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LOCALIZED VIBRATIONAL MODES OF DEFECT PAIRS IN SILICON

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INTRODUCTION

There have been many recent studies⁽¹⁾ of the effect of impurities, both substitutional and interstitial, on the vibrational modes of crystals. The conditions for introducing high frequency localized vibrational modes have been discussed in the literature, and experimental observation of infrared absorption bands associated with localized modes have been reported for a number of systems. Several cases have involved impurities, with concentrations ranging between 10^{16} and 10^{20} cm⁻³, in semiconductor crystals. In many cases the impurity used is an electrical dopant, and the resulting absorption from the large free carrier concentration must be reduced by the introduction of an electrically compensating impurity. This is the reason for some cases involving pairs of impurities.

Of interest to the present study is the experimental work done with B and B-Li impurities in Si. Measurements⁽²⁾ place the triply degenerate localized mode for isolated substitutional B near 624^{-1} cm⁻¹ at liquid nitrogen temperature for ¹¹B and 647 cm⁻¹ for ¹⁰B. Both frequencies are larger than the highest unperturbed silicon phonon frequency of ~ 518 cm⁻¹. When interstitial Li compensates B some rather striking effects have been reported^(3,4). Most of the triply degenerate B band is split, indicating doubly and singly degenerated modes separated by 90 cm⁻¹ with the doubly

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degenerate modes at higher frequency. In addition a band is observed slightly above the top of the unperturbed spectrum. The frequency of this mode is dependent upon the Li isotope but insensitive to the B isotope. A qualitative explanation has been offered in which these bands are related to the formation of ion pairs, $B_{Si}-Li_i$, where B_{Si} is B on a Si site and Li_i is interstitial Li. The point group symmetry at the B and Li sites is reduced from tetrahedral (T_d) to axial (C_{3v}) by the pairing.

This work is an experimental study of Si doped heavily with B and largely compensated with a substitutional donor impurity, i.e. P, As, or Sb. The compensation is completed by diffusing Li. New absorption bands have been observed which can be attributed to B-P, B-As, and B-Sb nearest neighbor pairs. In some cases, notably B-P, the strength of some of the absorption bands depends upon the time and temperature of Li diffusion. This latter effect is interpreted in terms of impurity precipitation.

EXPERIMENTAL METHOD

Silicon ingots were pulled from a melt of high purity Si and the desired impurities. The B and Sb were introduced in elemental form while P and As were added as $Ca_3(PO_4)_2$ and $Ca_3(AsO_4)_2$. In most cases B and the donor impurity were added to the melt simultaneously with concentrations adjusted to make the crystal p-type but, where possible, nearly compensated. The B concentration $[B]$ was always $\geq 10^{20} \text{cm}^{-3}$ while the donor concentrations varied from near 10^{20}cm^{-3} for [P], $5 \times 10^{19} \text{cm}^{-3}$ for [As], and $\sim 2 - 3 \times 10^{19} \text{cm}^{-3}$ for [Sb]. The samples were single crystal or polycrystalline with crystallinities of several nms. in dimension. The B used was enriched ^{11}B , i.e. 98% ^{11}B and 2% ^{10}B . Four point probe measurements of the resistivity ρ gave values consistent with the doping levels. The silicon was diffused with natural Li, i.e. $\sim 93\%$ ^7Li and 7% ^6Li . The resulting compensated samples had $\rho \geq 100 \Omega \text{cm}$. The times, temperatures, and conditions for Li diffusion have already been discussed^(4,5). Spectral half widths were always less than 1.0cm^{-1} wave number and generally near 0.5cm^{-1} . All optical measurements were made at liquid nitrogen temperature.

EXPERIMENTAL RESULTS

A. Localized Mode Frequencies

In Fig. 1 results are shown for three samples, each doped with ^{11}B , a substitutional donor, and Li. The term donor will be used only for the substitutional donor impurity and not for the diffused Li. The bands near 523, 536, 566, 586, 622, and 656 agree closely with bands reported for samples not containing the donor. These absorption bands are related to the presence of B

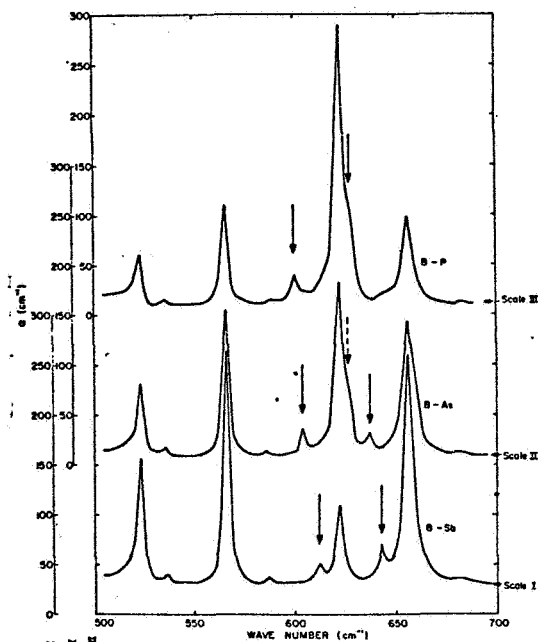


Figure 1

and Li. New bands⁽⁶⁾ have been observed for each donor, and their positions in Figure 1 are indicated by the arrows. There are two bands in each case with a possible third one in the B-As sample. The frequencies depend upon the donor employed. In a B-P crystal the new bands have very nearly the same isotope shift as isolated B band. Measurements at 5°K gave nearly the same results as those obtained at nitrogen temperature. The line widths and absorption peak positions as a function of temperature for the new band are, within experimental accuracy, the same as for the isolated B line. Several B-P doped ingots have been grown and the new bands are present

in all cases. An ingot was doped with B and elemental Ca, and Li compensated. The concentration of Ca introduced was the same as that by the $Ca_3(PO_4)_2$ and only B and B-Li bands were observed.

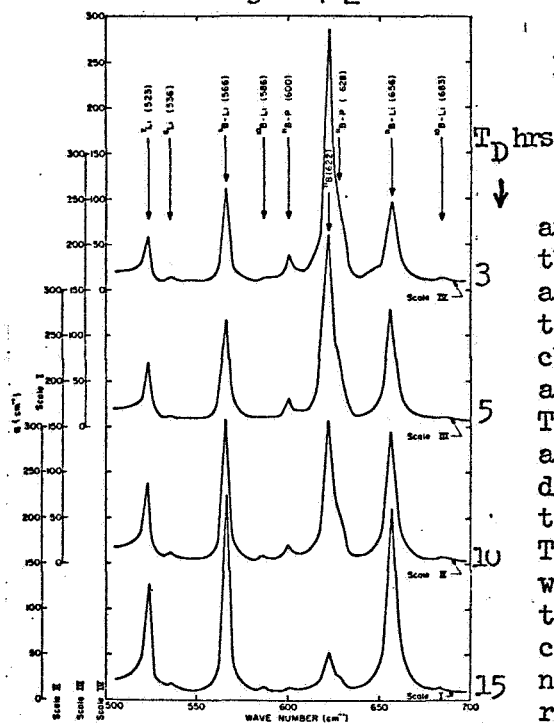


Figure 2

B. Dependence of Absorption Band Intensities on Li Diffusion Conditions

In B-P doped samples the relative intensities of several of the local mode absorption bands are a function of the time and temperature of Li diffusion. The change is indicated in Fig. 2 for a set of four B-P doped samples. The samples were adjacent to one another in the ingot and all Li diffused at 800°C. The diffusion time ranged from 3 to 15 hours. There is a decrease in strength with increase in the diffusion time for both the $622cm^{-1}$ with a concomitant increase in the bands near 656, 566, and $523cm^{-1}$. The relationship between these changes is demonstrated in Fig. 3 where

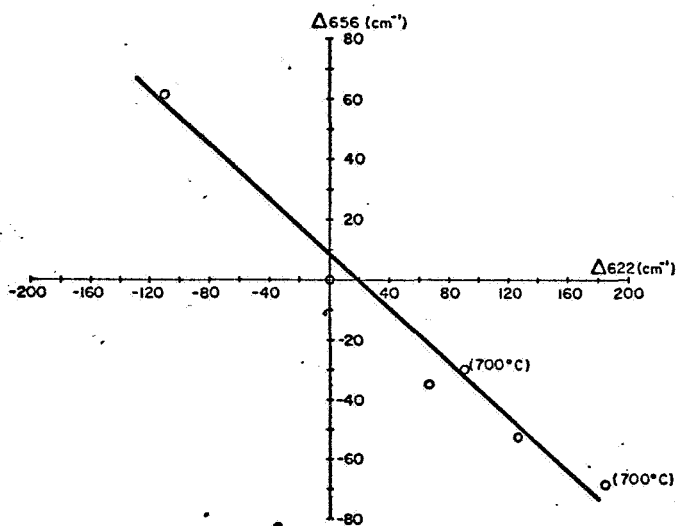


Figure 3

the scatter of the data, the points indicate a linear relation given by $\Delta 622 = -(0.45) \Delta 656$. The same result is obtained if the 566cm^{-1} band is used in place of the 656cm^{-1} .

No such effect has been observed in the B-As doped samples. The B-Sb samples show a small decrease in band strength for all bands with longer times of diffusion at 800°C as well as an increase in the apparent background absorption.

DISCUSSION OF RESULTS

A. Localized Mode Frequencies

Table I lists the local mode absorption bands observed in the present measurements. Frequencies are the position of the peak absorption coefficient. The new bands have been labeled as $^{11}\text{B-P}$, $^{11}\text{B-As}$, and $^{11}\text{B-Sb}$ pair bands. The reasons for this assignment are similar to those used to establish the identification of the B-Li pair bands⁽⁴⁾. The nearly full B isotopic shift, the proximity to the isolated B line, and the shift in frequency with change in donor species indicate the identification of the vibrational modes as ones which primarily involve B motion but the point group symmetry at the B site has been lowered from T_d to C_{3v} by the nearest neighbor substitutional donor. The triply degenerate isolated ^{11}B mode should be split into two bands with one twice the strength of the other. If the donor were a 2nd nearest neighbor, the symmetry becomes C_{2v} and three bands could result but with reduced splittings. In the B-P and B-Sb cases only two bands are observed. In the B-As case there is a third band near 627cm^{-1} . We tentatively ascribe this latter band to an unresolved second nearest neighbor interaction where the remaining structure is

the change in the 622cm^{-1} band peak height is plotted against that of the 656cm^{-1} band. The changes are measured with respect to the second sample from the bottom in Fig. 2 where both bands are nearly the same. Included in Fig. 3 are two samples labeled (700°C) . One was diffused for 8 hours (point with $\Delta 622=186\text{cm}^{-1}$) and the other for 96 hours at that temperature. Within

- Fig 3

TABLE I

Liquid Nitrogen Temperature Frequencies of Absorption Bands

Band	$^{11}\text{B}-^7\text{Li}$	$^{10}\text{B}-^7\text{Li}$	$^{11}\text{B}-\text{P}$	$^{11}\text{B}-\text{Sb}$	$^{11}\text{B}-\text{Sb}$
B-Li Pair	656.1 ± 0.6	683	---	---	---
Bands	566.1 ± 0.6	586	---	---	---
B Band	622.2 ± 0.5	647	---	---	---
Li Band	523.3 ± 0.5	523.3 ± 0.5	---	---	---
B-Donor	---	---	~ 628	636.7 ± 0.4	642.7 ± 0.3
Bands	---	---	600.1 ± 0.5	603.7 ± 0.3	611.9 ± 0.3
	---	---	---	~ 627	---

under the large 622 isolated ^{11}B line.

The relative strengths of the B-(Donor) bands are difficult to determine as they are weak and close to the strong isolated B and B-Li bands. An estimate is made by assuming the background in the region of B-D bands to be a constant plus the tails of the nearby major bands. The absorption tails are estimated by assuming at each local mode can be represented by a collection of non-interacting harmonic oscillators of resonance frequency ν_0 . This model gives an absorption coefficient

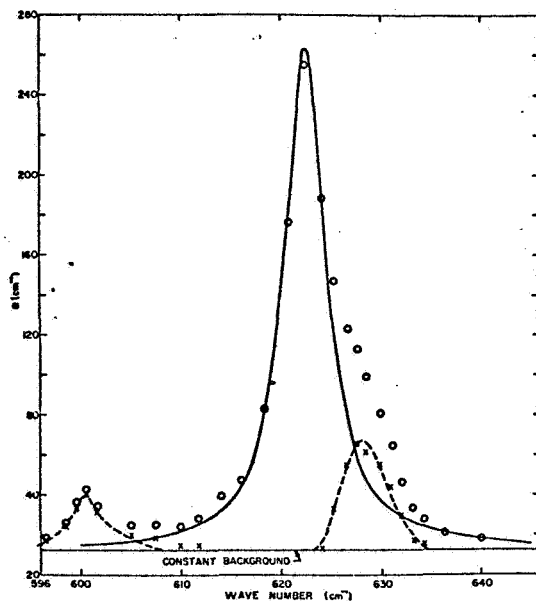


Figure 4

$$\alpha = \frac{C}{n} \left\{ \frac{\nu^2}{(1-\nu^2)^2 + \nu^2 \delta^2} \right\},$$

where ν and δ are the frequency and damping constant normalized by the resonance frequency, n the refractive index, and C a constant. It is assumed that n is independent of frequency. Figure 4 shows the curve fitting for a B-P sample. The only major band close enough to the B-P pair bands to have any effect is the isolated ^{11}B band at 622cm^{-1} . C/n was adjusted to give $\alpha_{\text{peak}} = 250\text{cm}^{-1}$ with δ of 0.008 (5.0cm^{-1}). Measurements over a more extended frequency range indicate that for this sample, $\alpha_{\text{background}} = 14\text{cm}^{-1}$. Subtraction of

TABLE II

Sample	$\int \omega_{adv} \text{ (cm}^{-2}\text{)}$	
	High frequency pair band	Low frequency pair band
B-P	297	133
B-P	200	132
B-As	65	110
B-Sb	120	90

$\alpha_{\text{background}}$ and the calculated curve from the measured data points give the dashed curves in Fig. 4.

The results for estimates of $\int \omega_{adv}$ for the pair bands in several samples are given in Table II.

While the results are not conclusive, they suggest that the high frequency band is the doubly degenerate one for B-P and B-Sb and the low frequency one for B-As. Comparison of the total integrated absorption of the B-Donor pair bands to that for isolated B gives $\Sigma_{\text{pair}} \int \omega_{adv} = 0.1$ to $0.2 \int \omega_{adv}$ for both B-P and B-As and 0.4 to $0.5 \int \omega_{adv}$ for B-Sb. The difference could arise either from a somewhat larger pairing energy for the B-Sb case or from the equilibrium configuration for B-Sb being characteristic of a somewhat lower temperature. The latter case would imply a larger diffusion constant for Sb than for As and P which is not in agreement with published data. (7)

The qualitative conclusions given here are in general agreement with the recent theory of Elliott and Pfeuty. (8) They calculate the effect of pairs of defects on the lattice modes by using Green's function methods. Of particular interest are their calculations for the frequencies of the localized modes of defect pairs in silicon where one of the defects is B_{Si} and the other a substitutional mass M_2 . Their results for no change in force constants are reproduced here in Figure 5. The solid lines are for ^{11}B , the dashed for ^{10}B , ω_M the maximum unperturbed Si phonon frequency, and M the Si mass. For the cases studied here the mass defect $\epsilon_2 < 0$ and only two modes should be observed, those labeled modes 1 and 2 on Fig. 5. The theory indicates that in both modes B motion dominates. The fact that the observed splitting of modes 1 and 2 is much larger than that given in Fig. 5 is evidence that a change in force constant is necessary. The increase in frequency of the pair bands as one goes from P to As to Sb is in the same order as the tetrahedral covalent radii which are

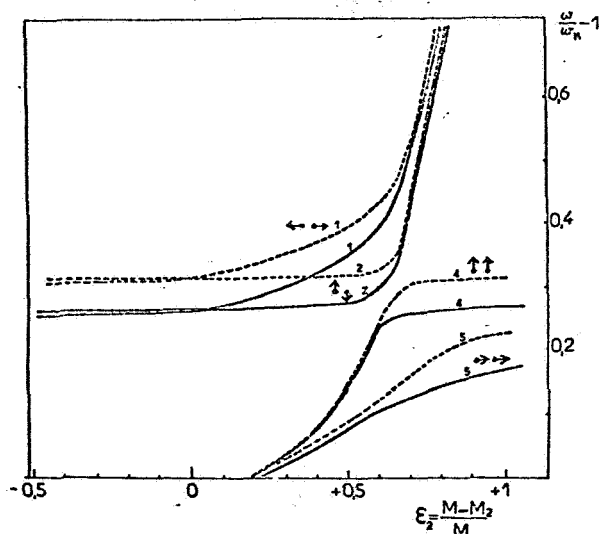


Figure 5

and M the Si mass. For the cases studied here the mass defect $\epsilon_2 < 0$ and only two modes should be observed, those labeled modes 1 and 2 on Fig. 5. The theory indicates that in both modes B motion dominates. The fact that the observed splitting of modes 1 and 2 is much larger than that given in Fig. 5 is evidence that a change in force constant is necessary. The increase in frequency of the pair bands as one goes from P to As to Sb is in the same order as the tetrahedral covalent radii which are

1.10, 1.18, and 1.36Å respectively.⁽⁹⁾

B. Impurity Precipitation Effects

It was observed that $\Delta 622 = -(0.45) \Delta 656 = -(0.45) \Delta 566$. With the half widths of 7.0cm^{-1} for the 656cm^{-1} band, 4.5cm^{-1} for 566cm^{-1} band and 5.0cm^{-1} for the 622cm^{-1} band it is observed that the change in f_{adv} for the isolated B band is equal and opposite in sign to the total f_{adv} for the B-Li pair bands. This result indicates that the total substitutional [B] does not change, and the total absorption strength per center is the same for isolated B and B-Li pairs. This result, the assumption that the isolated B concentration equals the isolated substitutional P concentration, and the data for B-Li doped samples may be used to express the strength of the bands in terms of the concentration of the different defects. In these estimates the B-D pairs were neglected since their absorption bands indicate the concentrations to be relatively small.

The results of Fig. 2 are consistent with a model involving P precipitation or any other process which removes P as an electrically active dopant. From the strength of the 622cm^{-1} band, the substitutional [P] is found to decrease from $9 \times 10^{19}\text{cm}^{-3}$ to $\sim 14 \times 10^{19}\text{cm}^{-3}$ after 15 hrs. of Li diffusion at 800°C . It is known⁽¹⁰⁾ that the solid solubility of a donor may be considerably enhanced by a large concentration of acceptors. Annealing of B-P doped samples for 17 hrs. at 740°C had no effect on either the resistivity or on the local mode strengths obtained after Li diffusion. During Li diffusion, Li compensates the excess [B] which leads to a decrease in the solubility of P to a value near that in Si without acceptors. Processes of precipitation of P in Si and in Ge-Si alloys have been reported^(11,12) for concentrations similar to those used in the present experiments. At 800°C the time constant for achieving the equilibrium [P] is ~ 10 hrs. while at 700°C the time constant ≥ 1000 hrs. These time constants are only approximate as the data are not sufficient to establish the kinetics of the process. Unfortunately, the present authors have been unable to find data on the P solid solubility in Si at 800°C .

The B-As doped samples with [As] of $5 \times 10^{19}\text{cm}^{-3}$ did not show any decrease in [As] with Li diffusion at 800°C indicating that the As solid solubility is above this concentration.

In the B-Sb case the [B] $\sim 1.9 \times 10^{20}\text{cm}^{-3}$ and [Sb] $\sim 2.5 \times 10^{19}\text{cm}^{-3}$. Although changes are small compared to those observed in the B-P case, comparison of samples Li diffused at 800°C indicates a decrease of $\sim 20\%$ in the isolated Sb concentration as a result of long term diffusion. The Sb concentration is close to the published⁽¹³⁾ solid solubility data at 800°C which indicates $\sim 2 \times 10^{19}\text{cm}^{-3}$. In addition a decrease is observed in the total

substitutional B concentration to $\sim 1.4 \times 10^{20} \text{cm}^{-3}$. This concentration is close to the [B] in the B-P doped samples where no B precipitation was observed.

REFERENCES

- (1) For a discussion of this topic see A.A. Maradudin, Solid State Physics (Edited by F. Seitz and D. Turnbull, Academic Press, New York, 1966) Vols. 18, 273.
- (2) J.F. Angress, A.R. Goodwin, and S.D. Smith, Proc. Roy. Soc. (London) 287A, 64 (1965).
- (3) M. Balkanski and W.A. Nazarewicz, J. Phys. Chem. Solids 27, 671 (1966).
- (4) M. Waldner, M.A. Hiller, and W.G. Spitzer, Phys. Rev. 140, A172 (1965); also W.G. Spitzer and M. Waldner, J. Appl. Phys. 36, 2450 (1965).
- (5) E.M. Pell, J. Phys. Chem. Solids 3, 77 (1957).
- (6) V. Tsvetov, W. Allred, and W.G. Spitzer, App. Phys. Letters, 10, p. 326 (1967).
- (7) H. Reiss and C.S. Fuller, Semiconductors (Edited by B. Hannay, Reinhold Publishing Co., New York, 1959) p 244.
- (8) R. Elliott and P. Pfeuty, J. Phys. Chem. Solids (to be published).
- (9) L. Pauling, The Nature of the Chemical Bond (Cornell Univ. Press, Ithaca, New York, 1960) p 246.
- (10) H. Reiss, C.S. Fuller, and F.J. Morins, Bell System Technical Journal 35, 535 (1956).
- (11) M.L. Joshi and S. Dash, IBM Journal of Research and Development 10, 446 (1966).
- (12) L. Ekstrom and J.P. Dismukes, J. Phys. Chem. Solids 27, 857 (1966).
- (13) F.A. Trumbore, Bell System Technical Journal 39, 205 (1960).