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Dynamics of H trapped by defects in type IV and III–V semiconductors

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Abstract

Recent progress and new results are discussed from anelastic spectroscopy studies of H complexes with substitutional dopants and vacancies in Si, GaAs and InP. Anelastic relaxation processes due to the reorientation of H around dopants are found in the case of acceptors (B in Si and Zn in GaAs) but not of donors (P in Si, and $\mathrm{Si_{Ga}}$ in GaAs). It is argued that this is an indication of bond-center occupancy in the first case and anti-bonding in the second one, in accordance with theoretical predictions. The reorientation rate of H around B in Si can be followed over 11 orders of magnitude, including the data from infra-red spectroscopy, and a deviation from an Arrhenius law with effective barrier of 0.22 eV at low temperature indicates the involvement of tunneling in the reorientation process. The relaxation rate of H and D in GaAs:Zn is much faster than any other dopant-H complex studied so far, and the analysis of the process demonstrates a totally non-classical nature of the H motion. This also provides evidence of off-centre occupation of H from the Zn–As bond. In InP, a new relaxation process has been found, which is present only in the semi-insulating state. It is argued that the defect is an In vacancy with the P dangling bonds partially saturated by H, and that such vacancy-H complexes have a role in obtaining semi-insulating InP, which is of technological interest.

Keywords: H in semiconductors; Anelastic spectroscopy; H tunneling; Dopant-H complexes; Vacancy-H complexes

PACS: 66.35.+a Quantum tunneling of defects; 61.72.Ji Points defects (vacancies, interstitials, color centers, etc.) and defect clusters; 62.40.+i Anelasticity, internal friction, stress relaxation, and mechanical resonances; 81.05.Ea III-V semiconductors

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1. Introduction

Hydrogen in semiconductors is rousing no less interest than in metals. It is often introduced in uncontrolled amounts during the material preparation and subsequent fabrication of devices. Although H has a much lower solubility in pure semiconductors than in many metals, its presence can drastically modify the electrical properties of semiconductors, thanks to its ability of combining with almost any defect or impurity and neutralizing its electrical activity [1]. The study of the complexes of H with various defects and impurities is therefore of both technological and fundamental interest.

A technique widely used in this field is the infrared (IR) spectroscopy [1], which is sensitive to the local vibration modes (LVM) of the H atoms bound at the various defects; each configuration has a characteristic frequency, and can be identified with the help of theoretical models. By making time- and polarization-resolved experiments [2], it is possible to follow the relaxation of the populations of differently oriented bonds under stress, measuring relaxation times of seconds or longer for the reorientation of H around impurities.

Later, the anelastic spectroscopy [3,4] has also been employed with success in this field, allowing relaxation rates in the range of kHz and the symmetry of the complexes to be explored. We review some recent progress and present new results on anelastic spectroscopy studies of the reorientation and tunneling dynamics of H near substitutional dopants and within vacancies in Si, GaAs and InP.

2. Experimental

The anelastic spectroscopy measurements were made on thin bars cut from single-crystal wafers, generally $3-5$ cm long and $0.4-0.8$ mm thick, and electrostatically excited on their odd flexural vibration modes at frequency $\omega/2\pi$.

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In this manner, one measures the complex dynamic Young's modulus $E(\omega) = E' + iE''$, which is the reciprocal of the compliance s in the direction of the longer dimension, $s_{[100]}$ or $s_{[110]}$ in most measurements. We will discuss the elastic energy loss coefficient, Q^{-1}, which is related to the dynamic modulus by E''/E' or s''/s'. A simple relaxation process, like hopping or transitions between two sites or energy levels α and β with a relaxation time τ contributes to E'' with [5]

$$s'' = \frac{c}{v_0} \frac{n_\alpha n_\beta}{k_B T} (\lambda_\beta - \lambda_\alpha)^2 \frac{\omega\tau}{1 + (\omega\tau)^2} \tag{1}$$

where c is the total concentration of the defect, n_α the population of the defect in the α configuration and λ_α the corresponding elastic dipole, namely the long range component of the strain due to a unitary concentration of defects α. For a uniaxial compliance in the direction $\hat{\mathbf{n}}$, λ is the component of the elastic dipole along $\hat{\mathbf{n}}$. The spectrum is measured at fixed frequencies ω as a function of temperature, and contains a peak at the temperature for which $\omega\tau(T) = 1$.

Hydrogen or deuterium in Si and GaAs was introduced by low-energy ion-gun irradiation (~140 eV) at 300°C for several hours, or by exposing the sample to H plasma (0.5 mbar) at 300–420°C for few hours. In this manner the penetration occurred by diffusion and the damage due to the impinging ions was minimized.

3. Results and discussion

An important type of complex with H is the pair with a substitutional dopant. First principle calculations [1] indicate that H can form stable pairs with dopants, and the passivation of the electrical activity of most dopants by addition of H confirms this view. In the case of an acceptor, the most stable site for H is the bond center (BC) site [1,6], midway between the dopant and one of the first neighboring host atoms in the ⟨111⟩ direction (Fig. 1). Instead, in *n*-type Si the anti-bonding (AB) sites, again along ⟨111⟩ from a host atom but opposite to the dopant–host bond, are favored, together with the tetrahedral (T) site, also indicated in Fig. 1.

3.1. Complexes of H with acceptors: nearly classical reorientation

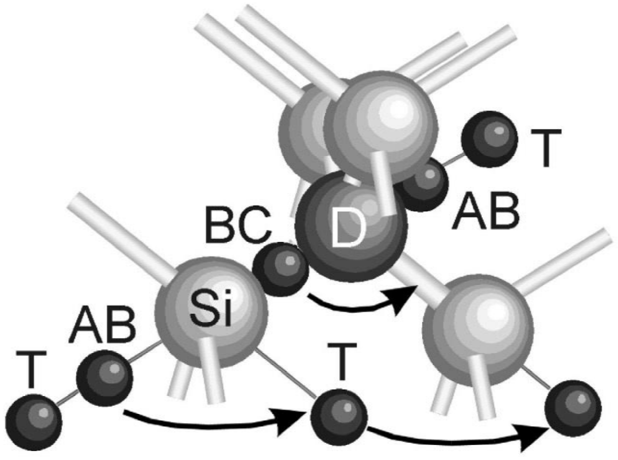

Fig. 1. Possible sites for H in Si near a dopant (D) atom. The large bonds represent the network of Si atoms. The bond center (BC) position is found near acceptors; the anti-bonding (AB) position is predicted near a donor, both on the donor and Si side. The jumps between BC and donor-AB sites are direct, while those between Si–AB sites require dissociation to a tetrahedral (T) site.

The B–H pair in Si has been studied by IR [6] and anelastic [3] spectroscopies. The complex has trigonal symmetry, as demonstrated by applying a uniaxial stress along different crystallographic directions and following the time evolution of the populations of the differently oriented B–H pairs with polarized IR spectroscopy [6]. Such a symmetry is confirmed by new anelastic spectroscopy measurements on two Si:B samples oriented along ⟨100⟩ and ⟨110⟩ and exposed together to H plasma. Fig. 2 demonstrates that the dissipation peak is observed in the ⟨110⟩ sample but is totally absent for the ⟨100⟩ one. Reminding that the flexural vibration of a sample with length along ⟨100⟩ is equivalent to non-homogeneous uniaxial strain along ⟨100⟩, the absence of relaxation in such a sample implies a trigonal symmetry of the defects, in accordance with a H occupation along the ⟨111⟩ bonds. The B–H peak measured at different frequencies [3]

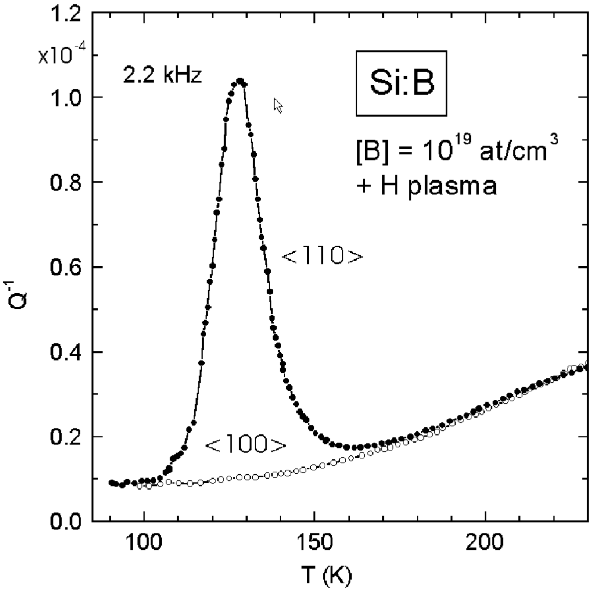

Fig. 2. Elastic energy loss versus temperature of two Si:B samples exposed together to 1 Torr H plasma at 180°C for 8 h; the RF frequency was 2.5 MHz and the samples were 10 cm from the plates, shorted with the cold plate.

closely follows Eq. (1) with a relaxation rate $\tau^{-1} = \tau_0^{-1} \exp(-W/k_B T)$, $\tau_0 = (8 \pm 4) \times 10^{-14}$ s and $W = (0.22 \pm 0.01)$ eV. These observations are in agreement with the theoretical calculations, which indicate that H occupies the BC position between B and Si and is mainly bound to the Si atom. In addition, according to ab initio pseudopotential calculations [7], the potential energy rises very slowly when H is displaced off-centre perpendicularly to the Si–B bond. This fact has been confirmed by further calculations showing that the BC site is a marginal equilibrium position, which evolves to off-centre positions with increasing size of the dopant atom [8]. This flat potential in the off-axis direction has been invoked in order to explain anomalies in the LVM in terms off-centre occupation of H at high temperature [6], but it is also the reason for the relatively high reorientation rate of H around the acceptor impurities, compared to the donor ones. The activation energy for reorientation, 0.22 eV, is even much smaller than the binding energy, estimated around 0.6 eV (Ref. [6]).

The data of the reorientation kinetics of B–H in Si from anelastic and IR spectroscopy span 11 orders of magnitude of the rate [9] and, similarly to the case of the local (around O impurities) and long range diffusion of H in Nb, Ta and V [10], the rates at lower temperature are higher than the extrapolation from the high temperature data (Fig. 3). This fact indicates that the reorientation of H between the BC sites occurs through tunneling assisted and not purely classical over barrier jumps. The data of the B–H reorientation from IR and anelastic spectroscopies have been fitted [9] with the expression by Flynn and Stoneham [11] for polaron-like hopping, although several models of quantum diffusion can reproduce a thermally activated behavior with a crossover to tunneling assisted hopping [12].

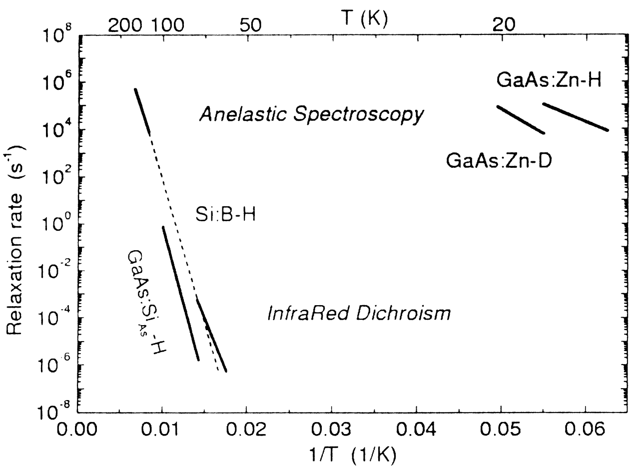

Fig. 3. Arrhenius plot of some reorientation rates of H and D around acceptor impurities in Si and GaAs.

3.2. Complexes of H with donors: anti-bonding versus bond-center occupation

The anelastic spectrum of Si:P charged with H and D under the same conditions which produce intense B–H peaks in Si:B is flat between 1 and 550 K (Ref. [13]). The undetectability of any anelastic relaxation process in H-doped Si:P is not due to the absence of the P–H complex, which is known to exist from the neutralization of the P donors by H addition. Rather, it must be due to the different structure of the P–H pair. In fact, in *n*-type Si the stable position of H is in sites with a lower electronic density, like the AB or T sites (Fig. 1); in particular for H trapped at P calculations predicted that the most stable position is AB to one of the Si atoms surrounding P [14]. There are three reasons why the intensity of the anelastic relaxation of such a pair is expected to be much lower than that for the dopant-H pair in BC configuration.

The reorientation between the AB coordinated with the Si instead of the dopant atom requires a dissociation of the P–H pair, since the sites are too far apart from each other for an elementary jump to occur. A possible reorientation path via a T site is shown in Fig. 1. Even though the exact intermediate configuration is not known, the reorientation requires at least a partial dissociation of the P–H pair, and the energy difference between the AB configuration and the dissociated one should be of the order of 0.5–1 eV, a typical energy separation between different states of H in Si. In particular, the energy difference between H in T occupation, E_T, and bound in AB configuration to a P donor, E_b, has been estimated by self-consistent pseudopotential calculations [15] as $E_T - E_b = 0.5 \div 1$ eV, depending on the H charge status. The reorientation process is therefore characterized by an intermediate state with energy $E_T - E_b \gg k_B T$ and also a barrier for the partial dissociation, $W_b = E_s - E_b$, much higher than that for retrapping, $W_T = E_s - E_T$, where E_s is the saddle point energy. The resulting relaxation modes correspond to the dissociation/retrapping process and to the reorientation one. The dissociation/retrapping mode has a rate $\tau^{-1} \simeq \nu_0 \exp(-W_b/k_B T) + \nu_0 \exp(-W_T/k_B T) \simeq \nu_0 \exp(-W_T/k_B T)$, which may well be comparable to that for the acceptor-H reorientation, but the relaxation strength is negligible due to the factor $n_T n_b \propto \exp[-(E_T - E_b)/k_B T]$ in Eq. (1). Instead, the reorientation mode has a much slower rate $\tau^{-1} \sim \nu_0 \exp(-W_b/k_B T)$ and therefore may be observable at much higher temperature. However, it is likely that also the intensity of the reorientation mode of an AB pair is smaller than that of a BC pair. From Fig. 1 it appears that the BC occupation requires a strong shift of the dopant and Si atoms, while H in AB occupation fits a large site with low electronic density. Then the $\langle 111 \rangle$ component of the elastic dipole λ of H in $\langle 111 \rangle$ BC occupation is larger than that in AB occupation, and the square of the anisotropy of λ in the relaxation strength may be considerably reduced for the AB occupation. A small distortion and therefore small relaxation intensity is expected for an AB donor-H pair both for H in AB_{Si} and AB_D (D being the dopant). In the latter case the reorientation path is direct, like the BC pair, but the activation energy could again be higher than that for BC reorientation, since the flatness of the potential perpendicularly to the bond axis has been verified for BC occupation [8] but not for AB.

We conclude that the anelastic relaxation process due to the reorientation of a donor-H complex, predicted to be in AB configuration, occurs with rate and intensity much smaller than the reorientation of an acceptor-H pair in BC configuration, making its observation difficult. It should be noted that both the BC and AB dopant-H pairs have trigonal symmetry; therefore, the lack of observation of an intense and fast reorientation process in hydrogenated samples is an important experimental indication of AB occupation.

This is further confirmed by the anelastic spectra of hydrogenated and deuterated $GaAs{:}Si_{Ga}$, which do not show any relaxation process attributable to defect reorientation [4]. In those samples Si substitutes Ga and acts as a donor, for which we do not expect intense relaxation; instead, the reorientation process of the Si_{As}-H pair has been observed by IR measurements [16] on $GaAs{:}Si_{As}$, which is *p*-type with predicted BC occupancy. The relaxation rate is slightly slower than that of B–H in Si, as shown in Fig. 3.

3.3. The Zn–H complexes in GaAs: off-centre occupation and tunneling

An anelastic relaxation process with an extraordinarily fast rate has been found [4] in $GaAs{:}Zn_{Ga}$ charged with D. The spectrum contains a peak at 20 K for $\omega \sim 10$ kHz, and the effective rate $\tau^{-1}(T) \sim \omega$ derived at the peak maxima measured at different ω is plotted in Fig. 3: it has an apparent activation energy of 0.034 eV, 6 times smaller than that for the reorientation of the B–H in Si. The process can also be observed after irradiation of the sample with H instead of D ions, with a sizeable isotope dependence (Fig. 4).

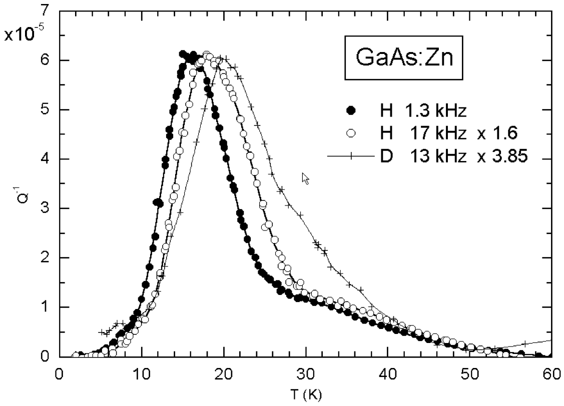

Fig. 4. Elastic energy loss of GaAs:Zn charged with H and D by ion gun irradiation (~7×10^{18} ions/cm^3, 140 eV at 300°C for ~7 h). A background has been subtracted and the peaks have been normalized in intensity with the factors indicated in the legend.

The Zn substitutional is an acceptor and H is expected to occupy the BC site [1,7,8], as explained above. In addition, the Zn atom could be large enough to push the H atom off-centre with respect to the BC site, as shown in Fig. 5. In that case, H could be delocalized over a ring of 3 or 6 off-centre sites around the Zn–As bond, and the distance between the adjacent rings would be smaller than that from BC sites, resulting in a faster reorientation rate. A progressive shift of H off-centre from the BC site at high temperature has been proposed in order to explain anomalies in the H LVM [6], but the present measurements would be the first experimental indication of off-centre occupation of H at low temperature. Such a picture predicts two relaxation processes: a slower one for the reorientation among the different bonds around Zn, and a faster and less intense one due to the transitions within the tunnel system (TS) formed over the ring. Since no other peaks attributable to reorientation processes are observed up to 550 K, the peak at 20 K is most likely due to the reorientation among different bonds. A puzzling feature of this peak is that it is several times broader than a pure Debye relaxation, Eq. (1), with $\tau(T)$ derived from the peak shift at different frequencies. The Zn concentration $[Zn] = 10^{19}$ cm^{-3}, corresponding to ~200 at ppm, does not justify site energy shifts due to a direct interaction between the Zn–H complexes; rather, a higher concentration of un-

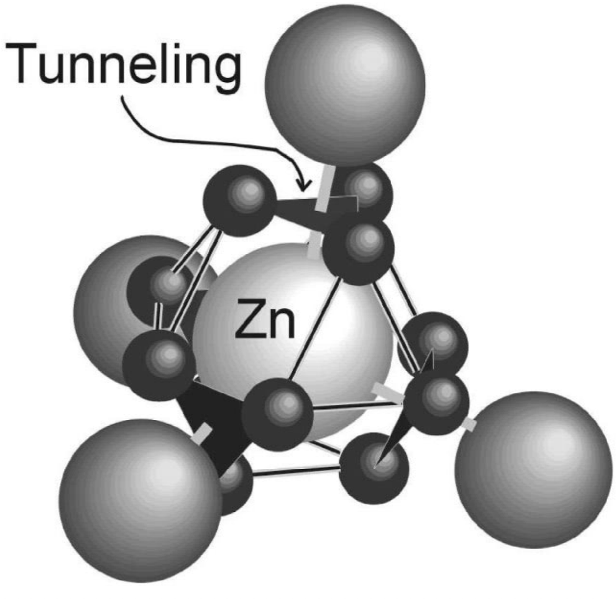

Fig. 5. Network of the off-centre sites for H near a dopant Zn in GaAs.

trapped H and possibly lattice damage from the ion gun irradiation should be responsible for the lattice disorder. In addition, GaAs is known to contain Ga vacancies. The wide distribution of relaxation rates necessary to explain the peak shape rules out an explanation in terms of overbarrier hopping with $\tau=\tau_0 \exp(W/k_B T)$, since a distribution of τ_0 over some orders of magnitude would be necessary. This is unphysical, since classically τ_0^{-1} is mainly determined by the curvature of the potential minima, which is little affected by strain. A tentative fit of the data was proposed [4] in terms of the Flynn–Stoneham formula; [11] in the approximation $T > \Theta_D$ it is close to a Arrhenius law, but the pre-exponential factor contains the square of an effective tunneling matrix element, which in principle could strongly depend on lattice disorder. A serious problem with this interpretation is that one needs to adopt the $T > \Theta_D$ approximation at 20 K, whereas $\Theta_D \gtrsim 250$ K. Recently, a comprehensive formulation of the dynamics of a tunneling particle interacting with the phonon bath has been proposed [12], with expressions of the relaxation rates which explicitly take into account the site energy shifts also in the high temperature incoherent tunneling regime, and the analysis of the 20 K peak in terms of that theory is in progress. Actually, from new measurements on H-doped GaAs:Zn (Fig. 4) it appears that there are two distinct peaks, at ~17 K and ~34 K; the origin of two distinct peaks in the above model is not clear and complicates the analysis.

3.4. Hydrogen and In vacancies in InP

Indium phosphide is of great technological interest for optoelectronic applications, when it is in the so-called semi-insulating (SI) state. The crystals are grown with the liquid encapsulated Czochralski (LEC) method, with a capping liquid B_2O_3 in order to prevent P loss, but have a too low resistivity for the applications. The main defects have been identified [17] with In vacancies with the four P dangling bonds saturated with H, here labeled as V_{In}–H_4, and are generally neutralized by addition of about 10^{16} cm^{-3} Fe acting as a deep acceptor. A drawback of the Fe addition is a low homogeneity, mainly due to Fe segregation, and therefore other methods are attempted. It has been found that crystals with a starting concentration of carriers below 4×10^{15} cm^{-3} can be made SI by a thermal treatment (TT) at ~950°C for hours or days [18] (in a phosphorous atmosphere in order to prevent P loss). Recently, we started a study of the mechanisms of the SI conversion in InP [19]; a correlation between an anelastic relaxation process near room temperature and the SI state, allowed a model of the SI conversion to be proposed. The peak appears only in the SI state, the one shown in Fig. 6 is measured on as-grown Fe-doped InP, but is observed also in high-purity InP made SI by TT. The peak is well described by a pure Debye relaxation, Eq. (1), with $\tau=3\times10^{14} \exp(-0.67\ \mathrm{eV}/k_B T)$ (solid lines in Fig. 6), and is stable against vacuum annealings up to at least 850 K, when decomposition of the sample with P loss starts; around the same temperature outdiffusion of H is observed [19]. The peak has been attributed to the reorientation of H among the P dangling bonds of a V_{In}, namely the reorientation of the complex V_{In}–H_n with $1 \leq n \leq 3$. The H saturated V_{In} are supposed to form during the LEC crystal growth in the presence of the capping liquid contaminated with water vapor; the formation of a high concentration of V_{In}–H_4 would be possible thanks to the low-energy of the strong P–H bonds, analogously to the formation of superabundant vacancies in metals in the presence of H (Ref. [20]). The subsequent TT at 950°C (which involves H outgassing) or the presence of Fe (which forms Fe–H pairs) would subtract H from the H-saturated V_{In}–H_4 complexes, expected to be donors contributing to the unwanted initial high conductivity. The conversion into V_{In}–H_n complexes with $n \leq 3$ on one hand would lower the concentration of donors and create new deep acceptors which neutralize the residual impurities; on the other hand it would create complexes with trigonal ($n = 1, 3$) or ⟨110⟩ orthorhombic symmetry ($n = 2$), whose reorientation causes the room temperature peak. New measurements on as-grown InP:Fe oriented crystals supplied by Wafer Technology demonstrate the trigonal and/or ⟨110⟩ orthorhombic symmetry of the defects causing this peak: in fact, the peak is observed on ⟨110⟩ but not on the ⟨100⟩ oriented sample (Fig. 7).

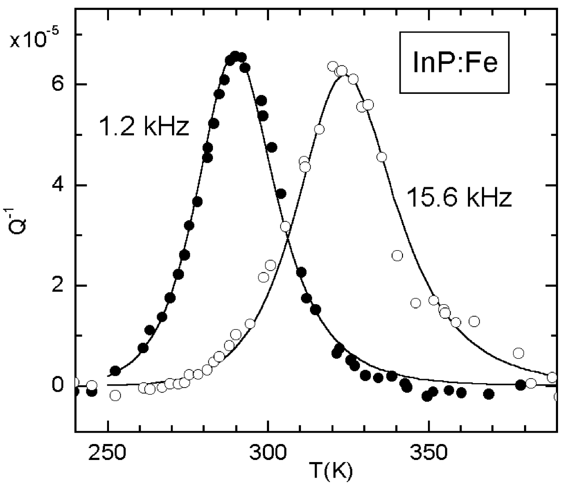

Fig. 6. Elastic energy loss of undoped InP after background subtraction. The sample, supplied by Venezia Tecnologie, was made SI by a high temperature treatment.

4. Conclusion

Regarding the structure of the dopant-H complexes, the anelastic relaxation experiments so far conducted on *n*- and *p*-type Si and GaAs are in agreement with the existing

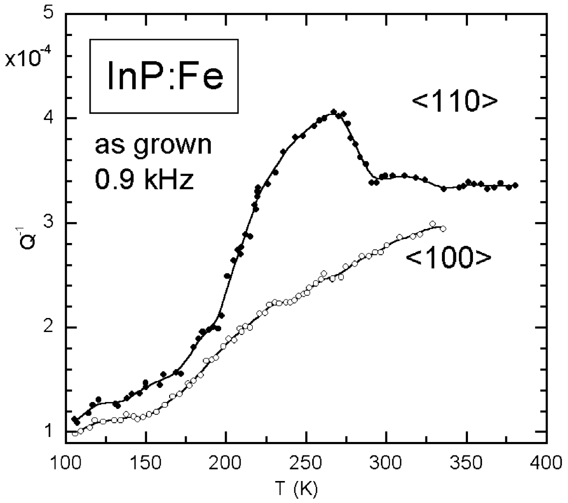

Fig. 7. Elastic energy loss of InP:Fe supplied by Wafer Technology, measured with flexural vibrations of bars with the longer dimension parallel to [110] and [100].

infrared data and first principle calculations. Furthermore, the anelastic spectroscopy extends to much higher relaxation rates the well established time- and polarization-resolved infrared measurements of the H local vibration modes, for studying the structure and dynamics of H complexes in semiconductors. In this manner, it is possible to obtain information also on fast dynamic processes governed by quantum tunneling.

The B–H pair in Si has a bond-center occupation, and the reorientation occurs over an effective barrier of 0.22 eV. The slight deviation of the reorientation rate from the Arrhenius law at low temperature can arise from quantum effects due to a sizeable delocalization of H in a potential which is flat perpendicularly to the Si–B bond. On the contrary, the donor-H complexes (P–H in Si and Si_{Ga}–H in GaAs) do not produce detectable anelastic relaxation effects below 550 K. This can be due to a reduced distortion of the donor-H pair with respect to the acceptor-H pair and to a higher barrier for reorientation. Both effects are in agreement with the predicted anti-bonding occupation of H in *n*-type Si and GaAs. Therefore, the absence of an easily detectable anelastic relaxation process in samples containing dopant-H pairs is an important indication of AB occupancy.

The anelastic spectra of GaAs:Zn_{Ga} charged with H and D provide the first evidence of off-centre occupation of H around the dopant–host bond, with a tunneling driven dynamics of H.

In InP, a new relaxation process from the reorientation of trigonal or ⟨110⟩ orthorhombic defects has been found, which is present only in the semi-insulating state. By studying the anelastic spectra of both Fe-doped and undoped InP subjected to various thermal treatments it is concluded that the defect is an In vacancy with the P dangling bonds partially saturated by H. A role of these defects has been proposed in connection with the technologically interesting methods for obtaining semi-insulating InP.

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