obtained by neutron scattering[11] is excellent. The force-constant model of Chung et al.[10] for Mg_2Ge and of Whitten et al.[9] for Mg_2Si gives values of ν_R in good agreement with our measurements.

It has been suggested[12] that the linewidth W of the one-phonon line is determined mostly by decay into two phonons of roughly the same energy, and hence its temperature dependence is given by

$$W(T) = W(0)\{1 + 2/[\exp(h\nu_R/2kT) - 1]\}. \qquad (2)$$

Figure 3 shows the corrected linewidths of Table I as a function of T/ν_R and the curve of Eq. (2). This curve represents well the experimental temperature dependence of W for Mg_2Si and, in view of the uncertainties in the correction of Eq. (1), for Mg_2Ge as well. For Mg_2Sn, Fig. 3 suggests some additional temperature-independent broadening mechanism. The same conclusion can be drawn from the temperature dependence of the restrahlung linewidth of Mg_2Sn, shown in Table II.

Note added in proof. We have measured the dependence of the one-phonon Raman line of Mg_2Sn on hydrostatic stress and we have found the corresponding Gruneisen constant to be close to 1, in agreement with the conjecture made in the discussion. Raman data for these materials and for Mg_2Pb have been also presented recently by Anastassakis and Perry [Bull. Am. Phys. Soc. 16, 29 (1971)].

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Dopant Diffusion in Silicon. III. Acceptors

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Aluminum, gallium, indium, and thallium acceptors have been diffused into (111) silicon from doped epitaxially deposited source layers in a flowing hydrogen atmosphere. As in the case of P, As, Sb, and Bi donors reported earlier, all these acceptors show significantly lower mobilities when freed from surface effects. The temperature dependence of the intrinsic diffusion coefficients, obtained above 1120 °C, are characterized by the following preexponential and activation-energy parameters: 1.385, 0.374, 0.785, (1.37) cm²/sec, and 3.41, 3.39, 3.63, (3.70) eV/atom for Al, Ga, In, Tl, respectively. An analysis of these diffusion characteristics indicate a similar point-defect mechanism for both group-III and group-V dopants in silicon.

I. INTRODUCTION

This is the third in a series of papers dealing with the intrinsic diffusion of group-III and group-V dopants in silicon.[1,2] All the group-V donors were found to migrate by a closely coupled donor-vacancy pair.[2] On the other hand, the diffusion behavior of the boron acceptor was found to be very

similar to that of the phosphorus donor.[1] Conse-
quently, for an elucidation of the diffusion mechan-
ism of boron it was considered to be of interest to
investigate the intrinsic diffusion behavior of other
group-III acceptors. Moreover, since some of the
group-III dopants have been traditionally used as
elemental diffusion sources, the relative impor-
tance of the two extrinsic effects arising from the
silicon free surface and the phase-boundary redox
reaction[3] could also be further clarified by such a
study.

II. EXPERIMENTAL

The detailed experimental technique used here
was identical to that used for B, P, As, Sb, and
Bi.[1,2] Doped, 5-11-μ-thick epitaxial silicon (dif-
fusant) source layers were grown on (111) Czo-
chralski silicon wafers (10-15 mils) of different
resistivity type and level. The deposition reaction
involved was the pyrolysis of 0.15% silane in pal-
ladium-purified hydrogen at 1050-1100 °C in an
induction-heated horizontal silicon epitaxial reac-
tor. Aluminum and gallium were incorporated into
the epitaxial layer by bubbling hydrogen through
"electronic grade" trimethyl aluminum and tri-
methyl gallium, respectively, and mixing this dop-
ant-saturated gas with the reactant gas stream (si-
lane in hydrogen) at the reactor entrance. Since the
corresponding organo-indium and organo-thallium
compounds (trimethyl and triethyl) had too low a
room-temperature vapor pressure and were too
unstable to be similarly used, indium- and thallium-
doped epitaxial layers were grown from elemental
vapor sources maintained on the susceptor (from
99.9999% metal at 900-1100 °C). Even then, the
maximum indium and thallium concentrations were
~2 × 10^{16} cm^{-3} and ~6 × 10^{15} cm^{-3}, respectively. As
before, special care was taken to produce a δ-func-
tion-type impurity profile at the substrate-epi in-
terface. The diffusion couples were finally covered
with a 2500 ± 500-Å layer of amorphous silicon ni-
tride at 800 °C (by the reaction of silane and am-
monia) to serve as an out-diffusion barrier.

All the diffusion experiments were done under
intrinsic conditions, as described earlier[1,2] and
the impurity profile determined by the spreading
resistance technique. The absolute reliability of
such data was demonstrated earlier.[1]

III. RESULTS

Under the boundary condition used here, the con-
centration profile of the diffusant is given by[4]

$$N(x, t) = \frac{N_0}{2} \left[\text{erf}\left(\frac{h+x}{2(Dt)^{1/2}}\right) + \text{erf}\left(\frac{h-x}{2(Dt)^{1/2}}\right) \right], \quad (1)$$

where N_0 is the initial uniform dopant concentration
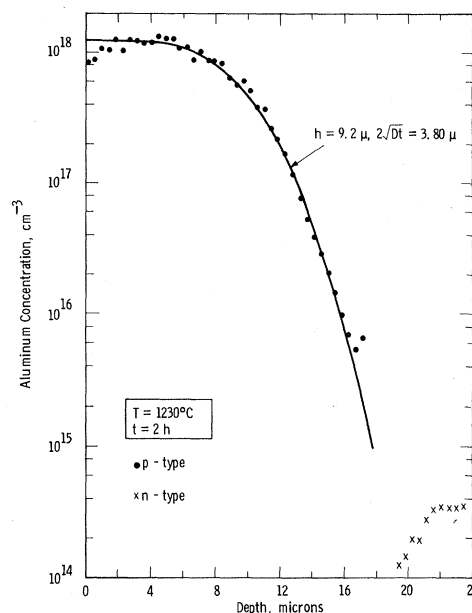in the epitaxial source of thickness h. The usual

FIG. 1. Typical fitted concentration profile of alumi-
num in silicon showing out-diffusion tail.

constraints of $t < h^2/D$ and $x > Dt/h$ for the conform-
ity of impurity profiles to Eq. (1) were properly
maintained. The experimental profiles were fitted
with calculated theoretical profiles to a maximum
accuracy of ± 0.05 μ in $2(Dt)^{1/2}$. All the concentra-
tion profiles for Al, Ga, In, and Tl exhibited excel-
lent Fickian behavior and were similar to those of
B, P, As, Sb, and Bi reported earlier.[1,2] Only in
the case of aluminum, at high temperatures and
long diffusion times, could small out-diffusion tails
be observed near the surface. But, with thick
enough epi-source layers, they did not interfere
with the accuracy of the curve fitting procedure,
and consequently, with the determined diffusivities.
Figure 1 represents a typical fitted concentration pro-
file of aluminum in silicon showing the out-diffusion
tail near the surface.

The calculated intrinsic diffusivities of Al, Ga,
In, and Tl, obtained as a function of inverse absolute
temperature, are shown in Figs. 2 and 3. The avail-
able literature data on their diffusivities are also
shown on the corresponding plots for comparison.
Table I summarizes their diffusion parameters as
obtained from the least-squares analysis of the dif-
fusion data.

As shown in Fig. 2, no effort was made to obtain
aluminum and gallium diffusivities in silicon under
widely varying surface concentrations and bulk con-
ductivity types and levels. Such studies, performed
earlier,[1,2] for boron, phosphorus, and arsenic in
silicon had produced no detectable dependencies.
As for other dopants, the type of the silicon ma-
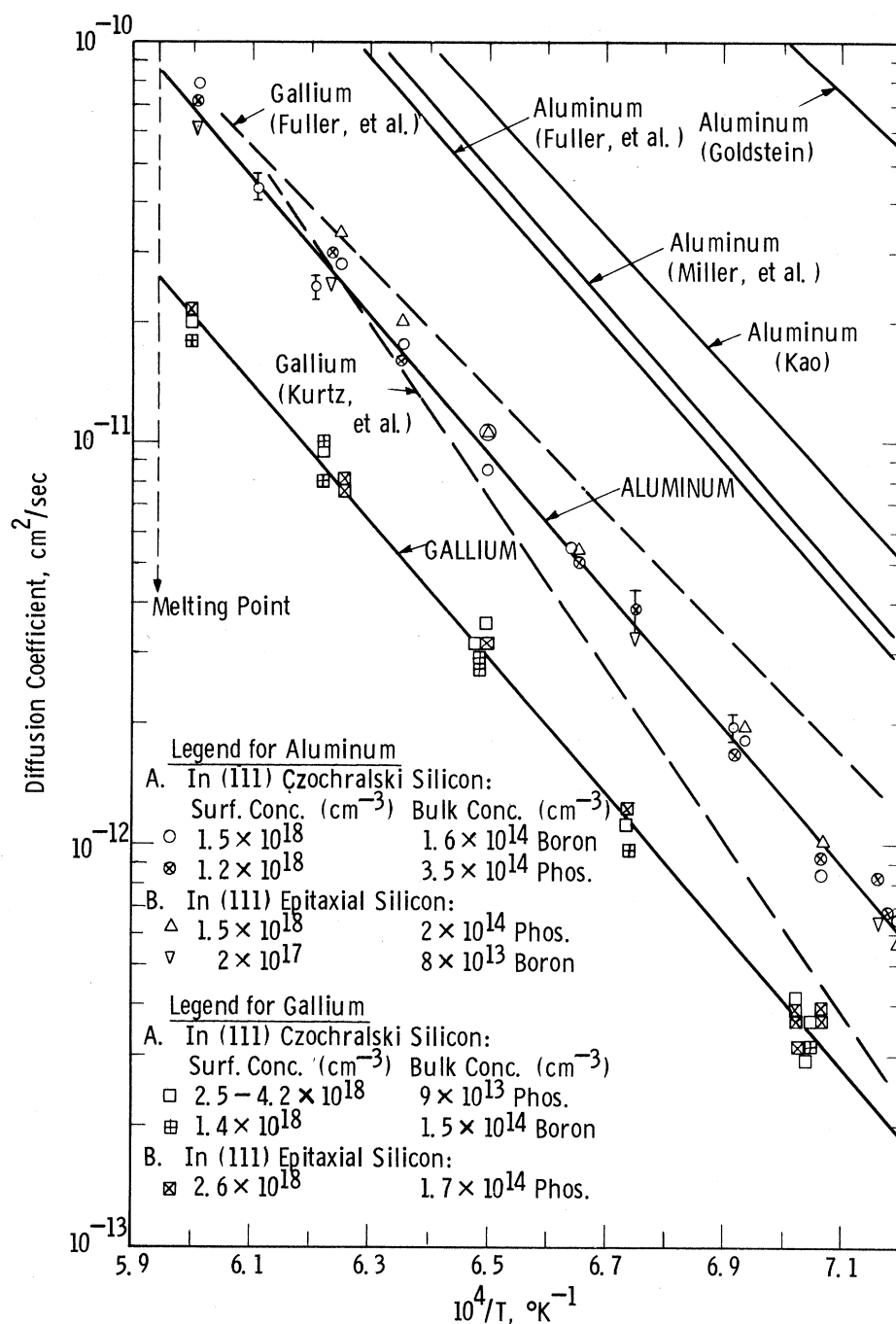terial (epitaxial or Czochralski) made no difference

FIG. 2. Arrhenis plot of aluminum and gallium diffusivities in silicon.

as to the diffusion behavior of both aluminum and gallium. Consequently, the different types of diffusion couple preparation was further simplified for indium and thallium. Even then, only one set of acceptable thallium-doped structures was possible. As a result, only a very limited number of thallium diffusivity data could be obtained. Thus, the diffusion parameters for thallium in silicon, reported under parentheses in Table I, were derived from the few diffusivity data obtained with an esti-

mated value of the activation energy (discussed later). No further effort was considered significant in that direction.

IV. DISCUSSION

A. Comparison with Literature Data

Compared to boron and phosphorus,[1] the reported diffusion studies of aluminum,[5-8] gallium,[5,9,10] indium,[5] and thallium[5] in silicon are, indeed, scanty. Aluminum was almost always used in the elemental
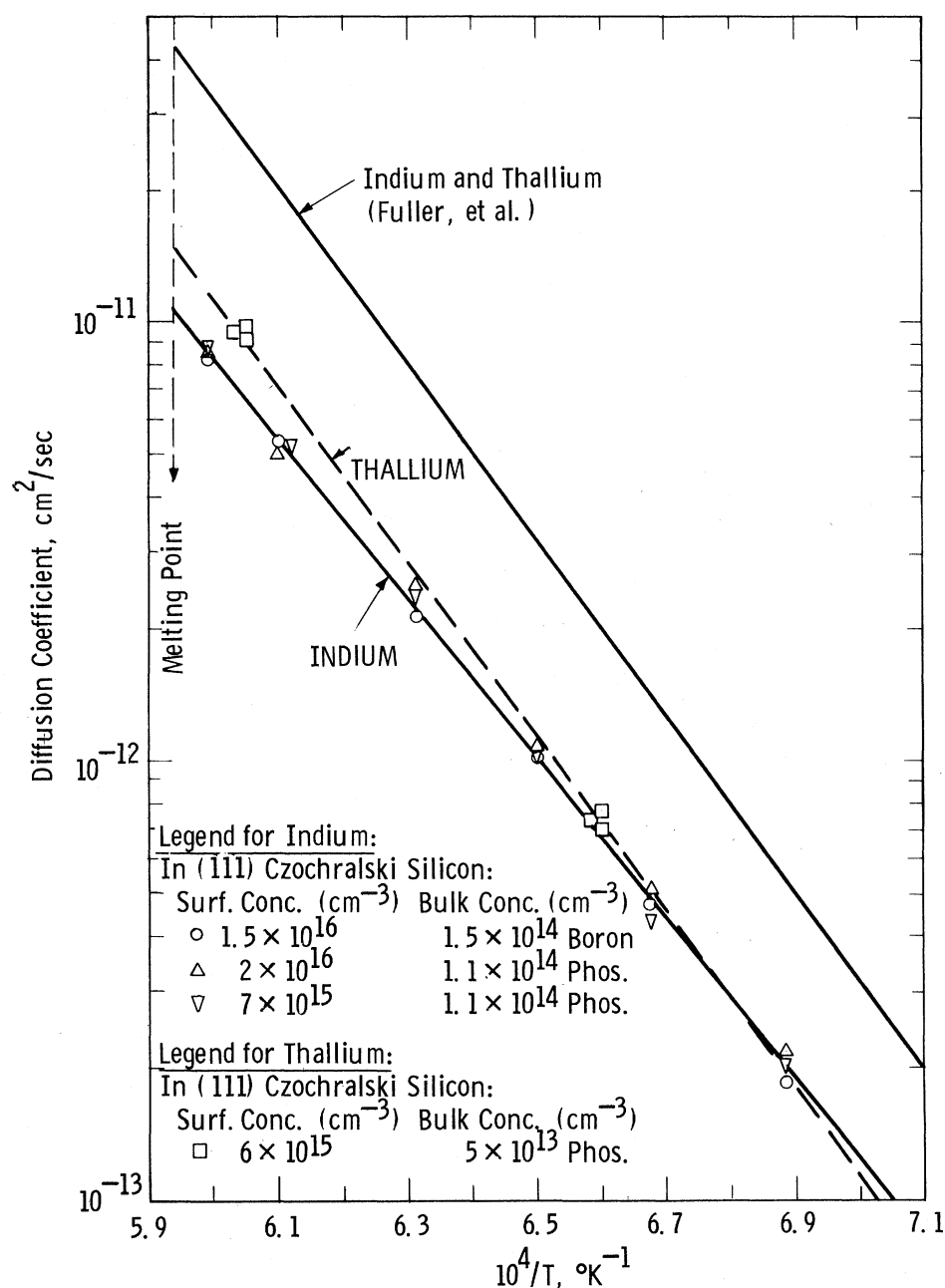
FIG. 3. Arrhenis plot of indium and thallium diffusivities in silicon.

form either in a sealed quartz tube[5,6,8] or in an inert atmosphere.[7] (Too high diffusivity values of Goldstein[6] were probably caused by the fast penetration of the Al-Si eutectic front into the silicon.) Consequently, the difference between the aluminum diffusivity values in the literature and the present work (Fig. 2) can almost be completely ascribed to the effect of the free silicon surface, except for the redox effect of any residual oxygen in the experimental environment. However, the consequences of including this extrinsic surface effect in the diffusion of aluminum in silicon are seen to be far greater in magnitude than in the case of phosphorus.[3]

The relative importance of the free silicon surface, and the oxidation-reduction reactions on it, is probably best illustrated by gallium in silicon. Us-

TABLE I. Acceptor diffusion parameters in silicon $(D = D_0 e^{-E/kT})$.

Acceptor	Temp. range (°C)	D_0 (cm²/sec)	E (eV/atom)
Aluminum	1119–1390	1.385	3.41 ± 0.03
Gallium	1143–1393	0.374	3.39 ± 0.04
Indium	1180–1398	0.785	3.63 ± 0.04
Thallium	1244–1338	(1.37)	(3.70)
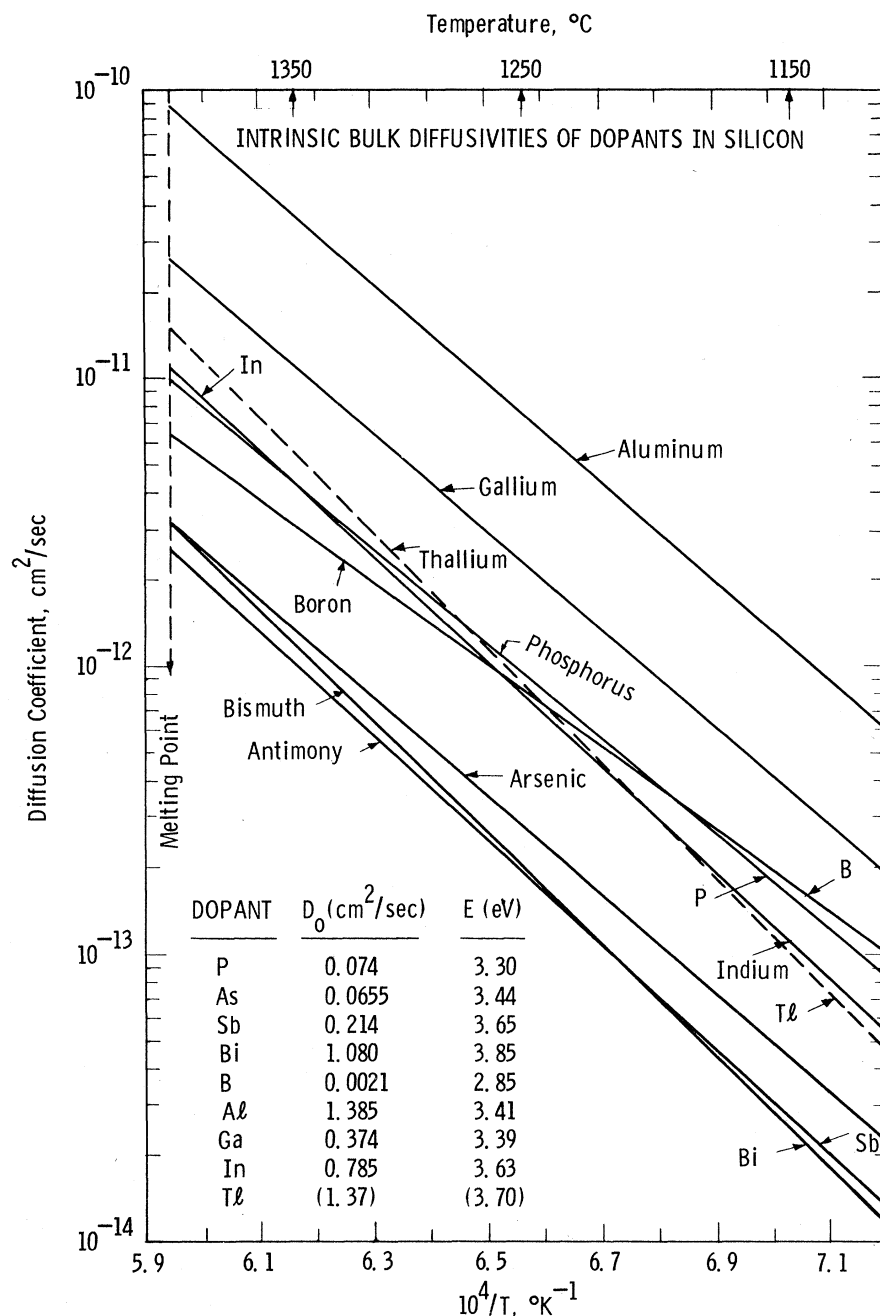
FIG. 4. Intrinsic bulk diffusivities of dopants in silicon free from surface effects.

DOPANT	$D_0 (cm^2/sec)$	E (eV)
P	0.074	3.30
As	0.0655	3.44
Sb	0.214	3.65
Bi	1.080	3.85
B	0.0021	2.85
Aℓ	1.385	3.41
Ga	0.374	3.39
In	0.785	3.63
Tℓ	(1.37)	(3.70)

ing Ga_2O_3, Fuller and Ditzenberger[5] obtained higher diffusivities than Kurtz and Gravel,[9] who used elemental gallium. Above ~1100 °C, their data, in turn, are much higher than those obtained in the present study, where both of these effects were eliminated. The same explanation is valid for the departure of the present indium and thallium diffusion data (Fig. 3) from that in the literature.[5]

B. Mechanism of Acceptor Diffusion

The intrinsic diffusivities of all the group-III and group-V dopants in silicon, determined as a func-

tion of temperature, during this series of investigations are summarized in Fig. 4. As is evident, except for aluminum and gallium, the donors and acceptors are equally slow diffusers. Most of them have very similar activation energies and preexponentials. Any minute difference between their diffusion behaviors may be sought, in turn, in the kinetic properties of the respective point defect predominantly responsible for the diffusional motion. This is rather well understood for the donors[2] in silicon (lattice vacancy-donor associates). Similar information is unavailable for the lattice vacan-

cy-acceptor associates. The limited information on their existence and identification[11,12] points out the instability of such entities.[13] However, certain similarities between the activation energies of diffusion of the donors and acceptors in silicon are observed. This is shown in Fig. 5, where the activation energy of diffusion is seen to be linearly dependent on the covalent radius of the impurity. The vertically lower displacement of such a relationship for group-III dopants probably indicates a lesser intensity of electronic interaction of the vacancy with the acceptors compared to that with the donors. (The activation energy of thallium diffusion, as shown in Table I and Figs. 3 and 4, was extrapolated from this figure to generate the stated preexponential from the limited diffusivity data.) Similar relationship for the activation energy of motion of the donor-vacancy associates was obtained by Hirata et al.[14] Figure 5 also shows the linear relationship of the entropy of donor diffusion with the square of the difference of covalent radii of silicon and the donor atom. It is to be noted that the latter quantity is directly proportional to the strain energy in silicon produced locally by the replacement of a host atom by a substitutional dopant atom.[15]

It would now appear that the mechanism of acceptor diffusion in silicon also involves acceptor-vacancy pair formation and migration. The simple lattice vacancy in such a case would have to behave as a donor. This is consistent with the known amphoteric nature of the silicon lattice vacancy.[12] However, until and unless such defects are properly

characterized, it is probably too premature to analyze the present acceptor diffusion parameters in silicon along the same line as was done for the donors.[2] Furthermore, without more information on the energetics of such point defects, the use of the proper correlation factor remains uncertain.

C. Nature of Extrinsic Effects

The effect of the free surface on the diffusivity of substitutional dopants in silicon can be best visualized by considering the mechanism of the instantaneous evaporation-condensation process simultaneously occurring at the surface. Even in the case where no net mass transfer occurs, the vacant site left behind by the instantaneous removal of a surface atom has a finitely large probability to diffuse into the solid. This is probably particularly true in a case where the mobility of free vacancy is quite large in the solid, as in this case.[16] Now, this in-diffused vacancy can be caught by a substitutional dopant atom to form a pair, with the consequent increase in the effective concentration of the point defect responsible for the dopant diffusion. However, if the starting diffusion front of the dopant is removed far enough from the free surface, the effect of this excess defect concentration, localized near the surface, on the concentration profile (and hence the effective diffusivity) will not be detectable. It appears from general considerations that the depth of separation of this starting diffusion front from the free surface will depend on the intrinsic diffusivity of the dopant, the binding energy of the vacancy-dopant complex (and hence the motion energy), and the temperature of diffusion. The value of this minimum depth of separation, at any temperature, can be experimentally determined by measuring the effective diffusivities of a dopant as a function of the thickness of the epitaxial diffusion source. In the case of indium at 1265 °C, this distance is about 6.2 μ, for a 7-h anneal, i.e., for this time-temperature anneal the indium concentration profile will correctly determine its diffusivity only for starting epi-source thickness of 6.2 μ or more. Otherwise, the apparent diffusivity will be higher than intrinsic. (Similar data for other dopants are not detailed enough to be specific.) This type of procedure was followed throughout this series of investigations for all the group-III and group-V dopants in silicon. It is *particularly noteworthy* that this type of surface effect is unknown in any other diffusand at present.

The nature of the oxidation-reduction reaction between the dopant oxide and elemental silicon on the surface to yield doped silicon was mentioned by Fuller and Ditzenberger[5] and elaborated for aluminum in silicon by Bollough et al.[17] This process also generates free-vacant sites on the surface by the consumption of lattice silicon atoms. It would
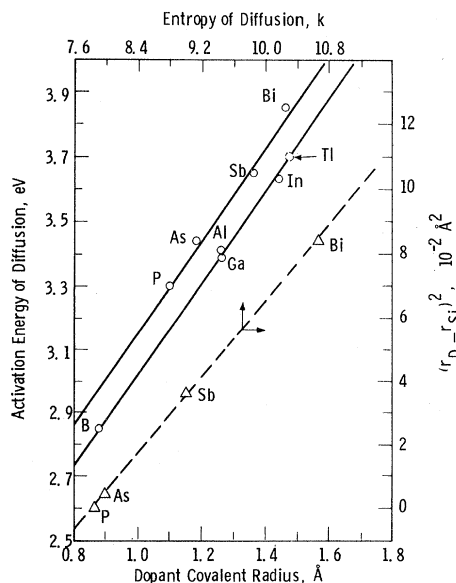

FIG. 5. Observed relationships of the activation energy of diffusion and the entropy of donor diffusion with the covalent radius of the dopant.

thus appear that the rate of this surface oxidation reaction will profoundly influence its effect on the determined diffusivity of a dopant, in addition to all the factors (mentioned earlier) influencing the magnitude of the free-surface effect. It does not appear experimentally possible, however, to determine the effect of this process on the substitutional diffusion in silicon, unequivocally.

D. Further Implications

It is now in order to consider the greater implications of the present dopant diffusion data. First and foremost is the distinct possibility of the existence of such surface effects in the substitutional diffusion in germanium. The activation energy of simple vacancy motion[18] and the literature diffusivity of a particular substitutional dopant (at the same T/T_m, where T_m is the melting point) are very similar for germanium and silicon. These, along with other relevant similarities between these two diamond-structure semiconductors, would cause one to expect, in all probability, that the available literature data on the diffusivity of group-III and group-V dopants in germanium are extrinsic.

Inspection of Fig. 4, along with the recent determinations of self-diffusivity in silicon,[19-21] makes another anomaly evident. Self-diffusion data of Peart[20] and Ghoshtagore[19] are now seen to lie well above, and those of Masters et al.[21] lie very near to the diffusivity data of As, Sb, and Bi near the melting point of silicon. Actually, Ghoshtagore's[19] self-diffusion study in silicon was not pursued to completion because some surface effects were suspected in silicon (of the type described in this paper). It would now be possible to determine intrinsic self-diffusivity in silicon by the present experimental technique using Si-31 tagged SiCl₄ to deposit the epitaxial diffusion source. In the light of a recent determination of the divacancy diffusivity in silicon,[22] the results are expected[23] to be described by $D_{sd} \simeq 30e^{-(4.45eV)/kT}$ cm²/sec in p-type material and $D_{sd} \simeq 15e^{-(4.30 eV)/kT}$ cm²/sec in n-type material. This would lead to a self-diffusivity of $\sim 10^{-12}$ cm²/sec at 1395 °C by the divacancy mechanism.[23] These values of silicon self-diffusivity are very near to those determined by Yoshida et al.[24,25] from the properties of nickel in silicon.

V. CONCLUSION

Under intrinsic conditions, Al, Ga, In, and Tl − like B, P, As, Sb, and Bi − diffuse much more slowly in silicon than has been believed. They are all affected to some extent by the free silicon surface and the oxidation-reduction reactions on it. Both of these extrinsic effects pump vacancies (nonequilibrium) into the host lattice undergoing diffusion. An analysis of the group-III acceptor diffusion data in comparison with the group-V donor diffusion data indicate that both these types of substitutional dopants diffuse by the migration of dopant-vacancy associates, in accordance to an earlier postulation.[23] An extension of the present work is seen to encompass the entire area of substitutional diffusion in silicon and germanium (including self-diffusion).

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Symmetry Analysis of Electroreflectance Spectra

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A systematic study is undertaken of the polarization anisotropies observed in electroreflectance, with the objective of obtaining information about the Brillouin zone (BZ) location and $E(k)$ topology of the transition. The analysis permits the extraction of such symmetry information from properly designed experiments, independent of the details of the spectral line shape, and magnitude and inhomogeneity of the modulating field. It is shown that transitions originating from $\langle 111 \rangle$ and $\langle 100 \rangle$ directions in the BZ can be identified. Criteria are established for determining the validity of the weak-field approximation in calculations of the electro-optic effect, and for determining the effect of the electric field on the transition matrix element. The effect of the electric field on band degeneracies is considered, and their correlation to observed anisotropies is discussed. Comparison of the analytical results with electroreflectance measurements in germanium is made.

I. INTRODUCTION

Semiempirical band models depend on an accurate correlation of optical spectra to critical points in the band structure, as characterized by transition energy, location in the Brillouin zone (BZ), and topology of the interband energy surface.[1] Only the first of these criteria of identification can be directly read out from static reflectance spectra. Consequently, band-structure analysis faces the problem of unfolding the observed one-dimensional sequence of transition energies into the three dimensions of the BZ.

As the source of experimental information in this assignment procedure, modulated reflectance is superior to static reflectance for two reasons. First, the modulated response correlates to localized rather than extended regions in the BZ,[2] thereby giving experimental information which is more directly comparable with calculated energy gaps. Second, modulation by an electric field or a stress establishes a preferred direction and lowers the symmetry of the sample crystal; consequently, anisotropies of the reflectance response are observed as the modulating vector rotates relative to the crystal frame.[3-6] Of the two, the latter has received the least attention. It is the object of this work to examine the diagnostic potential of these anisotropies in electroreflectance (ER).

In an attempt to explain these anisotropies, Phillips[7] suggested that they occur at two different levels. *Nontensorial* anisotropies arise from the

intraband mixing caused by the electric field (the electro-optic effect), complemented by tensorial anisotropies expected to arise from the transition matrix elements. Furthermore, these anisotropies when considered in properly designed ER experiments would then provide information about the BZ location and interband topology of the transition under study.

The present study executes Phillips's suggestion and presents a general method for analyzing directional ER experiments in a manner which allows a direct correlation of the spectra to features of the band structure. It leads considerably beyond a previous study of Bottka and Rössler[8] and generalizes Aymerich and Bassani's treatment of a special case.[9] In goal and spirit, this study is similar to the symmetry analysis of piezoreflectance spectra recently presented by Sell and Kane.[10]

We introduce in Sec. II the basic definitions and assumptions of the symmetry analysis, justifying them by experimental facts. The correlation between the observed change in reflectance $\Delta R/R$ and the dielectric function is then presented.

We describe the change in reflectance by a product — or the sum of products — of two factors representing separately the two levels of anisotropies, tensorial and nontensorial.[7] The nontensorial electro-optic effect is assumed to depend only upon the modulating field. This dependence is strong, both in the magnitude and direction of the electric field. The tensorial factor representing the sampling of the field-perturbed dielectric function by the inci-