Orientation Dependence of Electron Radiation Damage in InSb*

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The damage rate in (111)-oriented samples of InSb has been measured with the (111) face perpendicularly exposed to the incident electron beam and with the $(\bar{1}\bar{1}\bar{1})$ face similarly exposed. When the damage is separated into the portion which recovers in stage I and that which recovers in stage II, it is found that the defects which annihilate in stage II are produced at lower energies than those annihilating in stage I. Also, the defects annihilating in stage II are produced at a higher rate in samples with the (111) face exposed to the electron beam than in samples with the $(\bar{1}\bar{1}\bar{1})$ face exposed. The production rate of defects annihilating in stage I is higher when the $(\bar{1}\bar{1}\bar{1})$ face is exposed to the beam. These data are interpreted in terms of the polarity of the InSb lattice in the ⟨111⟩ direction to show that the defects which annihilate in stage I are produced by the displacement of antimony atoms with a threshold displacement energy lying between 8.5 and 9.9 eV, and the defects which annihilate in stage II are produced by the displacement of indium atoms with a threshold displacement energy of about 6.4 eV. It is also possible to conclude that the likely direction of the minimum displacement energy in InSb is the ⟨111⟩ direction.

I. INTRODUCTION

A KNOWLEDGE of the threshold displacement energy, i.e., the minimum pulse of energy required to displace a lattice atom to an interstitial position, is fundamental to the understanding of the production of radiation damage in solids. The measurement of this quantity has been carried out in several semiconductor materials. The most extensive study of this nature was carried out in germanium by Brown[1] and involved the measurement of the dependence on crystallographic orientation of damage production (i.e., the rate of change of electrical conductivity), in addition to measurement of the threshold displacement energy. Threshold measurements have been carried out in silicon and germanium by Rappaport and Loferski[2] and in InP, GaAs, and InAs by Bauerlein[3] using a technique which is sensitive to changes in minority carrier lifetime. In InSb, previous measurements[4] by the author indicate that the threshold electron energy for damage production in *n*-type InSb is near 250 keV, corresponding to an energy transfer of about 6 eV to an indium or antimony atom. These data were analyzed subsequently by Bauerlein[3] in a manner which indicated that there were two thresholds observed and the lower energy threshold was taken as that for indium displacements with the higher one being attributed to antimony displacements. There was, however, no direct experimental evidence that this assignment of thresholds was correct. The present work makes use of the polarity of the InSb lattice in the ⟨111⟩ direction to obtain experimental evidence for the assignment of threshold energies for indium and antimony displacements. The results show that the threshold for indium is indeed lower than that for antimony; but that the higher threshold energy revealed by Bauerlein's analysis of the earlier data is not that for antimony.

II. EXPECTED EFFECTS OF ⟨111⟩ POLARITY IN InSb ON DAMAGE PRODUCTION RATES NEAR THE THRESHOLD DISPLACEMENT ENERGY

The identification of indium and antimony threshold energies is made possible by the fact that, viewed along the [111] direction, the order of the atoms in InSb, which crystallizes in the zincblende structure, is In, Sb, −, −, In, Sb, −, −, (− indicates an empty position which could be occupied by an indium atom or an antimony atom without appreciable distortion of the lattice) and in the $[\bar{1}\bar{1}\bar{1}]$ direction the order is reversed[5] (see Fig. 1). It is reasonable to assume, therefore, that it is easier to displace an indium atom in the $[\bar{1}\bar{1}\bar{1}]$ direction than in the [111] since it would be moving into an empty space in the $[\bar{1}\bar{1}\bar{1}]$ displacement but would encounter an antimony atom in the [111] displacement. Likewise, it should be easier to displace an antimony atom in the [111] direction than in the $[\bar{1}\bar{1}\bar{1}]$ direction.

Kohn[6] has suggested that displacements in germanium should be easiest if the struck atom moves in the ⟨111⟩ direction, this being the direction of maximum symmetry with respect to its neighbors. It seems reasonable to believe that this may also be the easiest direction in which to produce displacements in InSb.[7]

* This work was in part supported by the U. S. Atomic Energy Commission.

[1] W. L. Brown and W. M. Augustyniak, J. Appl. Phys. **30**, 1300 (1959).

[2] J. J. Loferski and P. Rappaport, Phys. Rev. **111**, 432 (1958).

[3] R. Bauerlein, Z. Naturforsch. **14a**, 1069 (1959); *Radiation Damage in Solids* (Academic Press Inc., London, 1963), p. 358; Z. Physik **176**, 498 (1963).

[4] F. H. Eisen and P. W. Bickel, Phys. Rev. **115**, 345 (1959).

[5] The faces and directions are labeled as in C. Hilsum and A. C. Rose-Innes, *Semiconducting III-V Compounds* (Pergamon Press, Inc., New York, 1961), p. 8. The notation [111] is used to indicate a particular direction, whereas ⟨111⟩ indicates a class of directions which includes the [111], $[\bar{1}\bar{1}\bar{1}]$, $[\bar{1}11]$, etc.

[6] W. Kohn, Phys. Rev. **94**, A1409 (1954); and (private communication).

[7] It is possible that neither of the two empty positions through which a displaced atom would pass along the ⟨111⟩ direction would be stable interstitial positions, but that some position further from the vacancy and somewhat off a line in the ⟨111⟩ direction might have to be reached in order to produce a stable defect. In this case the direction of minimum displacement energy might be slightly off the ⟨111⟩ direction. The considerations as to whether indium or antimony displacements should be easier in a given ⟨111⟩ direction should still hold in this case.

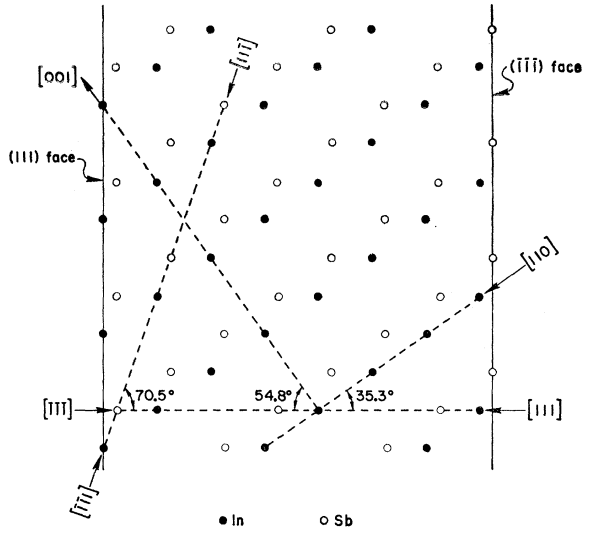

FIG. 1. Plan view of the (1̄10) plane in InSb. Note that, as mentioned in the text, if electrons are incident from the left perpendicular to the (111) surface they travel in the [1̄1̄1̄] direction in the crystal so that indium displacements are "easy" since the indium atom can move into empty spaces in the lattice. If the electrons are similarly incident from the right on the (1̄1̄1̄) surface they travel in the [111] direction and indium displacements are "hard" since an indium atom would collide with an antimony atom in moving in the [111] direction. Likewise the [11̄1̄] direction which is also shown in the figure is seen to be an "easy" direction for indium displacements and the [1̄11] is seen to be a "hard" direction. The relationship of the ⟨100⟩ and ⟨110⟩ directions to the ⟨111⟩ is illustrated by the labeling the [001] and [110] directions which also lie in the (1̄10) plane. Note the lack of polarity in either of these directions, so that the probability of a displacement in one of these directions is independent of whether the electron beam is incident on the (111) surface or the (1̄1̄1̄) surface.

Let us assume this and consider the displacement of indium atoms in a pair of samples, one with the (111) face perpendicularly exposed to the incident electron beam so that, neglecting the multiple scattering of the electrons, electrons travel in the [1̄1̄1̄] direction in the sample and indium displacements are easy; the other, with the (1̄1̄1̄) face exposed so that indium displacements are hard. The energy, T, which is transferred to a lattice atom by an electron is given by:

$$T = T_m \cos^2\gamma, \tag{1}$$

where T_m is the maximum possible energy transfer to an atom by an electron and γ is the angle between the incident electron direction and the direction of the initial impulse given by the electron. We denote the threshold energy for displacement of indium atoms in the [1̄1̄1̄] direction by $\bar{T}_d$ and that for the [111] direction by T_d. In the (111)-oriented sample, displacements will begin to be produced when $T_m = \bar{T}_d$. In the (1̄1̄1̄)-oriented sample displacements would be produced when $T_m = T_d$, which is expected to be substantially higher than $\bar{T}_d$. There is another manner in which displacements may be produced in this sample stemming from the fact that the [1̄11], [11̄1], and [111̄] directions are crystallographically and polarigraphically equivalent to the [1̄1̄1̄] direction and are thus easy displacement directions with displacement energy $\bar{T}_d$. These directions make angles of 70.5° with the direction of the electron beam in the (1̄1̄1̄)-oriented sample. Displacements would be produced along these directions when the electron energy becomes high enough that

$$T_m = \bar{T}_d/\cos^2\gamma = 9\bar{T}_d.$$

Thus, if electrons were not scattered in the sample, the production of indium displacements in the (1̄1̄1̄)-oriented sample would begin at $T_m = 9\bar{T}_d$ or $T_m = T_d$, whichever is lower. The effect of the multiple scattering of the electrons is to wipe out the original orientation of the beam in the sample in distances of the order of 0.001 in. in InSb. It then becomes possible for electrons of lower energy to produce displacements in the (1̄1̄1̄)-oriented sample in oblique [1̄1̄1̄]-type directions, since the scattering gives rise to reduced values of γ in Eq. 1.

It is difficult to calculate precisely the effects due to multiple scattering of the electrons. Near threshold, the displacement rate for indium would be much lower in the (1̄1̄1̄)-oriented sample than in the (111)-oriented sample. This is due to the fact that as the electrons penetrate the sample they lose energy in addition to being scattered, and as the average angle through which the electrons have been scattered increases the average energy of the electrons decreases. Therefore, close to threshold few if any of them will be scattered sufficiently and still have enough energy to produce displacements when the (1̄1̄1̄) face is exposed to the electron beam. As the bombarding energy is increased the ratio of the damage rate in the (1̄1̄1̄)-oriented sample to that in the (111)-oriented sample should increase, since more electrons will now be scattered and still be energetic enough to produce displacements. The damage rates for the two differently oriented samples may remain unequal at energies which are quite far above threshold and in samples which are thick enough that the original orientation of the electron beam has been completely wiped out. This follows since there can be no displacements of indium atoms in the (1̄1̄1̄)-oriented sample (assuming the electron energy is not sufficiently high that $T_m \geq T_d$ or $T_m \geq 9\bar{T}_d$) until some scattering of the bombarding electrons has occurred. This will result in a region near the surface of the (1̄1̄1̄)-oriented sample in which the defect concentration is lower than it is near the surface of the (111)-oriented sample, producing a difference in the measured damage rates for the two differently oriented samples which may persist at electron energies which are considerably higher than the threshold electron energy for damage production. Wolff[8] has calculated the effects of multiple scattering of the electrons on the orientation dependence experiments in germanium and his results are similar to

[8] P. A. Wolff (private communication).

the qualitative considerations presented above. In summary, considering only the displacement of indium atoms and if the threshold displacement energy has a minimum in the ⟨111⟩ direction in InSb, then we expect to observe a difference in damage rates between the (111) and $(\bar{1}\bar{1}\bar{1})$-oriented samples and a decrease in the ratio of the damage rate in the (111)-oriented sample to that in the $(\bar{1}\bar{1}\bar{1})$-oriented sample as the electron energy increases.

It is also of interest to consider the possibility that the threshold displacement energy may be lower in the ⟨100⟩ or ⟨110⟩ direction than in the ⟨111⟩ direction. There is no polarity of the lattice in these directions, so that displacements will be produced at the same rate whether the (111) face or the $(\bar{1}\bar{1}\bar{1})$ face is exposed to the electron beam. Assuming for the moment that the threshold energy is an absolute minimum in one of these directions (we denote this energy by T_d' without designating the direction for which such a minimum exists) and neglecting the scattering of the electrons, displacements can only be produced in that direction if T_d' is not greater than the maximum possible energy transfer in that direction; i.e., if $T_d' \leq T_m \cos^2\theta$, where θ is the angle between the direction of the absolute minimum threshold energy and the ⟨111⟩ direction ($\theta = 35.3°$ for the ⟨110⟩ direction and 54.8° for the ⟨100⟩ direction). If $T_d' < \bar{T}_d \cos^2\theta$, damage would be observed with equal damage production rates in the (111)-oriented and $(\bar{1}\bar{1}\bar{1})$-oriented samples when the electron energy is below the threshold for the production of displacements in the $[\bar{1}\bar{1}\bar{1}]$ direction but still high enough to transfer an energy T_d' in a direction making an θ with the $[\bar{1}\bar{1}\bar{1}]$ direction (we are still considering only the displacement of indium atoms), i.e., when $T_d'/\cos^2\theta < T_m < \bar{T}_d$. If $T_d' > \bar{T}_d \cos^2\theta$ displacements can only be produced, for $T_m < \bar{T}_d$, as a result of the multiple scattering of the electrons. In this case damage would be produced when $T_d' < T_m < \bar{T}_d$ but the damage rate for a given value of T_m would decrease as T_d' approached $\bar{T}_d$ and therefore the tendency for the damage production rates in the two samples to become equal as T_m approaches or becomes slightly less than $\bar{T}_d$ would decrease and eventually disappear.

III. EXPERIMENTAL

To search experimentally for polarity effects, a pair of 0.005-in.-thick, bridge cut, n-type InSb samples were mounted together so that one sample had the (111) face exposed to the incident electron beam and the other had the $(\bar{1}\bar{1}\bar{1})$ face exposed. It was possible to reverse the orientation of the pair of samples so that damage-rate data were obtained with each side of both samples exposed to the electron beam. The samples were cut from oriented slices obtained from Cominco Products, Spokane, Washington, polished by the supplier to a Linde "B" finish. They had electron concentrations of about 10^{14} cm^{-3} and mobilities of 4.5×10^5 cm^2/V sec. Identification of the faces was accomplished by the use of a chemical etch (0.4N Fe^{3+} in concentrated HCl) which develops etch pits on {111} faces but not on $\{\bar{1}\bar{1}\bar{1}\}$ faces[9] (the {111} faces are the (111), $(\bar{1}\bar{1}1)$, $(\bar{1}1\bar{1})$, and $(1\bar{1}\bar{1})$ faces; the $\{\bar{1}\bar{1}\bar{1}\}$ faces are the $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}11)$, $(1\bar{1}1)$, and $(11\bar{1})$ faces).

The samples were irradiated simultaneously with electrons from a horizontal Van de Graaff accelerator. The beam was passed through a 0.00025-in. aluminum scattering foil in order to insure uniform irradiation of both samples. For energies above 300 keV the foil was about 20 in. from the samples. For lower energies it was 5 in. from the samples. The accelerator voltage was stable to within ± 2 keV. The generating voltmeter was calibrated against the threshold for the $C^{12}(d,n)N^{13}$ reaction at 328 keV.[10] The high-energy limit of the accelerator was about 500 keV.

The samples were mounted in a cryostat designed for use with the horizontal accelerator. A heat switch, basically the same as that previously described for use with a vertical accelerator,[11] was used with a heater and temperature control system, of the type previously described,[11] to permit annealing of the irradiated samples. Most irradiations and subsequent measurements were carried out at liquid-nitrogen temperature, though some were performed at liquid-helium temperature, as will be discussed later. Measurement of the Hall coefficient and electrical conductivity were carried out by standard potentiometric techniques. The carrier removal rate, $d\bar{n}/dN_e$ (carrier concentration change per cm^3/number of bombarding electrons per cm^2), was calculated from the change in the Hall coefficient. The Hall coefficient was used instead of the electrical conductivity because appreciable changes in the electron mobility were produced by the irradiation; the use of conductivity to compute the change in carrier concentration, assuming no change in mobility, would result in carrier removal rates which were approximately a factor of 2 too high. It is assumed that the carrier concentration calculated from the measured Hall coefficient is approximately the average carrier concentration in the sample, even though the carrier concentration is somewhat nonuniform in the direction of the electron beam (due to the decrease in damage production rate which results from the degradation of the electron energy as the electrons penetrate the sample), especially near the threshold energy. This assumption is supported by the observation of an initial linear dependence of the change in carrier concentration on integrated beam current and by the fact that the ratio of the $d\bar{n}/dN_e$ computed from the Hall coefficient change to that computed from the change in electrical conductivity, assuming constant mobility, is nearly independent of the bombarding

[9] H. C. Gatos and M. C. Lavine, J. Electrochem. Soc. **107**, 427 (1960).
[10] T. W. Bonner, J. E. Evans, and J. E. Hill, Phys. Rev. **75**, 1398 (1949).
[11] F. H. Eisen, Advan. Cryog. Eng. **8**, 437 (1963).

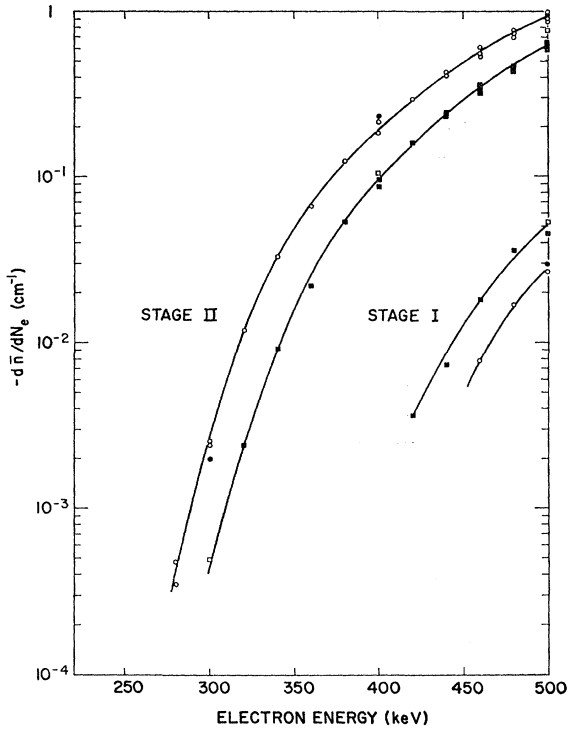

FIG. 2. Carrier removal rate, $-d\bar{n}/dN_e$, for (111)- and ($\bar{1}\bar{1}\bar{1}$)-oriented samples, separated into the portion which recovers in stage I and that which recovers in stage II, versus bombarding electron energy. Circles represent data obtained when irradiating the (111) surface and squares are for the ($\bar{1}\bar{1}\bar{1}$) surface. Filled symbols are for sample 1 and the empty symbols are for sample 2.

electron energy. Therefore, only the absolute value of the carrier removal rate is effected by the choice between the Hall coefficient and the electrical conductivity as the parameter from which to compute the carrier-removal rate.

Previous work[12] has shown that electron irradiation of *n*-type InSb results in a decrease in the electron concentration and that recovery of the electron concentration on annealing the irradiated sample occurs in five distinct recovery stages. After irradiation near the threshold displacement energy the recovery is limited to stages I and II (numbered in order of increasing recovery temperature). In the present work the Hall coefficient change was divided between that portion which recovers in stage I (centered at about 83°K in these samples) and that which recovers in stage II (centered at about 128°K), to permit computation of the carrier removal rate for the portion of the damage which recovers in each of these stages.

IV. RESULTS

The irradiation data are presented in Fig. 2. The portion of the damage rate (i.e., carrier-removal rate) which recovers in stage I is shown separately from that which recovers in stage II. It is seen that for both portions of the damage there is a substantial difference between the damage rate measured with the (111) face exposed to the electron beam and the damage rate measured with the ($\bar{1}\bar{1}\bar{1}$) face exposed. However, the damage rate of the portion of the damage which recovers in stage I is higher when the ($\bar{1}\bar{1}\bar{1}$) face is exposed to the beam; whereas, the damage rate for the portion which recovers in stage II is higher when the (111) face is exposed. In accordance with the discussion above of the expected dependence of the damage rate on whether the (111) face or the ($\bar{1}\bar{1}\bar{1}$) face is exposed to the electron beam, these data indicate that the defects annihilating in stage I are produced by the displacements of antimony atoms and those annihilating in stage II are produced by the displacements of indium atoms. Note that at 300, 400, and 500 keV, where data is available for each sample with the (111) face exposed to the electron beam and with the ($\bar{1}\bar{1}\bar{1}$) face exposed to the beam, the portion of the damage rate obtained for a given stage with a given face exposed to the beam agrees for the two samples. This agreement between corresponding faces of *different* samples is evidence that the effect is not a spurious one, but that there is a real difference in the damage rates which depends on whether the (111) or the ($\bar{1}\bar{1}\bar{1}$) surface is being irradiated.

The measurement of the damage production rate, separated into stages I and II portions, is complicated by several factors. First, at liquid-nitrogen temperature where the irradiations and measurements were carried out, stage I recovery takes place at a low rate during irradiation. Irradiations and measurements carried out at liquid helium temperature indicate that the true damage rates may be about 15% higher than those presented in Fig. 2 but that the ratio of the rates for (111)-oriented to ($\bar{1}\bar{1}\bar{1}$)-oriented samples is not affected by this recovery. Several "background" effects also complicate the resolution of the measurements for stages I and II. There is recovery of the Hall coefficient and electrical conductivity which takes place in the temperature region between stages I and II and which proceeds in the same direction as in these stages.[13] It is, however, possible by careful annealing of the sample to separate out this effect. Some recovery is observed in the temperature region of stage II which may be the continuation of the above effect or an independent one. This only becomes important at low energies and places a lower limit on the energy at which the damage pro-

[12] F. H. Eisen, Phys. Rev. **123**, 736 (1961).

[13] The recovery in this temperature region was labeled as stage I in Ref. 4. This is inconsistent with later work (Ref. 11) in which recovery in about the same temperature region was observed following higher energy (1.0 MeV) irradiation. Since the latter recovery seems to be due to the annihilation of defects throughout the volume of the sample while the present effect only shows up as a background at low energies and may be due to a surface effect, the notation of Ref. 11 will be followed. This confusion in the identification of stage I has resulted in an error in Fig. 6 of Ref. 11. The point plotted for stage I at 240 keV is incorrect and the curve for stage I should descend sharply below 400 keV as the present data shows.

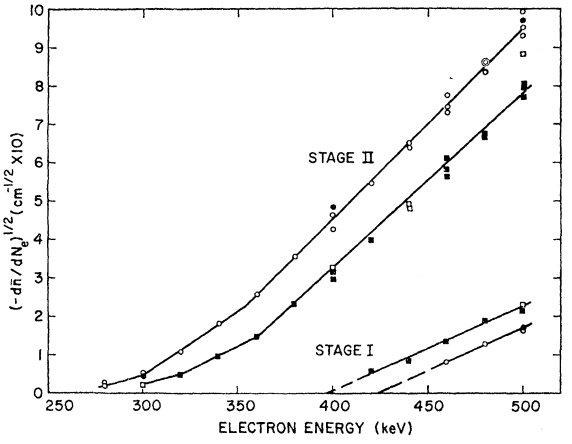

FIG. 3. The data of Fig. 2 presented with $(-d\bar{n}/dN_e)^{1/2}$ plotted versus bombarding electron energy. The meaning of the symbols is the same as for Fig. 2.

duction rate for the portion of the damage which recovers in stage II can be measured. There is also an effect, which can be annealed out near room temperature, in which the Hall coefficient changes in the direction opposite to the changes in stages I and II. The nature of all these effects is not understood. They may be, in part or in total, due to surface effects. In general, they are relatively independent of the bombarding electron energy and do not cause experimental problems at energies above about 350 keV.

V. DISCUSSION

It is possible to draw some conclusions concerning the values of the threshold energies in IbSb from the present data. Bauerlein[3] has suggested that near threshold $d\bar{n}/dN_e$ should be linearly related to $(E-E_d)^2$, where E is the energy of the bombarding electrons and E_d is the threshold electron energy, and that this relation may be used in extrapolating damage rate data to obtain the threshold energy. Figure 3 shows $(d\bar{n}/dN_e)^{1/2}$ plotted versus E for the present data. Consider first the data for stage II which is shown broken down into three straight-line segments. Extrapolation of the lowest energy segment of the upper curve to zero damage rate gives 268 keV as the minimum electron energy required to displace an indium atom. This corresponds to an energy transfer of 6.4 eV. This value is not very precise since there is not enough data available close to threshold, because of the previously mentioned background effects which made it impossible to obtain data at lower electron energies, to precisely determine how to draw this segment of the curve. In the earlier data for InSb,[4] this background was separated out and probably accounts for the long "tail" on the damage rate curve. It is possible that the change in slope which is shown at 300 keV actually occurs at a lower energy, so that a lower threshold energy would result. The curve is drawn as shown because the analysis by Bauerlein,[3] of the earlier work[4] indicated a change in slope at 300 keV. Bauerlein has interpreted this change in slope as being due to the introduction of antimony displacements and obtained a value for the displacement energy for antimony on this basis. The present work indicates that this assumption is incorrect since, if antimony were being displaced above this energy, there ought to be a tendency for the difference in damage rate between the two orientations, due to the polarity effects, to decrease as previously discussed. If the change in slope at about 300 keV is due to a new displacement process, then the damage rate attributable to that process ought to be equal to the difference between the measured damage rate and an extension of the straight-line segment lying below 300 keV in Fig. 3 to higher energies. If the extrapolation and subtraction are performed it is found that the difference is higher for the (111)-oriented sample than for the $(\bar{1}\bar{1}\bar{1})$-oriented sample, as is the total damage rate.

Other data[14] for InSb indicates the production of two different close pair defects which annihilate in stage II and it is possible that the change in slope at 300 keV indicates the position of the threshold for the production of the second kind of these close pairs. The significance of the change in slope at about 350 keV is not clear at present. It may have no special significance since the data fits a straight line at energies which are far beyond the range of validity of Bauerlein's simple analysis.

On the same basis it is possible to obtain an indication of the threshold energy for antimony from the upper curve for stage I. The lower threshold for stage II results in a background for stage I, that eventually produces an apparent nonlinear dependence of the portion of the damage which recovers in stage I on the integrated beam current and, therefore, limits the energy at which damage rate for stage I can be obtained. There is a possibility that the slope of the curve for stage I may decrease in the energy range where it was not possible to obtain data. If this were the case, it does not seem likely that the threshold would go below about 350 keV, judging from the shape of the curve for stage II. If there is no such decrease in slope, the electron threshold is at 398 keV. The range of energy transfers corresponding to these limits is then 8.5 eV to 9.9 eV.

While the present irradiations were carried out only in ⟨111⟩-oriented samples, it is possible to learn something concerning the orientation dependence of the displacement energy. From the earlier discussion of the expected effects of the ⟨111⟩ polarity we know that if the displacement energy were lower in the ⟨110⟩ or the ⟨100⟩ direction than in the ⟨111⟩ we would expect to see the damage rates for the (111) and $(\bar{1}\bar{1}\bar{1})$-oriented samples approach each other as the electron energy approaches the threshold for the ⟨111⟩ direction. There is no indication from the data for stage II that this takes place. By applying the analysis of Wolff[7] to this situation, one is led to conclude that (in the notation used previously)

[14] F. H. Eisen, Bull. Am. Phys. Soc. 8, 235 (1963).

if T_d' is lower than $\bar{T}_d$ by about 1 eV or more, this would be detected from the shape of the curves for the two faces. Within this limit then, the displacement energy for indium is a minimum in the ⟨111⟩ direction in InSb.

VI. CONCLUSIONS

(1) The defects which annihilate in stage I in InSb are produced by the displacement of antimony atoms and those which annihilate in stage II are produced by the displacement of indium atoms.

(2) The threshold displacement energy for indium in InSb is about 6.4 eV and the threshold displacement energy for antimony lies between about 8.5 eV and 9.9 eV.

(3) The likely direction of minimum displacement energy in InSb is the ⟨111⟩ direction.

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Direct Transition and Exciton Effects in the Photoconductivity of Gallium Phosphide

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Photoconductivity spectra between 0.6 and 3.3 eV of vapor-grown, high- and low-resistivity, GaP whiskers and of high-resistivity floating-zone-refined crystals of GaP were measured as a function of temperature. Structure seen in the spectra of high-resistivity whiskers and interpreted as direct exciton formation (with subsequent dissociation) permitted a determination of the energy gap at $\mathbf{k}=0$ and its temperature variation. It could be fitted by $E_G=2.895\pm0.004-(1.17\pm0.01)\times10^{-6}\ T^2$ in eV for temperature below 300°K. This structure was seen as a result of an anomalously large photoconductive response in the direct transition region, which was attributed to a mobility increase from optical excitation similar to that seen previously in InP, CdSe, and GaAs. In low-resistivity, sulfur-doped whiskers photoconductivity arising from absorption in bound exciton states associated with neutral sulfur donors was observed. The photoconductive lifetime at 296°K in high-resistivity whiskers was found to be 3×10^{-9} sec.

INTRODUCTION

THE fundamental absorption edge of gallium phosphide arises from indirect transitions from the valence-band maximum to conduction-band minima in the [100] directions.[1,2] The forbidden energy gap between these band extremes is 2.325±0.003 eV at 0°K.[3] The determination of the energy gap at $\mathbf{k}=0$ ("the direct band gap") has been a more difficult task. A number of experiments[2,4–6] aimed at its determination have not definitely located it. Observation of direct transitions in optical absorption[2] has been prevented by difficulties in preparing GaP crystals less than 8μ in thickness with polished faces. This limited the study of absorption to absorption coefficients below 8×10^3 cm^{-1}. On the other hand, absorption coefficients somewhat greater than this are necessary to be observable in reflectivity measurements. Recently, however, a very weak maximum in the reflectivity has been observed[7] at 2.8 eV at 300°K. From its pressure dependence it was identified as due to the direct band gap.

The first report in the literature concerning the direct band gap in GaP was that of Spitzer *et al.*[2] They observed an absorption band in the infrared near 3 μ which was present only in *n*-type material. This indicated a conduction-band minimum about 0.31 eV above the [100] minima. They also observed enhanced absorption at 0.35 eV above the forbidden gap energy in a study of the fundamental absorption edge. They suggested that the observed conduction-band minimum at 0.31 to 0.35 eV above the [100] minima was that at $\mathbf{k}=0$.

The lack of a significant wavelength shift of the 3-μ absorption band with pressure led Paul and Zallen[5] to conclude that the higher conduction band minima responsible lay directly above the [100] minima rather than at $\mathbf{k}=0$ (see Fig. 1).

Allen and Hodby[8] studied the shift of the 3-μ band

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