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Hopping and tunnelling of H(D) in semiconductors

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Abstract

The dynamics of H and D in p-type Si:B and GaAs:Zn in n-type Si:P and GaAs:Si, have been studied by acoustic spectroscopy measurements in the temperature range 1 K-550 K and at frequencies between 1 and 30 kHz. By combining the data from anelastic relaxation and from the dichroism decay, the relaxation rates of the H–B pair are obtained over 11 decades and there are clear indications of a deviation at low temperature from the classical dependence. However, no conclusions can be drawn at present on the mechanism governing the H(D) transitions. The complete absence of relaxation effects in Si:P may confirm that H occupies backbonding sites in this system. In deuterated GaAs:Zn, a new peak is observed at 20 K. This peak is much broader than a single-time Debye peak, and is due to a species performing unexpectedly high transition rates: more than 15–20 orders of magnitude higher than in all the other semiconductors measured so far. This species has been identified as the D–Zn complex. The analysis of data demonstrates that the nature of the relaxation is strongly quantistic. Measurements on GaAs:Si–D suggest that the energy barrier separating the four D antibonding sites around Si may be rather high.

Keywords: Hydrogen (Deuterium)-Semiconductor Systems; H(D) Hopping and Tunnelling; Anelastic Relaxation

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1. Introduction

The diffusion coefficient of hydrogen and its isotopes in semiconductors may be several orders of magnitude lower than in metals; nevertheless this light particle can display, locally, a remarkably high mobility. In boron-doped silicon loaded with hydrogen, measurements of infrared absorption [1] and anelastic relaxation (elastic energy loss and modulus) [2] have shown that H is rather mobile around the substitutional dopant acting as a trapping centre. The measurements of Ref. [2] revealed a thermally activated process due to the H reorientation around B with an activation energy of $W=0.22$ eV. The pre-exponential factor of the relaxation rate, as derived from the classical Arrhenius law, is $\tau_0^{-1}=1.2\cdot10^{13}$ s^{-1}, typical of point defect relaxation. The infrared absorption measurements at low temperature [2] gave a rather similar value for the activation energy of the H reorientation around B ($W=0.19$ eV), but the extrapolation of the relaxation rate to infinite temperature gave a markedly lower value ($\tau_0^{-1}=9.1\cdot10^{10}$ s^{-1}), two orders of magnitude slower than that of point defect motion in solids. This observation suggested that under-barrier jumping may take place at low temperature for $\tau^{-1}(T)$. The combination of the infrared absorption and of the anelastic relaxation data gives the H jumping rate in an exceptionally wide range (12 orders of magnitude) and indicates that a deviation of $\tau^{-1}(T)$ from the classical law takes place at low temperature. A fit of the Flynn–Stoneham model [3] to the data from the two types of experiments was recently accomplished [4] and led the authors to the conclusion that phonon-assisted incoherent tunnelling for the H motion could take place at low temperature.

Direct and unambiguous evidence of quantum tunnelling in semiconductors was recently reported in an anelastic relaxation study of the deuterium dynamics in GaAs doped with Zn [5]. A relaxation of D occurring at 20 K in the kHz range has the highest jumping rate found so far for a hydrogen isotope in a semiconductor and cannot be explained in a classical framework.

This paper reports on the H(D) behaviour in p-type and n-type doped Si and GaAs.

2. Experimental procedure

The samples were four rectangular bars of 40×5×0.4 mm^3: (i) p-type Si:B with [B]=10^{19} cm^{-3}; (ii) n-type Si:P with [P]=5×10^{18} cm^{-3}; (iii) p-type GaAs:Zn$_{Ga}$ with [Zn]=10^{19} cm^{-3}; (iv) n-type GaAs:Si$_{Ga}$ with [Si]=2×

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10^{18} cm^{-3}. Hydrogen and deuterium were introduced: (i) by low-energy ion-gun irradiation (~140 eV) at 300°C for 450 min for a H or D dose of 6.7×10^{18} H ions cm^{-2}; (ii) by low pressure plasma (0.5 mbar) at 300–420°C for 180–500 min. In this way, H(D) penetration occurs via thermal hopping and the lattice damage is minimized, if not avoided.

The acoustic spectroscopy measurements were carried out between 1 K and 550 K by electrostatically exciting flexural vibration modes of the bars which were suspended by thin wires on their nodal lines. The first, third, and fifth modes were excited, for resonant frequencies spanning from about 1 kHz to 30 kHz.

3. Experimental results and discussion

3.1. Si:B and Si:P systems

Fig. 1 shows the elastic energy dissipation curve of Si:B as a function of temperature. The sample in the H-free state displays a monotonical decrease of dissipation with decreasing temperature. After hydrogenation, a well developed peak appears above the background at about 125 K (at 2.4 kHz). The main features of that peak are reported in the following. The peak shifts in temperature with frequency, indicating a thermally activated nature, and is described by a single-time Debye curve. In the temperature range of the energy-loss measurements, the relaxation time is well fitted by an Arrhenius law ($\tau=[(8\pm4)\cdot10^{-14}$ s]$\cdot\exp[(0.22\pm0.01)\mathrm{eV}/kT]$). The peak is stable (the cooling curves are retracted on heating), with a height increase depending on the H content, whilst the temperature at which the maximum occurs is concentration independent; the elastic interactions among the B–H complexes do not appear to affect the H jumps within the experimental uncertainty, and an upper limit of less than 10 meV is estimated for the random shifts of the H site energies due to such interactions. As hydrogen and its isotopes are expected to have a bond-centre occupancy in p-type doped Si (in the middle of the bond between the substitutional dopant and the host Si atom), this peak has been attributed [2] to the stress-induced reorientation of H among the four bond-centre sites around B. Considering the relatively low dopant concentration (~10^{19} B atoms/cm^{-3}), the single-time nature of the relaxation process is justified by the energy equivalence (in the unstrained crystal) of these positions.

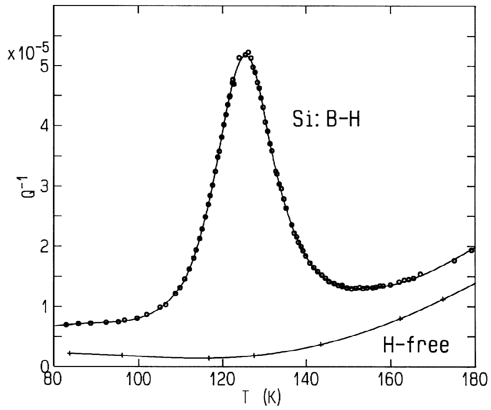

Fig. 1. Elastic energy dissipation coefficient versus temperature of H-free and hydrogenated Si:B. The (thermally activated) relaxation peak is due to the reorientation of H around B.

Hydrogen in n-type semiconductors is expected to occupy sites different from the bond-centre positions generally expected in p-type semiconductors. To test the different H occupancy, we carried out acoustic spectroscopy measurements in n-type, H(D)-charged Si:P. In this system, P is expected to occupy the site on the P–Si bond line, back to the Si atom such that Si bridges the H and P atoms (backbonding site, see Fig. 2). Fig. 2 presents the dissipation curves versus T of deuterated Si:P and of Si:B as a reference. Whilst the peak due to the stress-induced reorientation of D among the bond-centre sites around B appears in Si:B–D, no process has been observed in Si:P–D in the same temperature range. It is surprising that even in the extended range 1 K-550 K, no relaxation process could be detected in Si:P. As the backbonding sites are far apart (see sketch in Fig. 2), it is conceivable that the H(D) transitions among the four energetically equivalent positions cannot occur via direct jumps. Therefore, energy loss is not expected in this case, and the absence of relaxation processes in Si:P supports the backbonding occupancy for H(D) in n-type doped Si.

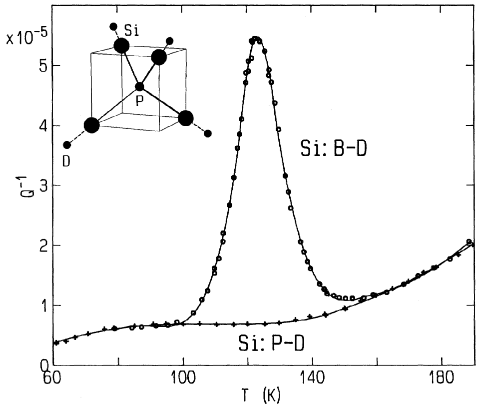

Fig. 2. Elastic energy dissipation coefficient versus temperature of p-type Si:B–D displaying the peak due to the B–D relaxation, and of n-type Si:P–D showing the absence of any process (in the range 1 K-550 K; only a limited range is shown in the figure). The sketch shows the backbonding positions of H(D) in Si:P.

3.2. GaAs:Zn and GaAs:Si systems

The coefficient Q^{-1} of the elastic energy dissipation of deuterated GaAs:Zn at two different frequencies (1 and 13 kHz) is plotted in Fig. 3. A well developed peak appears at

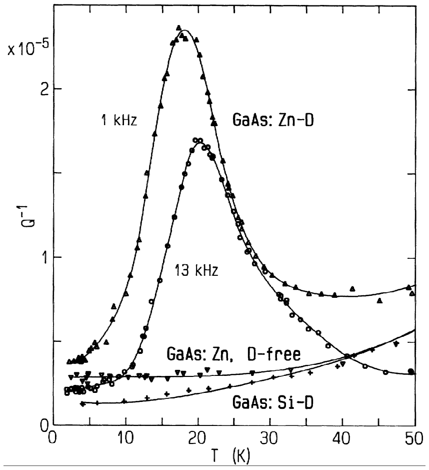

Fig. 3. Elastic energy dissipation coefficient versus temperature of p-type GaAs:Zn–D at 1 and 13 kHz showing the thermally activated Zn–D peak around 20 K, of D-free GaAs:Zn, and of n-type GaAs:Si–D displaying only background dissipation.

about 20 K. It shifts with frequency thus indicating that the process is thermally activated. The peak is governed by unexpectedly high H transition rates, more than 15–20 orders of magnitude higher than in all the other semiconductors measured so far. Moreover, the peak is much broader than a single Debye process. In the same Fig. 3 the dissipation curves of deuterium-free GaAs:Zn and of D-loaded GaAs:Si are also plotted. In all cases the peak is absent, indicating that the presence of both Zn and D is necessary for the appearance of the peak. Although the above observations suggest that the peak is caused by the relaxation of D around the Zn trapping centre, an attribution to a particular complex symmetry and mechanism is not possible at present.

The above Zn–D peak cannot be described by classical hopping. In fact the single-time Debye curve, traced by using the Arrhenius law for $\tau(T)$ and the activation energy W_S obtained from the peak shift with frequency, is far too narrow with respect to the experimental curve. The curve broadening can be explained in terms of a distribution of the D site energies, i.e. of both the activation energies W and site asymmetries caused by the elastic interactions between the Zn–D complexes. However these interactions have been shown to be negligible in Si:B–H at the low dopant concentrations used (~10^{19} cm^{-1}), where the B–H relaxation gives rise to a single Debye process [2]. In an attempt to introduce large distributions of W and τ_0^{-1} into the classical formulae, τ_0^{-1} had to be varied of orders of magnitudes in order to obtain a reasonable fit to the experimental curves, and assumed completely unphysical values.

Two possibilities have been considered for quantum tunnelling of D in GaAs: the *incoherent* and the *coherent* D tunnelling. A widely used model for incoherent tunnelling is the model of Flynn and Stoneham [3], in which the H atom is supposed to be self-trapped in a given site and to tunnel to an adjacent site when the two site energies are made equivalent by thermal fluctuations. A tentative fit in terms of this model was accomplished [2] and the result was only partially satisfactory, because of the large variation introduced for the tunnelling matrix element J in order to fit the data. Although the values assumed for J are not as unphysical as in the case of τ_0^{-1}, they are rather high for a tunnelling process. Moreover, the distribution for J is too broad to be caused by elastic interactions, at least at the low Zn and D concentrations presently used.

On the other hand, coherent tunnelling has been reported in H(D)-metal systems. In the present case, H(D) can be shifted by the large and heavy substitutional Zn to three equivalent off-axis positions around the Zn–As bond. The confinement of H(D) in these sites should give rise to three-level tunnel systems at low temperature and the H(D) transitions among quantized energy levels could then be the origin of the observed relaxation. Also the tunnelling among the sites of the four different bonds around Zn cannot be excluded. The analysis of the dynamic regime for H or D in GaAs:Zn is in progress.

Lastly, the absence of any peak (Fig. 3) over the range 1 K-550 K in the n-type GaAs:Si–D system, where H and its isotopes are expected to occupy antibonding sites (on the Si–As bond line, back to the Si atom such that Si bridges the H and As atoms) may indicate that the height of the energy barrier separating the four equivalent antibonding sites around Si is fairly high.

4. Conclusion

The relaxation of H–B pairs in Si gives rise to a nearly Debye process. The relaxation rates, considered separately from the anelastic relaxation or from the decay of dichroism, are well fitted by a classical Arrhenius law. The combination of data from the two types of experiments reveal a deviation from the exponential behaviour at low temperature. A preliminary attempt in terms of a small polaron model of the phonon-assisted incoherent tunnelling has been accomplished. The absence of relaxation effects in the Si:P–D system is consistent with the backbonding occupancy of H(D) in n-type doped Si. A new peak observed in GaAs:Zn–D at 20 K, much broader than a single Debye curve, is caused by a very mobile species identified as the Zn–D complex. The mechanism causing the process cannot be explained classically, and at present the under-barrier H hopping or H tunnelling between definite lattice sites should both be considered. Finally, the deuterated n-type GaAs:Si system, where H(D) is expected to occupy Si antibonding sites, does not display relaxation processes, thus indicating a rather high activation energy for the reorientation of D around Si in GaAs.

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