the discussion which follows, it is convenient to introduce a partition coefficient k_g defined by $k_g = N_e/N_g$, where N_g is the concentration of the diffusant in the gaseous phase in equilibrium with a concentration N_e in the solid. It will be assumed that k_g is not dependent on diffusant concentrations. This assumption will be discussed in a later section. If the diffusion system is such that the only source of diffusant is the doped sample, and that the rate at which the gaseous diffusant leaves the volume in which the diffusion is carried out is given by LN_g atoms sec^{-1} , then the appropriate boundary condition has been shown to be¹

$$D \left[\frac{\partial N(x,t)}{\partial x} \right]_{x=0} = \frac{L}{A} N_g = \frac{LK}{L+k_gKA} N(0,t) = K'N(0,t). \quad (2)$$

In this expression L is the pumping speed of the connecting channel from a high vacuum to the chamber in which the sample is placed and A is the total area of the diffusion sample. Thus, Eq. (2) has the same form as Eq. (1) except that K is replaced by K' . Note that as L becomes much larger than k_gKA , K' becomes equal to K . Then, for $N(x,t) = N_1$ for $t=0$ and $x \geq 0$, the

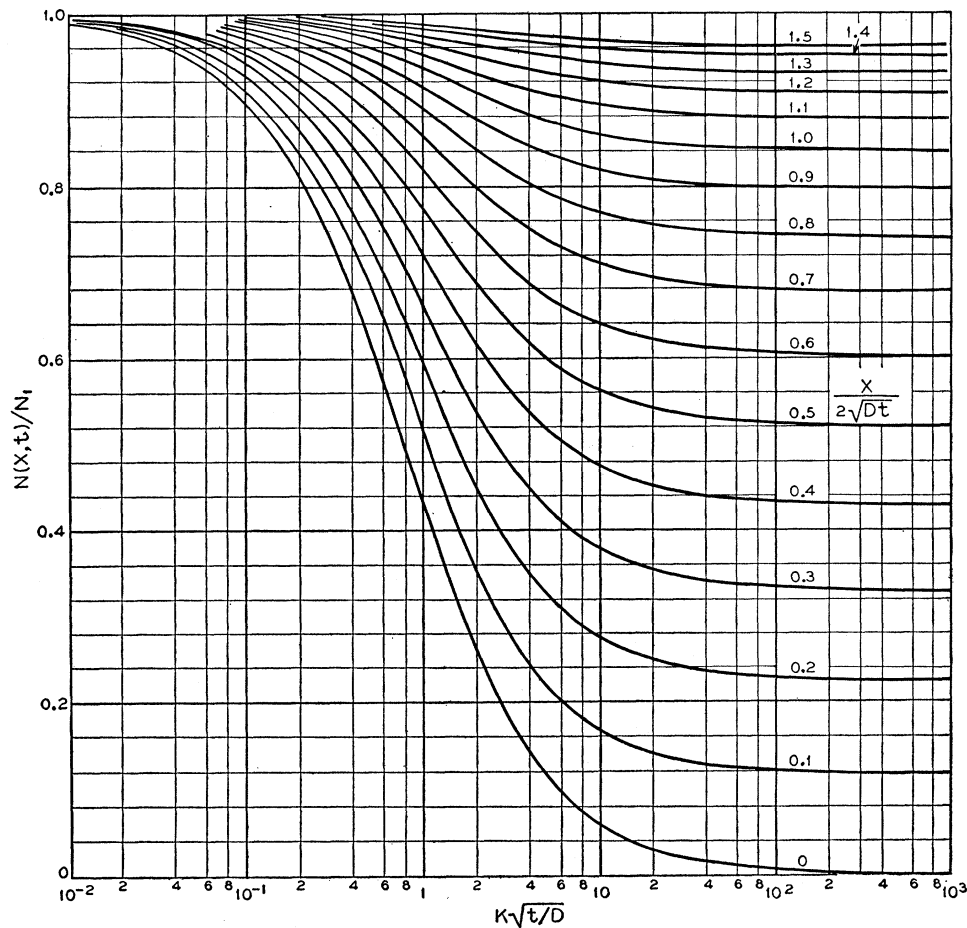


FIG. 1. Graphical solution to the diffusion differential equation for diffusion out of a doped sample taking into account the rate limitation at the surface. These curves were taken from H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Clarendon Press, Oxford, 1948), Fig. 7, p. 54.

solution to the diffusion differential equation is^{1,2}

$$N(x,t)/N_1 = \operatorname{erf} \frac{x}{2(Dt)^{1/2}} + \left\{ \operatorname{erfc} \left[\left(\frac{x}{2(Dt)^{1/2}} \right) + K' \left(\frac{t}{D} \right)^{1/2} \right] \right\} \times \exp \left[\frac{K'x}{D} + \frac{K'^2 t}{D} \right]. \quad (3)$$

A graphical solution of Eq. (3) is shown in Fig. 1. Note that an experimental determination of $N(x,t)$ as a function of x is sufficient to determine both D and K' directly. The measurement of K' as a function of L enables one to obtain the interfacial conductance K and the partition coefficient k_g . Finally, it is also possible to determine the sticking coefficient s from the same data, where the sticking coefficient is the probability that a diffusant atom incident on the solid will become part of the solid phase. For at equilibrium,¹

$$KN_e = Kk_gN_g = (N_g/4)\bar{v}s, \quad (4)$$

where \bar{v} is the average thermal velocity of the gaseous diffusant atoms. Therefore, one obtains

$$s = 4k_gK/\bar{v}. \quad (5)$$

² $\operatorname{erfc} y = 2(\pi)^{-1/2} \int_0^y \exp(-z^2) dz = 1 - \operatorname{erfc} y$.

DIFFUSIONS AND RESULTS

The antimony-germanium system was selected for the experiments. Antimony was chosen as the diffusant for two reasons. First, it is a sufficiently fast diffuser in germanium to make these experiments relatively easy to perform. Secondly, an antimony radioactive isotope, Sb^{124} , with a half-life of 60 days, is readily available so that radiotracer techniques could be used. The vapor pressure of germanium³ is sufficiently small, about 10^{-12} mm of Hg, over the temperature range investigated so that any effects due to the evaporation of germanium are negligible insofar as this research is concerned.

The germanium single crystals had antimony concentrations of approximately 2×10^{17} atoms cm^{-3} as determined from the radioactive analysis. The crystal was cut so that the diffusion current was in the $[100]$ direction. The samples were lapped with silicon carbide and acid etched prior to the diffusions.

The diffusions were made in two types of quartz tubes shown in Fig. 2. The pumping speed of the straight quartz tube, $L = 900 \text{ cm}^3 \text{ sec}^{-1}$, will be shown to be sufficiently large so that $L \gg k_gKA$ and the K' deter-

³ A. W. Searcy, *J. Am. Chem. Soc.* **74**, 4789 (1952).

mined with this tube is equal to K . The constricted tube contains a capillary quartz length which reduces L to $0.223 \text{ cm}^3 \text{ sec}^{-1}$ so that it becomes comparable to $k_g K A$ and hence provides an external rate limitation. The pumping speeds of the quartz tubes were calculated from data given in the literature.⁴ Prior to use, the quartz tubes were etched in hydrofluoric acid for ten minutes, rinsed with de-ionized water, and finally fire-polished with an oxy-hydrogen torch. The amount of antimony removed from the system by chemical reaction with the quartz envelope prepared in this fashion, and by diffusion into the quartz walls, was found to be too small to measure and hence negligible insofar as this research is concerned.

After the diffusion sample is placed in the quartz tube, the apparatus is assembled as shown in Fig. 2 and the tube is evacuated to about 10^{-6} mm of mercury. When the constricted tube is used, one end of the tube must be closed after the sample is placed in the appropriate region of the tube. Care is taken to insure that the germanium does not heat up and therefore oxidize during the sealing procedure. After the tube is evacuated, the furnace is brought to about 500°C for a few hours to outgas the quartz and sample. The lower stopcock is then closed and the sealed off components are removed from the vacuum station by opening the ball joint just above the lower stopcock. After the furnace is brought up to the desired diffusion temperature, the evacuated diffusion tube is inserted in the furnace and reconnected to the vacuum station. Thus the tube and sample attain the diffusion temperature in a sufficiently short time interval so that the temperature transient has a negligible effect on the results. The diffusion temperature is held to within 1°C of the nominal desired temperature. After the diffusion period, the tube is removed in the same manner as described above.

The samples are then removed from the quartz tubes, trimmed around the edges to a depth several times the expected depletion penetration, and mounted in preparation for grinding. Layers parallel to the surface are ground off on silicon carbide paper and the activity on the paper is then counted with a Geiger counter. From the difference in weight of the sample plus the holder before and after each grinding, the area of the sample

TABLE I. Data and results for diffusions made in unconstructed quartz tubes, $L=900 \text{ cm}^3 \text{ sec}^{-1}$.

Diffusion time hours	Temperature $^\circ\text{C}$	D $\text{cm}^2 \text{ sec}^{-1}$	K cm sec^{-1}
68.0	900	2.3×10^{-10}	3.9×10^{-7}
6.47	900	2.7×10^{-10}	4.3×10^{-7}
6.50	900	2.9×10^{-10}	6.3×10^{-7}
72.0	850	7.0×10^{-11}	1.05×10^{-7}
72.0	850	8.7×10^{-11}	2.43×10^{-7}
76.0	800	3.5×10^{-11}	6.6×10^{-8}

⁴ S. Dushman, *Vacuum Technique* (John Wiley and Sons, Inc., New York, 1949).

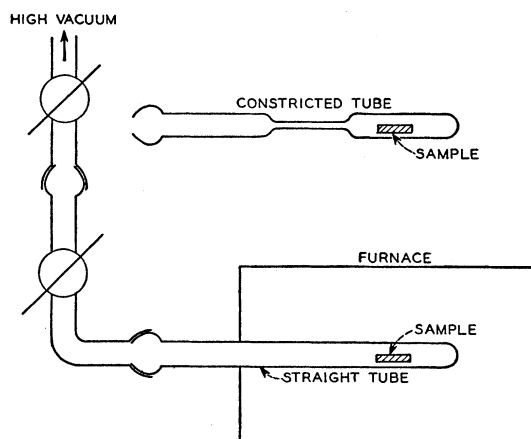


Fig. 2. Two types of quartz tubes used for the diffusions. The straight and constricted tubes have pumping speeds of 900 and $0.223 \text{ cm}^3 \text{ sec}^{-1}$, respectively.

surface and the counting rate, the specific activity can be calculated and a plot of the relative concentration versus distance can be made. The diffusivity and interfacial conductance K' which best fit the experimental data are determined from this plot with the aid of the graphical solutions given in Fig. 1.

The data for a sample which was heated in a straight quartz tube for 72 hours at 850°C are shown in Fig. 3. The experimental points are plotted as triangles. The solid curve is the theoretical curve which best fits the experimental data and was calculated from Eq. (3) with $K=2.43 \times 10^{-7} \text{ cm sec}^{-1}$ and $D=8.65 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$. A plot of the solution for the case when it is assumed that $N(0,t)$ is equal to zero at all times, i.e., no rate limitation, so $N(x,t)=N_1 \text{ erf}[\frac{1}{2}x/(Dt)^{\frac{1}{2}}]$ is also shown in the same figure as a dashed curve. It should be noted that the solid theoretical curve fits the experimental data. Table I contains the pertinent experimental data and results for the diffusions which were made with unconstructed quartz tubes. The logarithm of K versus T^{-1} is shown in Fig. 4. It is found that K

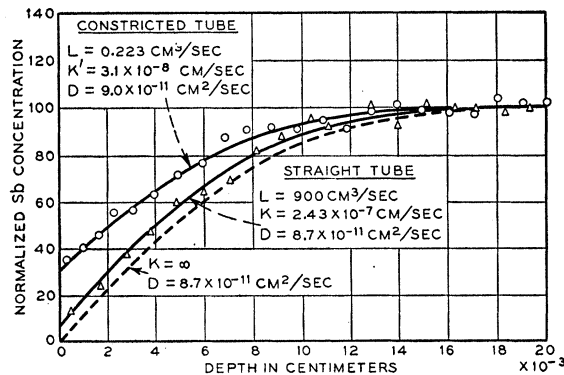


FIG. 3. Antimony distributions after heating for 72 hours at 850°C in a straight and a constricted tube. Note the effect of the constricted tube is to increase the antimony concentration above that obtained with the straight tube.

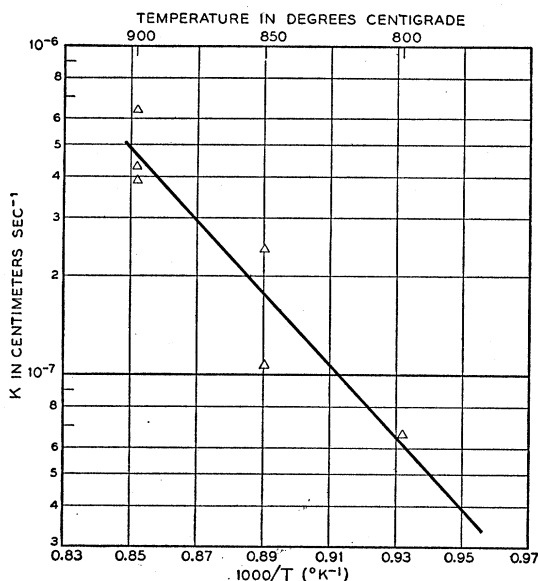


FIG. 4. The interfacial conductance K versus $1000/T$ $^{\circ}\text{K}^{-1}$. The activation energy is 2.19 ev.

can be represented by

$$K = K_0 \exp[-\Delta H/(kT)],$$

with K_0 and ΔH equal to $1.1 \pm 0.3 \times 10^3$ cm sec $^{-1}$ and 2.19 ± 0.28 ev, respectively. The constants have been determined from a least squares fit of the data and the probable errors in the constants have been evaluated by the method described by Birge.⁵

Figure 3 also shows a concentration versus distance plot for a sample which was heated in a constricted tube for 72 hours at 850°C. The experimental points are plotted as circles. The solid curve is the theoretical curve obtained from Eq. (3) with $K' = 3.1 \times 10^{-8}$ cm sec $^{-1}$ and $D = 9.0 \times 10^{-11}$ cm 2 sec $^{-1}$. This depletion curve can be compared with the one obtained for the other sample which was heated in a straight tube for the same time at the same temperature. One sees that the constricted tube provides an external rate limitation which results in an $N(x,t)$ greater than that found with

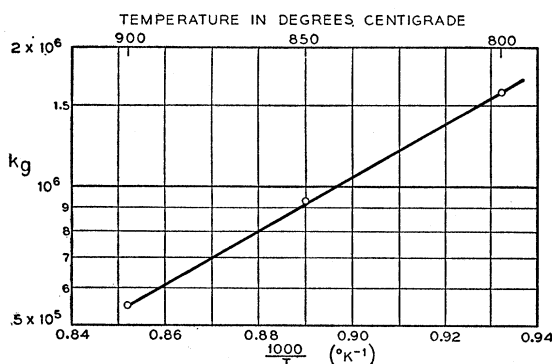


FIG. 5. The partition coefficient versus $1000/T$ $^{\circ}\text{K}^{-1}$. The slope gives an energy of 1.2 ev.

⁵ R. T. Birge, Rev. Phys. 40, 207 (1932).

the unconstricted quartz tube. Table II gives the significant data and results for the constricted-tube diffusions. To calculate s and k_g from Eqs. (2) and (5), the interfacial conductance K was taken from the least-squares fit of $\log K$ versus T^{-1} data shown in Fig. 4. It is clear from the values of k_g obtained in this fashion that $Kk_gA \ll 900$ cm 3 sec $^{-1}$ so that the interfacial conductance determined from the unconstricted-tube data is indeed equal to K . A plot of $\log k_g$ versus T^{-1} is given in Fig. 5. The partition coefficient can be represented by

$$k_g = k_{g0} \exp[-\Delta E/(kT)],$$

with k_{g0} and ΔE equal to 6.7 and 1.2 ev, respectively. Since there are only three values of k_g , uncertainties calculated in a formal manner are not given for the constants. It is estimated that each k_g is known to within 50%.

Figure 6 shows a plot of the $\log D$ versus T^{-1} where all the diffusions have been included. The diffusion constant can be expressed by

$$D = D_0 \exp[-\Delta H/(kT)],$$

with D_0 and ΔH equal to 1.3 ± 1.0 cm 2 sec $^{-1}$ and 2.26 ± 0.07 ev, respectively. The constants have been determined from a least squares fit of the data and the probable errors in the frequency factor and the activation energy calculated by the method given by Birge.⁵ Note that the activation energy given here for D is the same within the experimental uncertainties as that found for the interfacial conductance K . The diffusivities of antimony in germanium determined by Dunlap⁶ and Fuller⁷ are also shown in Fig. 6. Their values are about 25% smaller than those reported here, which is equivalent to a 10°C shift in the temperature scale. In the present work, the temperature measurement is thought to be within 5°C of the true temperature, so it is believed that the 25% discrepancy results from temperature uncertainties encountered in the three investigations.

DISCUSSION

From the data obtained in this research, it is possible to estimate the binding energy of an antimony atom in the germanium lattice. Consider the equilibrium



and let N_g be the concentration of antimony atoms in the gaseous phase and N_s the concentration of antimony

TABLE II. Data and results for diffusions made in constricted quartz tubes, $L = 0.223$ cm 3 sec $^{-1}$.

Diffusion time hr	Diffusion temp. $^{\circ}\text{C}$	D cm 2 sec $^{-1}$	K' cm sec $^{-1}$	s	k_g
21	900	2.7×10^{-10}	6.4×10^{-8}	2.1×10^{-5}	5.5×10^5
72	850	9.0×10^{-11}	3.1×10^{-8}	1.4×10^{-5}	9.4×10^5
89.5	800	3.4×10^{-11}	1.74×10^{-8}	9.4×10^{-6}	1.60×10^6

⁶ W. C. Dunlap, Jr., Phys. Rev. 94, 1531 (1954).

⁷ C. S. Fuller, Phys. Rev. 86, 136 (1952).

atoms in the germanium in equilibrium with N_g . At the pressures encountered in this work, of the order of 10^{-4} mm of mercury or less, it is certain that the gas phase can be considered as an ideal gas. Then, since the solid solutions are dilute and obey Henry's Law, it can be shown from thermodynamic arguments that the slope of the logarithm of k_g , where $k_g \equiv N_e N_g^{-1}$, versus T^{-1} will give the energy change ΔE for the reaction written as Eq. (6). The average energy of the gaseous antimony atoms is $3kT/2$, so that the binding energy, V_B , is $\Delta E - \frac{3}{2}kT$, which is found to be 1.0 ev in the temperature range investigated. This binding energy is the average energy difference between an antimony atom with zero kinetic energy outside the crystal and an antimony atom within the germanium lattice at the temperature of the system.

So far nothing has been said concerning the state of the antimony atoms within the lattice. In the temperature range investigated in this research, 800 to 900°C, the product of the electron and hole concentrations is in the neighborhood of 10^{38} .⁸ Since the concentration of antimony atoms is only 10^{17} per cc, the semiconductor may be considered to be intrinsic. If it is assumed at the diffusion temperatures that the Fermi level is in the center of the energy gap and that the impurity ionization energy is equal to the value usually employed at room temperature, 0.01 ev,⁹ the ordinary semiconductor Fermi-Dirac statistics indicate that about 25% of the antimony atoms should be un-ionized. However, as pointed out by Herring,¹⁰ this is not correct. The reason is that at these high temperatures the impurities are embedded in a dielectric which contains such large concentrations of holes and elec-

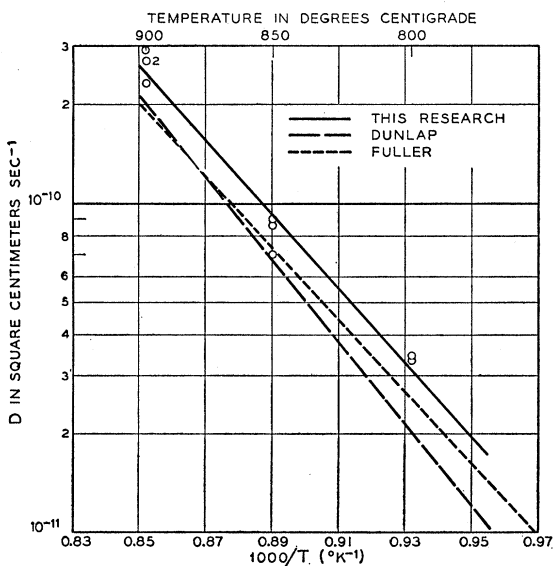


FIG. 6. The diffusivity versus $1000/T$ $^{\circ}\text{K}^{-1}$ found in this research and also the data of Dunlap and Fuller. The activation energy is found to be 2.26 ev.

⁸ F. J. Morin and J. P. Maita, Phys. Rev. **94**, 1525 (1954).
⁹ T. H. Geballe and F. J. Morin, Phys. Rev. **95**, 1985 (1954).
¹⁰ C. Herring (private communication).

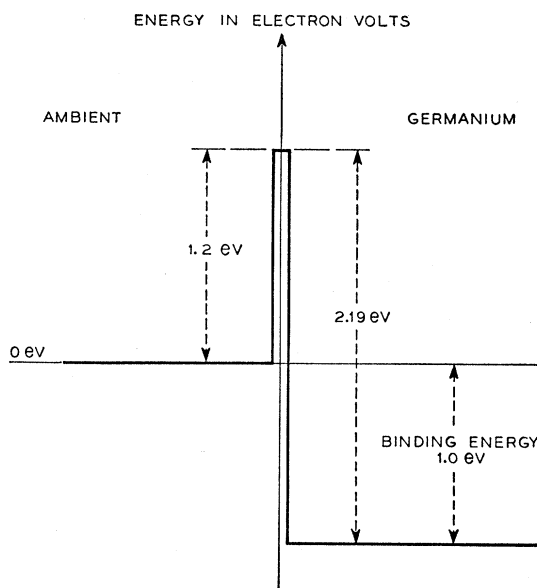


FIG. 7. An energy diagram capable of explaining the results. The activation energy for the interfacial conductance minus the binding energy leaves 1.2 ev which represents the potential barrier which an incident antimony must surmount to enter the crystal.

trons that there is a significant number of holes and electrons within the first Bohr orbit. Thus the Bohr theory of the hydrogen atom modified to take into account the dielectric constant of the medium and the effective mass of an electron in a periodic lattice is no longer valid. Estimates based on the Debye-Hückel theory of electrolytes indicate that the holes and electrons essentially screen the positively charged donor sites so that presumably all the antimony atoms are ionized.

The interfacial conductance K which describes the rate limitation on the transport of impurity atoms across the germanium-ambient interface can be interpreted in terms of a potential-energy barrier of height V_i which an average impurity atom must surmount to leave the crystal. Hence the slope of the logarithm of K versus T^{-1} enables one to determine the potential-energy barrier. This was found to be 2.19 ev atom⁻¹. Then if one assumes that the energy diagram given in Fig. 7 describes the case under investigation, the energy barrier V_1 which an antimony atom with zero kinetic energy must surmount in order to become part of the crystal lattice, is $V_i - V_B$ which gives 1.2 ev. Note that V_1 was obtained from the temperature dependence of K and k_g . The quantity V_1 will also be estimated from the absolute value of the sticking coefficient.

The sticking coefficient has been defined as the probability that an antimony atom from the ambient incident on the germanium surface will become part of the lattice and not be reflected off the surface. To calculate s one must determine the fraction of antimony atoms which possess sufficient energy to overcome V_1 . Assume that the gaseous antimony atoms possess a

TABLE III. Potential barriers V_1 calculated from sticking coefficients.

Temperature °C	s	V_1 electron volts
800	9.4×10^{-6}	1.07 ± 0.05
850	1.4×10^{-5}	1.07 ± 0.05
900	2.1×10^{-5}	1.08 ± 0.05

Maxwellian velocity distribution characteristic of the temperature of the diffusion enclosure. Then the fraction of the incident antimony atoms which possess velocities u in a direction normal to the germanium surface such that $\frac{1}{2}mu^2 \geq V_1$ will be the fraction of atoms which are able to enter the crystal, and therefore equal to s . With these assumptions, gas kinetic theory considerations give

$$s = \frac{\int_{u_1}^{\infty} u du \exp[-mu^2/(2kT)]}{\int_0^{\infty} u du \exp[-mu^2/(2kT)]} = \exp[-mu_1^2/(2kT)], \quad (7)$$

where $mu_1^2/2$ is equal to V_1 , so that

$$s = \exp[-V_1/(kT)]. \quad (8)$$

Note that s approaches unity as V_1 approaches zero which must be the case for this model. The values of V_1 obtained from Eq. (8) are given in Table III. From these data it is clear that the experimental values of the sticking coefficient can be represented by Eq. (8) with V_1 independent of temperature. The value of V_1 obtained from the temperature dependence of K and k_g was given as 1.2 ev and the uncertainty is thought to be ± 0.3 ev. To make a meaningful comparison of the two values of V_1 would require a more comprehensive analysis than presented here. Such an analysis seems unwarranted in view of the uncertainties in the experimental data.

It is interesting to consider some of the atomistic kinetics of diffusant atoms in solids at the solid-ambient interface. The diffusivity, in one dimension, can be expressed as $\lambda^2\dot{p}$, where λ is the distance between adjacent atomic planes and \dot{p} is the jump frequency in one direction, i.e., the average number of times that an impurity atom will jump a distance λ in a given direction in unit time. Likewise, the interfacial conductance K can be written as $\lambda\dot{p}_0$, where \dot{p}_0 is the escape frequency. It is difficult to say much about \dot{p} and \dot{p}_0 from theoretical considerations alone. It does seem reasonable that the activation energy for \dot{p}_0 should be equal to or greater than the binding energy of the impurity atom in the solid. In the case at hand, the activation energy for \dot{p}_0 is found to be approximately twice the estimated binding energy. All the diffusions made in this work were in the [100] direction so that λ is one-fourth the lattice constant, or $\lambda = 1.41$ A. Hence, from $D = \lambda^2\dot{p}$,

$$\dot{p} = 6.4 \times 10^{15} \exp[-2.26 \text{ ev}/(kT)],$$

and from $K = \lambda\dot{p}_0$,

$$\dot{p}_0 = 7.8 \times 10^{10} \exp[-2.19 \text{ ev}/(kT)].$$

The ratio of the antimony atoms leaving the crystal to those arriving at the surface per unit time per unit area is the transmission which is

$$\Gamma = \dot{p}_0/\dot{p} = 1.2 \times 10^{-5}.$$

An exponential factor has been omitted since the energy in this factor is considerably less than its uncertainty. Hence for all practical purposes the transmission is 10^{-5} . This is also the ratio of the antimony atoms leaving the germanium to those which return to the interior of the crystal per unit time.

The assumption has been made throughout this work that the only significant antimony species in the gaseous phase is the atomic species. It is known that other species of antimony exist, but the data on the molecular composition of gaseous antimony are meager. Rough estimates made on the basis of thermodynamic data collected by Stull and Sinke¹¹ indicate that the equilibrium ratio of antimony dimers to monomers at the highest pressure encountered in this work, approximately 10^{-5} mm of Hg, is about one. This high pressure is attained only when the constricted tube is used, and then only during the initial phases of the diffusion. With the straight tube, the ratio is approximately three orders of magnitude less. However, it is reasonable that the antimony leaves the germanium surface as atoms and since the mean free path is many times larger than the dimensions of the volume in question, the probability of forming dimers or other complex species is extremely small. Thus chemical equilibrium in the gas phase is probably not attained so that the unity ratio given above may be an upper limit.

Thus it has been demonstrated that the present boundary condition does indeed lead to solutions to the diffusion differential equation which accurately fit the experimental data on the diffusion of antimony out of germanium. The interfacial conductance which describes the flow of antimony across the germanium-ambient interface has been determined as a function of temperature and is found to have an activation energy equal to that found for the diffusion of antimony in germanium. Experimental data on the interfacial conductance and the partition coefficient have been used to calculate the binding energy of antimony in germanium and the sticking coefficient of antimony atoms incident on germanium.

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¹¹ D. R. Stull and C. C. Sinke, *Thermodynamic Properties of the Elements* (American Chemical Society, Washington, D. C., 1956).