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Local dynamics of H and D trapped by substitutional dopants in semiconductors

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Abstract

The motion regimes of hydrogen and deuterium in *p*-type Si:B and GaAs:Zn have been studied by anelastic spectroscopy (elastic energy loss and dynamic modulus) between 1 and 600 K in the frequency range (1–40) kHz. Interstitial H or D in Si:B are bound to the acceptor acting as a trapping centre, and display rather high jumping rates between the four equivalent bond centre sites around B; the respective relaxation peaks are nearly single Debye processes. The H(D) reorientation rate $\tau^{-1}(T)$ is satisfactorily interpreted by the classical Arrhenius law in terms of overbarrier hopping, within the temperature range of measurements. However, by joining the data from anelastic relaxation with those from infrared absorption, the range of the measured H(D) relaxation rates is widened to 11 orders of magnitude, and a slight deviation from the Arrhenius law to higher rates is observed below liquid nitrogen temperature. The analysis of the relaxation curves indicates that the models of incoherent tunnelling used to interpret the behaviour of hydrogen (deuterium) in metals hardly apply to the presently investigated systems. The influence of quantum tunnelling is even more evident in GaAs:Zn charged with H or D, which display relaxation processes at liquid helium temperatures characterised by transition rates of more than 10 orders of magnitude faster than all those previously reported in hydrogenated semiconductors. The mobility parameters obtained and the features of the relaxation spectra may suggest that the mobile species causing the effect performs coherent tunnelling within close sites, and the relaxation rates are not related to jumps, but to transitions among the quantized energy levels of the tunnel systems. Although the species causing the effect has not yet been univocally individualised, the data shows that the presence of both H(D) and Zn in the relaxing complex is required. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Semiconductors; H-tunnelling; Anelasticity

1. Introduction

Hydrogen as an unwanted impurity is hardly avoided in semiconductors due to its presence in the processing environment during the device fabrication and to its significant diffusivity. The studies of the motion of hydrogen (deuterium) in semiconductors are of growing interest from both the application and fundamental aspects, because of its important function of inhibiting the doping efficiency, and of its interesting dynamic properties. In fact, although the diffusion coefficient of hydrogen and its isotopes in semiconductors may be orders of magnitude lower than in metals, this light particle can display, locally, a remarkably high mobility, as it was found for H(D)-charged Si:B [1,2]. In addition, recent results and analyses have shown that H dynamics in semiconductors may deviate from classical behaviour, and that in some systems the H(D) motion is totally governed by quantum mechanical mechanisms at low temperature [3]. In the present paper diffusion data of H and D in Si:B and GaAs:Zn will be presented and discussed.

2. The anelastic spectroscopy technique and the samples

Anelastic spectroscopy is an effective tool for the investigation of the dynamics of atomic imperfections in solids. In a vibrating crystal the alternating stress due to the vibration interacts with the local distorsion associated with a mobile lattice imperfection perturbing its energy states. As a consequence, the imperfections thermally redistribute themselves among the perturbed states, so giving rise to a relaxation process, which manifests itself as a peak of the elastic energy loss Q^{-1} versus temperature. The anelastic relaxation curve is described by the

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Debye law and displays its maximum at a temperature where the reciprocal of the relaxation time $\tau(T)$ equals the angular vibration frequency ω:

$$Q^{-1} \propto \frac{c(\Delta\lambda)^2}{k_B T} \frac{\omega\tau}{1+(\omega\tau)^2}$$

where c is the concentration of the relaxing entity, $\Delta\lambda$ is the change in the local elastic distortion, and k_B the Boltzmann constant. The relaxation time $\tau(T)$, which in the classical case follows the Arrhenius law, is related to the type of interaction of the imperfection with the environment and is close to the mean time between two subsequent jumps. From the analysis of the relaxation curve at different vibration frequencies, the dynamics parameters of the imperfection can be evaluated.

The anelastic spectroscopy measurements were carried out between 1 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 to 30 kHz.

The samples were rectangular bars of $40\times5\times0.4$ mm^3 with the following dopant contents: (i) p-type Si:B with $[B]=10^{19}$ cm^{-3}; (ii) p-type GaAs:Zn_{Ga} with $[Zn]=10^{19}$ 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 $6.7\cdot10^{18}$ 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 minimised, if not avoided.

3. Results and discussion

3.1. The Si:B–H(D) system

Hydrogen in Si:B occupies a site called the bond centre (BC), along the bond between the B substitutional dopant and Si. There are four energetically equivalent BC sites around B, and the symmetry of the B–H complex is lower than that of the host lattice; therefore, relaxation consequent to the H–B reorientation is expected, and is actually observed by acoustic spectroscopy measurements (elastic energy loss and dynamic modulus) [2]. Fig. 1 shows the elastic energy dissipation curve of H free and H charged Si:B. The dissipation curve of the hydrogenated sample displays a well pronounced maximum at 125 K (for 2.4 kHz), having the following features. The peak height increases with increasing H content, but the peak temperature is concentration independent. The peak is stable, in fact the cooling curves are retraced on heating. In addition, the peak shifts towards higher temperature with an increase in frequency, indicating that the process is

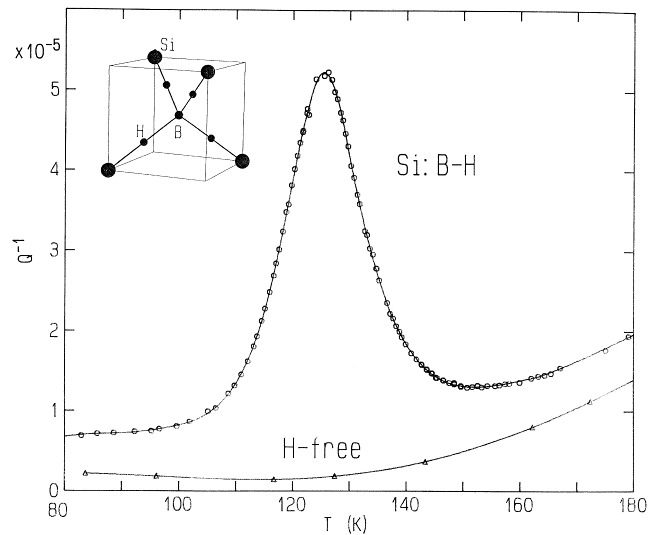

Fig. 1. Elastic energy dissipation coefficient versus temperature of H-free and hydrogenated Si:B. The thermally activated relaxation peak is due to the reorientation of H around B. The sketch shows the four equivalent bond-centre positions of H(D) in Si:B.

thermally activated. The effect has been attributed to the reorientation of H around B, and the analysis of the curves yields $W=(0.22\pm0.01)$ eV for the activation energy, and $\tau_0=(8\pm4)\cdot10^{-14}$ s for the pre-exponential factor of the relaxation rate. Fig. 2 shows the curves measured at different vibration frequencies, after normalisation in temperature and height. Also shown is the theoretical single-time Debye curve obtained with the activation energy $W=0.22$ eV. The excellent fitting to the experimental data proves unambiguously that the reorientation of H around B is governed by a single relaxation time. The analysis of the peaks gave the value of 7 meV for the upper limit of the random shifts of the H site-energies. This value is rather low and supplies the important information that the interaction among the H–B complexes is thoroughly negligible at the boron concentrations used, $c_B\sim10^{19}$ cm^{-3}.

The infrared absorption measurements at low temperature [1] 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 ($\tau_0^{-1}=9.1\cdot10^{10}\text{s}^{-1}$), two orders of magnitude slower than that of typical point defect motions in solids. This discrepancy suggested that tunnelling-assisted jumping might take place at low temperature for $\tau^{-1}(T)$. Indeed, the combination of the infrared absorption and of the anelastic relaxation data, which gives the H jumping rate over an exceptionally wide range (12 orders of magnitude), indicates that a deviation of $\tau^{-1}(T)$ from the classical law takes place at liquid nitrogen temperatures. The authors of Ref. [4] tried to interpret the behaviour of the relaxation rate derived by their and by our data in terms of the Flynn–Stoneham small polaron model [5] of the H phonon-assisted incoherent tunnelling. The

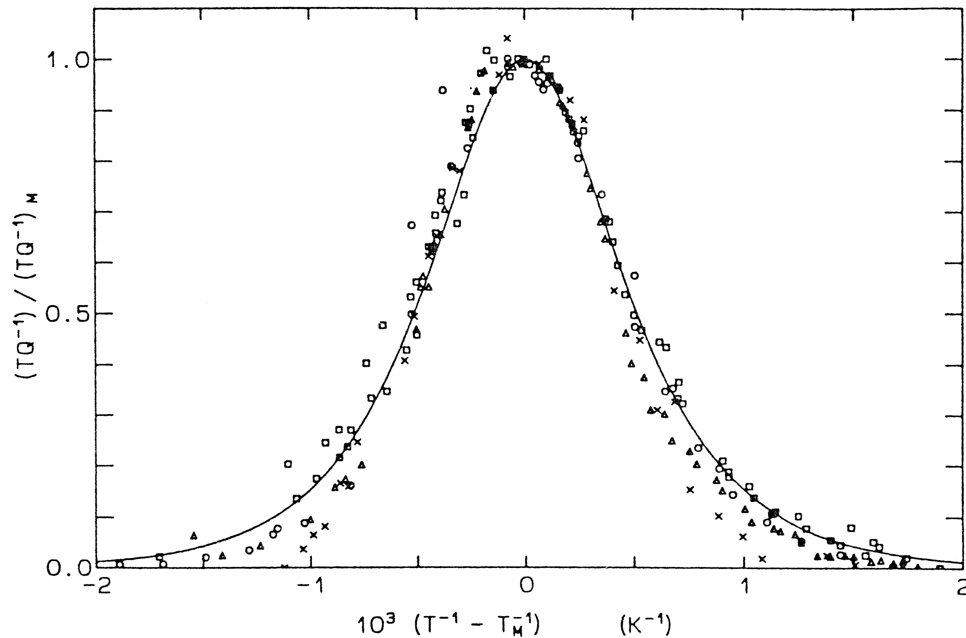

Fig. 2. Elastic energy dissipation peaks in Si:B–H at three frequencies (2.4, 13, and 32 kHz) after normalisation in temperature and height. The solid line represents the theoretical single-time Debye curve with $W=0.22$ eV.

use of that model, however, requires a Debye temperature $\Theta_D=187$ K, whereas the actual value for Si is $\Theta_D=450$ K.

In Fig. 3 we report the elastic energy dissipation coefficient as a function of temperature of the D charged Si:B sample. Again, a peak is found at low temperature by the deuterated sample. From the analysis of the peak it is derived that, within experimental error, the activation energy and the prefactor of the relaxation rate have the same values of H. This observation is rather unexpected, and indicates that at the temperature of the peak ($T\sim125$ K) the situation is different from that at about 60 K, where a reverse isotope effect has been reported [4]. To explain the faster jump rate of D with respect to H (a factor of 1.5) measured by the infrared absorption measurements, the presence of elastic interactions among the H–B complexes has been invoked [1]. However, this occurrence would not be confirmed by the features of the anelastic spectra; in fact, a significant complex interaction would cause a broadening of the dissipation curves, which on the contrary, is not observed by our measurements.

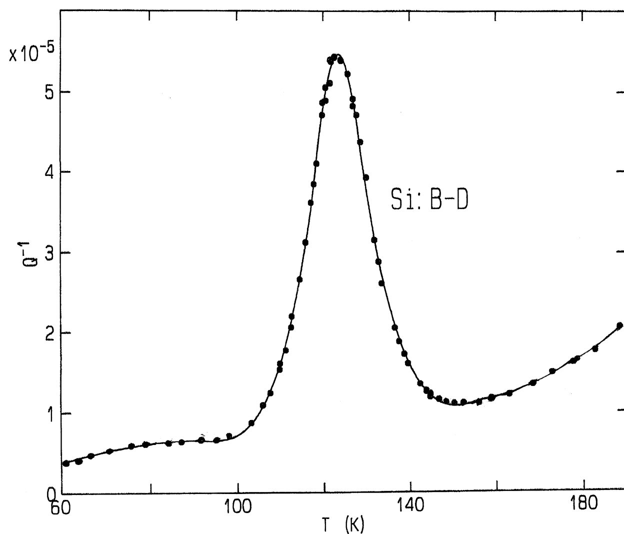

Fig. 3. Elastic energy dissipation coefficient versus temperature of *p*-type Si:B–D displaying the peak due to the D–B relaxation.

3.2. The GaAs:Zn–H(D) system

In deuterated and hydrogenated GaAs:Zn peak is observed at about 20 K in the kHz range [3]. This peak is governed by unexpectedly fast transition rates, which are the highest found so far for H(D) in a semiconductor; in fact, they are about 15 orders of magnitude faster than those of hydrogen in all other measured semiconductors. Fig. 4 shows the elastic energy dissipation curves of GaAs:Zn before and after the D charge, at 1 and 13 kHz, where the appearance of the effect is evident. The occupancy of H around Zn in GaAs has been calculated to be bond centre [6], but the actual defect configuration causing the peak is not known; at present it can only be said that the simultaneous presence of H(D) and Zn in GaAs is necessary for the peak to occur. If the peak is interpreted in terms of a classical over-barrier hopping of the mobile species causing it, an activation energy $W=37$ meV and a pre-exponential factor $\tau_0=1\cdot10^{-14}$ s are derived from the peak shift with frequency; the value of the prefactor is typical of point-defect relaxation. However, the peak is exceptionally broad, as shown in Fig. 5, where the experimental points are drawn together with the single-

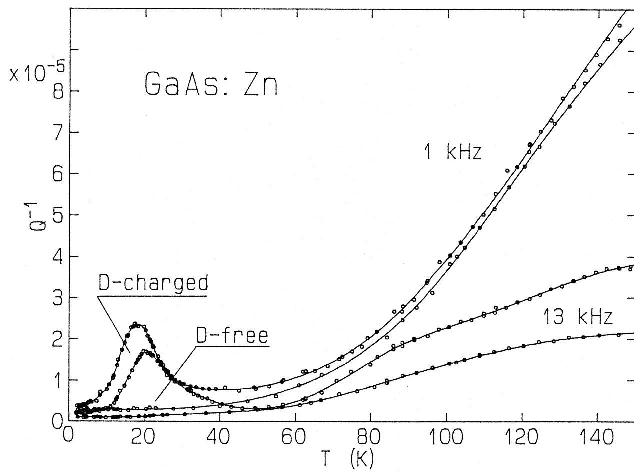

Fig. 4. Elastic energy loss of GaAs:Zn before and after the charge with D ($6.7 \cdot 10^{18}$ ions cm^{-2}), at 1 and 13 kHz.

time Debye curve obtained using the above parameters. In order to fit the data by the classical Arrhenius law, an unphysically broad distribution of W and τ_0 should be introduced, which would imply a strong elastic interaction among the Zn–D complexes. But a significant interaction is not expected at the dopant concentrations presently used ($c_{Zn} \sim 10^{19}$ cm^{-3}) as Si samples containing similar B concentrations and charged with H(D) under similar conditions displayed a nearly single Debye peak for the reorientation of the H–B complex [2].

The analysis mentioned above indicated that the process

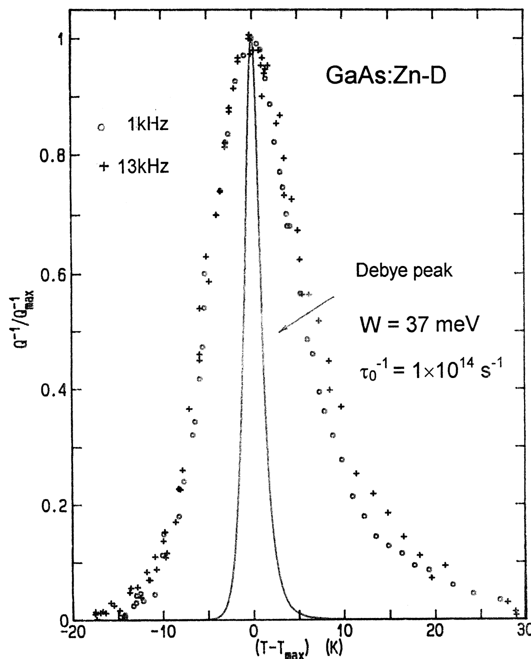

Fig. 5. The normalised relaxation process in GaAs:Zn–D at two frequencies (1 and 13 kHz). The continuous line represents the theoretical single-time Debye curve with the activation energy $W=0.37$ meV derived from the peak shift with frequency.

is non-classical and a quantum mechanical approach is necessary. However, an attempt to explain the peak as incoherent tunnelling, in terms of the small polaron phonon-assisted hopping [5] was also not satisfactory. Indeed, the theoretical curves are much narrower than the data, and broadening is again obtained by adopting large distributions in which, however, the tunnelling parameters vary over orders of magnitude. In addition, only the formula approximated for $T \gg \Theta_D$ can reproduce the data to some extent; such an approximation is certainly not valid at the peak temperature, $T=20$ K, since the Debye temperature for GaAs is $\Theta_D=270$ K. Even in this case, if attempts are made to reproduce the peak temperatures, the corresponding heights are not obtained.

In the framework of coherent tunnelling, it is possible to obtain broad curves without the necessity of introducing exceedingly strong interactions among defects. In fact, assuming a simple two-level system and taking into account the simultaneous contributions of one-phonon (giving relaxation rates following the linear law $\tau^{-1} \propto T$) and of two-phonon processes (giving rapidly varying laws $\tau^{-1} \propto T^n$) broad curves can be derived.

4. Conclusions

The relaxation of H–B pairs in Si gives rise to a single-time Debye process. The relaxation rates versus temperature from the anelastic relaxation and from the decay of dichroism, considered separately, are well fitted by a classical Arrhenius law, but the combination of data from the two types of experiments reveals a deviation from the exponential behaviour at liquid nitrogen temperatures. The attempts made in terms of a small polaron model are not quite satisfactory. In GaAs:Zn–D(H) a relaxation effect is observed at 20 K, which is much broader than a single Debye curve and is caused by a very mobile species, not yet identified. The mechanism causing the process cannot be explained classically and is hardly interpreted in terms of incoherent tunnelling. The possibility of a coherent tunnelling system making multiphonon assisted transitions should also be considered.

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