Threshold energy for atomic displacement in InP

B. Massarani* and J. C. Bourgoin
Groupe de Physique des Solides de l'Ecole Normale Supérieure, Université de Paris VII, Tour 23, 2 Place Jussieu, 75251 Paris Cédex 05, France
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The anisotropy of the defect introduction rates of two hole traps (H4 and H5) detected by deep-level transient spectroscopy measurements in room-temperature electron-irradiated p-type InP has been used to determine the sublattice to which the created defects belong. It appears that the H5 defect belongs to the indium sublattice and it is confirmed that the H4 defect belongs to the phosphorus sublattice. Using the variations of the introduction rates of H4 and H5 with the electron energy, a threshold energy of 8 eV is deduced for P-atom displacement and of 3 and 4 eV for In-atom displacement in the two crystallographic directions In[111] and P[111], respectively. A model taking into account the secondary collisions of the primary knock-on atom with the first and second neighbors is proposed to explain the complex behavior of the anisotropy ratio curve measured for the H5 defect.

I. INTRODUCTION

The determination of the threshold energy for atomic displacement is important for the understanding of the production of radiation defects. In compound semiconductors the anisotropy of this threshold energy can be used to determine the sublattice to which the created defect belongs. This has been clearly demonstrated in the case of GaAs.[1,2] For this, one compares the introduction rates of a given defect for irradiations along opposite [111] directions. This technique was first proposed by Eisen[3] and has been successfully applied for the identification of the displaced atom in several compound semiconductors.[1-5]

The first determinations of threshold energies were performed using resistivity or luminescence measurements and the results were not sufficiently accurate.[6] More accurate results are now obtained using deep-level transient spectroscopy (DLTS). This technique is very suitable for threshold energy determination because (i) it is a spectroscopic technique and (ii) it detects the irradiation-induced defects in a thin layer below the surface of the sample, i.e., in the region where the incident particles conserve almost their initial energy and initial direction. The conditions of a "thin sample" thus may be considered realized and surface effects are eliminated.

Many works have been devoted to the study of electron irradiation-induced defects in InP. DLTS measurements have shown the existence of a number of irradiation-induced trap levels in both n-type InP (Refs. 7-13) and in p-type InP (Refs. 8,9, and 13-16). These defects have been labeled E1 to E11 for electron traps[7,9,10] and H2 to H6 for hole traps.[9,14] Most of these traps are thought to be related to primary or complex defects in the P sublattice.[16] No defect in the In sublattice has been unambiguously identified yet.

In this paper we focus on two hole traps observed in irradiated p-type InP, namely the level ($E_v-0.37$ eV) labeled H4 and the level ($E_v-0.53$ eV) labeled H5. It has been shown[17] that H4 corresponds to a distribution of deep centers in the phosphorus sublattice. This defect anneals nearly completely at about 100° C.[9] As to the defect H5, it is usually undetectable directly after room-temperature irradiation: a thermal annealing around 100° C is necessary to reveal it. Its introduction rate increases with the increase in the acceptor impurity concentration.[18] This behavior suggests that H5 is a complex, formed by thermal annealing, composed of a created intrinsic defect, not detectable by DLTS, and of an acceptor atom. On the contrary to most irradiation-induced DLTS traps in InP which anneal nearly completely at about 100° C, H5 is stable above 150° C.

In this paper we shall show that the anisotropy of the introduction rate of H5 is characteristic of a defect which belongs to the In sublattice, and we shall determine the threshold energy for In atom displacement. The same study performed on H4 allows one to confirm the threshold energy for P-atom displacement already published as well and to gain some additional information about the anisotropy of the threshold energy.

II. EXPERIMENTAL PROCEDURE

We have used a series of identical Schottky diodes that were realized by Ti-Au evaporation on Zn-doped InP grown by liquid phase epitaxy on Zn-doped (100)-oriented p^+-type InP substrates, after providing ohmic contact on the backside by Au-Zn alloying.[4] The hole concentration at room temperature, determined from capacitance-voltage measurements, was 1.1×10^{17} cm^{-3}.

Irradiations were performed at room temperature using an electron Van de Graaff accelerator in the electron energy range 0.10 to 1.60±0.005 MeV. Two samples were irradiated simultaneously in such a way that the first received electrons along the In[111] direction while the second received electrons along the P[111] direction. Caution was taken to ensure that the two differently oriented samples receive exactly the same dose at the given electron

energy. Electron doses of irradiation were chosen in such a way that the concentration of free holes after irradiation did not differ by more than 10% from the initial value. The electron flux did not exceed 0.1 $\mu A\,cm^{-2}$ in the high-electron-energy range (1 to 1.6 MeV) and 0.5 $\mu A\,cm^{-2}$ in the low range (0.1 to 1 MeV) to ensure that the sample temperature did not rise more than 10°C during irradiation.

C-V curves and DLTS spectra, using a double lock-in detector,[19] were recorded before and after irradiation and after thermal treatment (1 h at 150°C) which has the effect to anneal about 95% of the H4 defects and to make the concentration of the H5 defect reach its maximum.

III. RESULTS

Figures 1 and 2 show the introduction rates of H4 and H5, in the two directions of irradiation In[111] and P[111], versus electron energy. As noticed by Sibille *et al.*[13] there is a continuous rise of the introduction rate with energy while the theory predicts a saturation. This is especially true in the case of H5. For this defect we observe two crossovers between the introduction rate curves (Fig. 2). This will be discussed later. In Figs. 1 and 2 we have also plotted the anisotropy ratios for H4 and H5, i.e., the ratio of the introduction rates for irradiations in the In[111] direction and in P[111] direction. We find here the same general features (rapid decrease at low energies, reverse ratio at higher energies) expected for the anisotropy ratio curves[2] as for other compound semiconductors. The results concerning H4 are in agreement with those previously reported[13] and allow one to deduce that H4 is in the P sublattice. The anisotropy ratio at low electron energy we have obtained (~ 6) is higher by a factor of about 2 than that obtained in Ref. 13. This is due to the fact that our samples are more heavily doped ($\sim 10^{17}$ cm^{-3}) than those in Ref. 13 and therefore DLTS detects the defects in a layer closer to the surface (where the direction of the incident electron is better preserved). For H5 it can be seen clearly that the introduction rates at electron energies (below 0.35 MeV) are larger for irradiations along In[111] direction than along the P[111] direction. This means that In[111] is the "easy" direction for H5 and hence it should be concluded that H5 is due to displacements of In atoms. The introduction rate behavior at higher energies will be discussed later.

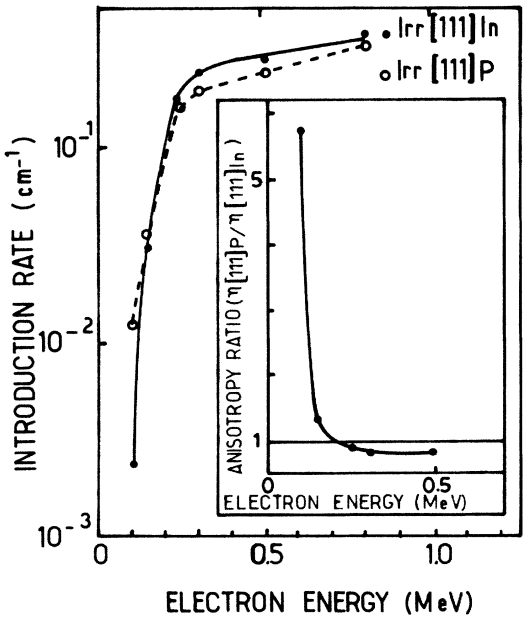

FIG. 1. (a) Introduction rates η of H4 defect versus electron energy for irradiations along the In[111] and P[111] directions. (b) Anisotropy ratio η(P[111])/η(In[111]) versus electron energy.

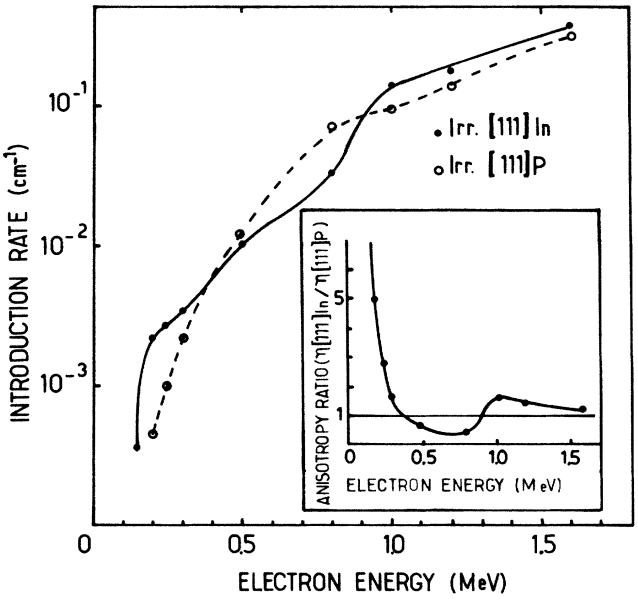

FIG. 2. (a) Introduction rates η of H5 defect versus electron energy for irradiation along the In[111] and P[111] directions. (b) Anisotropy ratio η(In[111])/η(P[111]) versus electron energy.

The measured introduction rates versus energy of H4 and H5, related to the P and In sublattices, respectively, are used to determine the threshold energies for P- and In-atoms displacements. It should be pointed out that since H4 and H5 are not primary defects, this assumes concentrations of the H4 and H5 defects proportional to the concentrations of displaced P and In atoms. We can assume that this is the case in view of the very low concentrations of H4 and H5 used in this study ($\sim 10^{14}$ cm^{-3}) relative to the acceptor concentration ($\sim 10^{17}$ cm^{-3}). In addition we have found that the H5 introduction rate at constant energy of irradiation is constant for successive irradiations at the same energy (see Fig. 3). In Fig. 4 we have plotted the curves corresponding to the variation of the cross section for atomic displacement calculated for the P atom using the McKinley-Feshback approximation[20] for different threshold energies. Because of the already-mentioned steady rise of the introduction rates with energy, we have preferred not to normalize the curves at a given energy but only to compare the experimental results for H4 corresponding to electron energies up to 0.5 MeV with the cross section curves. The fit with the curves corresponding to 7 and 8

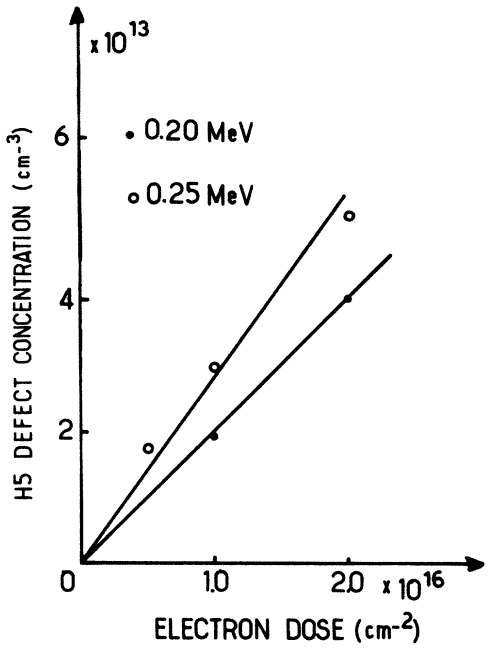

FIG. 3. H5 defect concentration versus electron dose at two constant energies of irradiation: 0.20 and 0.25 MeV.

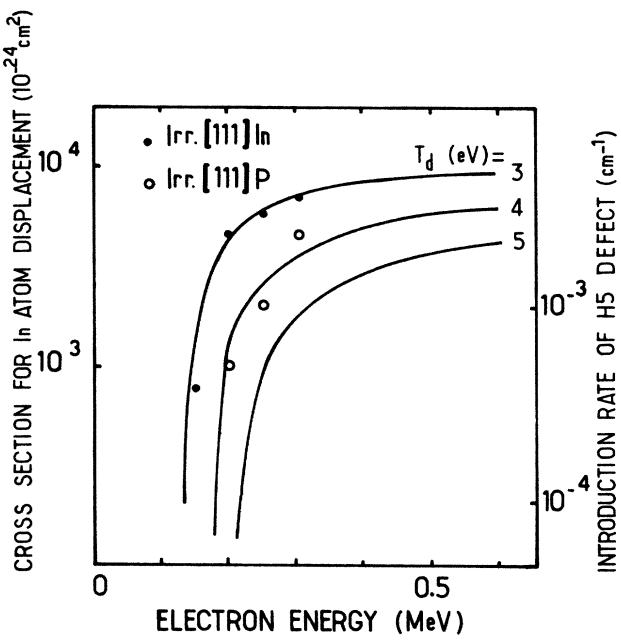

FIG. 5. Cross section for In-atom displacement versus electron energy and experimental results for H5 as in Fig. 4.

eV is fairly good. We can deduce from the lowest electron energy (0.1 MeV) able to produce H4 defects that the threshold energy for the P-atom displacement is lower than 7.8 eV, the maximum kinetic energy transferred to the P atom by collision with 0.1 MeV electron. This result is in agreement with the one previously reported by Sibille *et al.*[13]

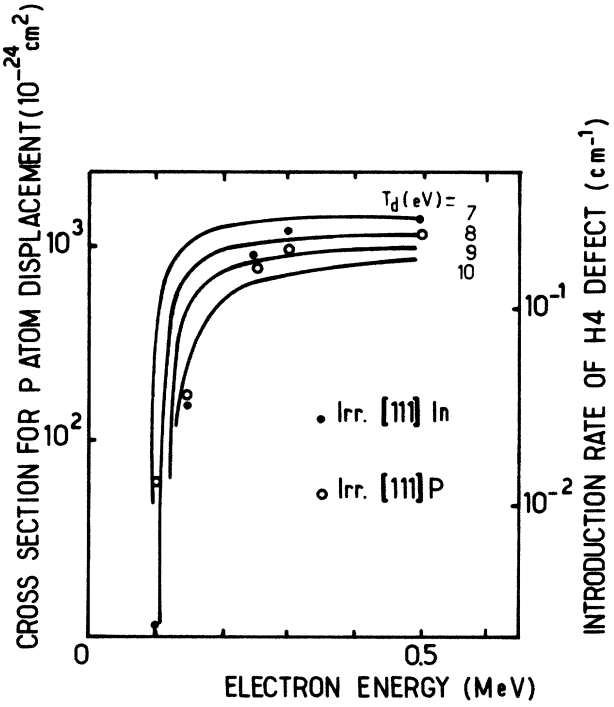

FIG. 4. Calculated cross section for P-atom displacement versus electron energy displaced vertically for best fit and the experimental introduction rate for the H4 defect in the In[111] and P[111] directions.

Because the crossover in the introduction rate curves happens to be at relatively low energy (about 0.2 MeV), it is difficult to resolve the two threshold energies for the P-atom displacement in the two [111] directions. Irradiations at electron energies lower than 0.1 MeV would give a more precise estimation of the threshold energy in these two directions. Unfortunately, the Van de Graff accelerator we used does not permit irradiations at energies lower than 0.1 MeV.

In Fig. 5 the experimental introduction rates of H5 for energies below 0.5 MeV are compared with the cross-section curves calculated for In-atom displacement. The fit is more satisfactory here and we can deduce a threshold energy T_d of 3 eV for the displacement of the In atom in the easy In[111] direction and 4 eV in the hard P[111] direction. It should be pointed out that, at an electron energy of 0.15 MeV, the defect H5 can still be produced when irradiating along the In[111] direction, but not along the P[111] direction, and that, at 0.1 MeV, it is not produced in any of the two directions. This implies that the threshold energy for the In-atom displacement in the In[111] direction is 2.7 ± 0.6 eV. The same can be said for the threshold energy in the P[111] direction for which we find 4 ± 0.6 eV. This is in good agreement with the values (3 and 4 eV) deduced from the comparison of the introduction rates with the cross-section curves.

IV. DISCUSSION

The anisotropy ratio curves for defects H4 and H5 (Figs. 1 and 2) make it unambiguously evident that H4 belongs to the P sublattice while H5 appears to belong to the In sublattice. The anisotropy reversal is due to the interaction of the knock-on atom with the off-axis atoms.

This is imposed by the tetrahedral geometry of the interacting potential and, as shown by Pons,[2] the crossover energy does not depend strongly on the interacting potential. Pons[2] has considered the secondary collisions of the primary knock-on atom (say A-atom) with the nearest neighbors only, i.e., with the three off-axis atoms of the other kind than the primary knock-on atom itself (say B atoms). Here we shall see that the results may be *a priori* better explained if we distinguish between the interactions of the primary knock-on A atom with the first neighbors B atoms and with the second neighbors A atoms as well. We shall see that the observed behavior of the introduction rate curves can thus be explained, i.e., a physical meaning can be given to the two crossovers between the introduction rate curves for the two [111] opposite directions.

In order to clarify the physical meaning of the observed crossover let us first consider the low-energy range. At electron energies close to the threshold energy for A-atom displacement, this atom will have a high probability of displacement when irradiating in the easy A[111] direction because the lattice is open in the direction of its displacement as its recoil angle is close to 0° at this energy. When the electron energy increases the recoil angle increases rapidly and the interaction with the surrounding off-axis A atoms increases and passes by a maximum when the recoil angle is equal to 35° which corresponds to the direction towards one of these atoms. The situation is the inverse in the case of irradiation along the B[111] direction: At electron energies close to the threshold energy the recoil angle is close to 0° and the probability of displacement for the A atom is very low because of the high interaction with the B atom just in front of it (hard direction). With the increase of the electron energy this interaction decreases because of the increase of the recoil angle. At 35° the situation is exactly the same for the two A atoms displaced by the irradiation along the two opposite [111] directions. At an electron energy corresponding to this recoil angle the two atoms have exactly the same probability of effective displacement, hence the same introduction rate will be measured for the two directions (the first crossover on the curves). Let us now consider the higher-electron-energy range corresponding to mean recoil angles larger than 35°. For irradiations along the A[111] direction the interaction of the displaced A atom will have another maximum for the recoil direction towards the nearest-neighbor B atom which corresponds to a recoil angle of 71°. For larger recoil angles the interaction decreases rapidly. The situation is different for irradiations along the B[111] direction. For recoil angles larger than 35° the interaction decreases and nothing special happens at 71°. A second crossover may than occur at higher electron energies but no special meaning can be attributed to it as it was the case for the first crossover at 35°. However, in order to confirm this qualitative analysis, it will be necessary to perform a simulation of all the interactions considered.

Here, in order to examine the validity of this model, we have calculated the mean recoil angle $\bar{\theta}$ corresponding to the mean energy transferred to the displaced atom using the formula given by Seitz and Koehler[21] based on the McKinley-Feshback approximation for both P and In atoms as a function of electron energy for different threshold energies (Fig. 6). In the case of P-atom displacement with threshold energy of 8 eV we find for the observed crossover energy between 0.15 and 0.20 MeV (Fig. 1) a mean recoil angle $\bar{\theta}$ between 26° and 36°. This is thus in correct agreement with the expected crossover recoil angle of 35°. The first crossover in the case of In-atom displacement is observed between 0.35 and 0.45 MeV (Fig. 2) and the corresponding mean recoil angle is between 36° and 44° if we consider a threshold energy of 4 eV. This is less consistent with the value of 35° but can still be considered satisfactory. In GaAs the crossover is observed at an electron energy of about 0.5 MeV.[1,2] At this energy the mean recoil angle, calculated for a threshold energy of 10 eV, is about 38°, which is not so far from the expected value of 35°. In addition it can be noticed that the anisotropy ratio results concerning InSb (Ref. 3) and GaSb (Ref. 4), reviewed by Pons,[2] can also be accounted for satisfactorily by this model.

On the other hand, in view of the precise physical meaning of the crossover, if the crossover energy is precisely determined experimentally, the threshold energy may then be deduced easily. Thus, the measurement of the crossover energy could be an alternative method for the determination of the threshold energy when the electron energies of irradiation needed for this determination are too low so that electron penetration into the sample to sufficient depths becomes a limiting factor. The crossover energy in the case of the P atom in InP is, as already mentioned, between 0.15 and 0.20 MeV (Fig. 1). This imprecision does not allow one to deduce a value of the threshold energy for the P-atom displacement better than 8 ± 1 eV, which is consistent with the previous estimation. In the case of the In atom, the first crossover is between 0.35 and 0.45 MeV which implies a threshold energy higher than 4 eV. This is somewhat less consistent with our pre-

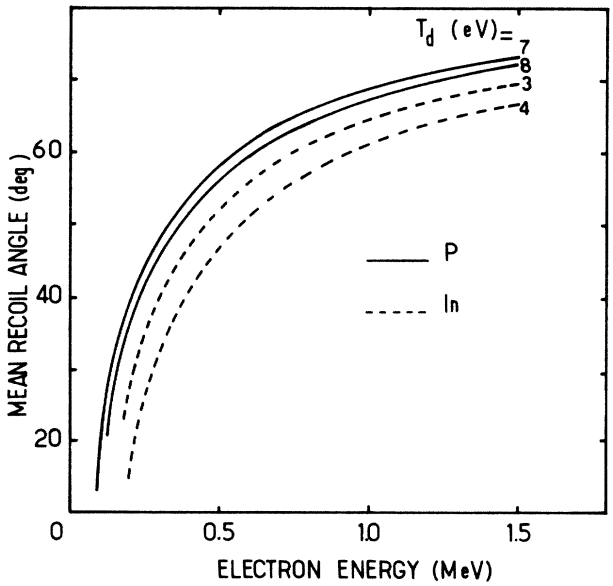

FIG. 6. Mean recoil angle versus electron energy of irradiation for P and In atoms for different threshold energies.

vious estimation. Numerical calculations taking into account the interaction of the knock-on atom with the first and second neighbors will be very useful for a better understanding of the experimental results.

Finally, it may seem surprising that the threshold energy for In-atom displacement is so low, about two times smaller than that for P-atom displacement. Indeed, one expects that the energy required to break four In bonds is identical to the one required to break four P bonds. This difference therefore strongly suggests that the threshold energy is not only the energy required to break the four bonds of the displaced atom but contains also a nonnegligible contribution due to the energy required to put the atom into an interstitial position. Namely, this last energy may be very different for the two kinds of atoms which have very different masses.

V. CONCLUSION

The displaced atom forming the complex defect H5 is identified to be the In atom and the previously reported result that the displaced atom forming the H4 defect is the P atom is confirmed. The threshold energy for the In atom is found to be about 3 eV in the easy In[111] direction and about 4 eV in the hard P[111] direction. A model taking into account the secondary collisions of the primary knock-on atom with the first and second neighbors seems to explain well the experimental results and attributes a physical meaning to the crossover between the introduction rate curves in the two opposite [111] directions.

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*Permanent address: Department of Physics, Faculty of Sciences, University of Damascus, Damascus, Syria.

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