PHONO-CONDUCTION SPECTROSCOPY OF SHALLOW STATES IN SEMICONDUCTORS

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1. INTRODUCTION

There is a long-standing interest in the problem of dynamics of carriers excited from and trapped by shallow states in semiconductors. High frequency phonons in many cases mediate the relaxation of the carriers from free to bound states. Specific experimental evidence of the phonons involved could give direct information on the processes effective in relaxation but as yet is missing.

The process inverse to relaxation, the excitation of carriers from bound to free states by nonthermal phonons has been developed in the last years as a new spectroscopic technique called PIC (phonon induced conductivity) [1] or phonoconductivity: Superconducting tunnelling junctions are used as high frequency phonon generators with a bias tunable sharp spectral component. Sensitive detection of the excitation is possible by the change in conductivity. It has been shown by this technique that

* Al-junctions transmit quasimonochromatic phonons up to at least 14 meV into Ge, i.e. frequencies well beyond the Debye frequency of the lowest TA-branch in Ge;

* strong phonon coupling to D^-/A^+ states of overcharged donors/acceptors allows sensitive investigation of their properties;

* one-phonon excitation from the ground state (GS) to the conduction band (CB) is possible for donors in Ge since the many valley structure of the CB facilitates the conservation of the large phonon k-vector in the transition.

A problem connected with such a one-phonon transition is that the deformation potential coupling may be drastically reduced by the condition of momentum conservation because the wavelength of the corresponding phonons may be much smaller than the extent of the wave function of the shallow bound states. Therefore, to understand the experimentally observed rapid decay of nonequilibrium free carriers at low temperatures intermediate states have been invoked for relaxation such as the quasi-hydrogenic ladder of excited states of the trap ("Lax cascade", [2]) or the weak binding of an additional carrier by a neutral trap in analogy to H^-. [3]

2. EXPERIMENTAL

A typical experimental setup may be as follows [4]: An Al-junction as tunable phonon source is evaporated on one of the 15 mm x 5 mm faces of the 2 mm thick samples. The junction films are relatively thin (~15 nm) to prevent excessive down-conversion of the high frequency phonons by reabsorption within the films. 100 nm thick Al-contact films are evaporated on the side opposite to the junction for measurement of the conductance change. It is the bias U to the superconducting tunnelling junction (bath temperature typically 1 K) that determines the maximum energy ($eU-2\Delta_{Al}$) of the phonons emitted by the tunnelling quasiparticles. This maximum phonon frequency is filtered by Lock-In technique if the junction bias is modulated (For a review see e.g. Eisenmenger [5]).

The side opposite to the junction is irradiated with visible light from an incandescent lamp on top of the cryostat via a glass fibre rod to produce free carriers (electron-hole pairs) for a finite resistance of the sample (typically 1 MΩ) to measure the phonon induced resistance changes. The carriers diffusing and drifting through the sample are partly trapped by the neutral donors/acceptors to form D^-/A^+-states with binding energies around 2 meV.

A property specific to phonoconductivity as opposed to FIR-photoconductivity is the strong gradient in phonon intensity away from the phonon generator not so much from geometrical spreading but more because of the small mean free path (mfp) of high frequency phonons. This allows distinguishing configurations for additional information as detailed in [6]: Measuring the resistance change between the contacts opposite to the generator means a long phonon path; measuring across the sample may mean a short phonon path if by appropriate polarity of the measuring bias the appropriate type of carriers for additional D^-/A^+ production is drawn underneath the phonon generator where the phonon intensity is high. Epitaxially doped layered samples additionally allow to locate the detection zone and thus e.g. to estimate the effective phonon mfp. A first example was given in [7]. A

low or ohmic contact resistance is not essential in these measurements but the modulation frequency is limited to about 1 kHz because of the large electronic time constant for a high resistance. Higher modulation frequencies are possible by the installation of a transimpedance amplifier with small heat dissipation close to the sample within the cryostat rendering a better signal to noise ratio and, in addition, some information on the carrier dynamics in the sample. Similar devices have been applied by several authors in low temperature photoconductivity (see e.g. Haller [8]).

Stress may be applied by tearing a yoke against the sample with a wire strained from top of the cryostat by a screw. It is measured either with resistive strain gauges near the top of the cryostat or with a piezoelectric strain gauge adjacent to the sample. The analysis of our experiments (see below) indicates that "zero" stress may be indefinite up to 50 bar because of the needs of a firm positioning of the narrow samples. Some inhomogeneous residual stress may be due to the fact that the electrical connection to the junction and contact films is made by indium cones pressed against the sample. Near the surface there is another source of residual strains: the surface damage that may be produced by polishing with .25 um diamond grain which was the case for most of the Ge measurements described below. These strains will be more important for the highest phonon frequencies where the mfp is in the um range. Two types of processes determine the phonon mfp at high frequencies and low temperatures: elastic isotope scattering - E_{ph}^{-4} and anharmonic decay - E_{ph}^{-5}. Only rough estimates are possible in the high frequency range: With dominant elastic scattering the resulting diffusion length may range from several 1000 um at 2 meV (- the threshold of the D^--states) to several um at 12 meV (- the binding energy of the D^o.) Thus the 2 meV phonons may excite the D^- across the whole thickness of the sample increasing the carrier density everywhere across the sample whereas the 12 meV-phonons ionize the D^o only in a thin layer beneath the junction generating a thin space charge layer which will mainly influence the contact resistance.

3. RESULTS

As mentioned before a basic problem in the phonoionization of shallow impurities in semiconductors is the k-conservation: the large extent of the impurity wavefunction as compared to the wavelength of the corresponding high energy phonons leads to a strong reduction of the interaction. There are two classes of shallow states where the restriction is relieved:

1) The binding energy of D^-/A^+-states is only 1/20 of that of the corresponding neutral states within the effective mass approximation

(EMA) whereas the extent of the wavefunction is larger by only a factor of about 2.
2) In the case of a many valley band structure such as the CB of Ge the bound neutral states are made up of Bloch functions of different valleys which may facilitate a large k-vector transfer by intervalley scattering in the transition.
Both situations have been investigated by PIC measurements.

3.1. Phonoconductivity response of D^-/A^+-states in Si and Ge

In the case of D^-/A^+-states in Si and Ge the same conductivity thresholds are found as with FIR-conductivity showing that the excitation is in fact by a one-phonon process. Differences to FIR connected with the nontheless large phonon vector show up in the steepness and most spectacularly in the stress dependence of the phonon response [9] [10]. By the inclusion of details of the valence band structure in the calculation Haug and Sigmund [11] obtained good qualitative agreement for the stress dependence of the phonoconductivity response in the case of $Si:B^+$ and $Si:In^+$. More detailed comparison of the phonoconductivity results with the so far restricted results of theory as well as FIR might be necessary for a complete understanding of the situation. Apart from the case of Si:B the only other acceptor where the stress dependence can be compared is the double acceptor Ge:Be [12] where quite similar characteristic differences are found as for Si:B as shown in Fig.1.

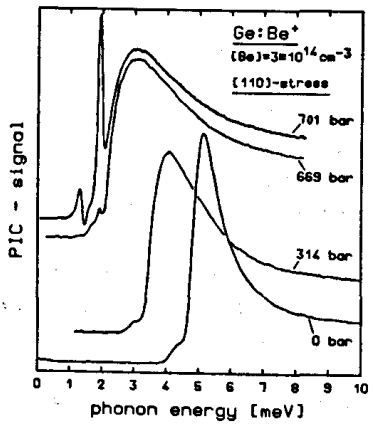

Fig. 1. Stress dependence of the phonoconductivity response of $Ge:Be^+$. The sharp peak appearing with increasing stress is similarly observed [14] in the case of $Si:B^+$, $Si:Al^+$, $Si:Ga^+$. It is, however, not found in the stress dependence of the FIR response for the measured cases of $Si:B^+$ and $Ge:Be^+$.

So far we have found no indication of the existence of excited A^+-states in Si as postulated from a model to explain the multiplet structure of acceptor bound excitons in Si [13]. In contrast to the continuous chemical shift of the multiplet splitting seen in the exciton case for the acceptors B, Al, Ga, and In we find for the binding energy of the corresponding A^+-states only for In^+ a chemical shift (i. e. influence of the central cell potential) from the effective mass value of about 2 meV (as observed for B^+, Al^+, Ga^+) to

about 6 meV [4]) which may be regarded as another example for the so-called shallow-to-deep instability of the binding energy with increasing central cell attraction.

The phonon interaction with these states is rather strong. From the resistance under illumination it is estimated that the detection threshold is below 10^9 cm^{-3} D^-/A^+ centers for our standard experimental set up. At lower illumination intensities depopulation by the phonon irradiation is observed [14]).

3.2 Phonoconductivity response of D^o-states in Ge

We have found phonon induced conductivity thresholds corresponding to the respective D^o-binding energies for Ge-samples containing Sb, P, and As with dopant concentrations of $<10^{12}$ cm^{-3} to 6×10^{14} cm^{-3} [15]). This means that Al-junctions emit primary phonons as determined by the junction bias up to the Debye frequencies of the transverse acoustic phonon branches in Ge. Fig. 2 gives an overview of the phonoconductivity response in n-Ge: The threshold near 2 meV is due to the excitation of the D^--states and the steps near 9.9 meV, 12.4 meV and 13.4 meV are ascribed to the one-phonon ionisation of Sb^o, P^o, and As^o, respectively. The high sensitivity for Sb is evident from the PIC signal of the As-doped sample where the Sb concentration should be below 10^{12} cm^{-3}, the detection limit in photoluminescence measurements of the sample (K. Thonke, Stuttgart, private communication). The Sb^o-signal of a sample doped with 3×10^{14} cm^{-3} Sb is shown in Fig. 3 in detail. The threshold at 9.9 meV (obtained by extrapolating both the

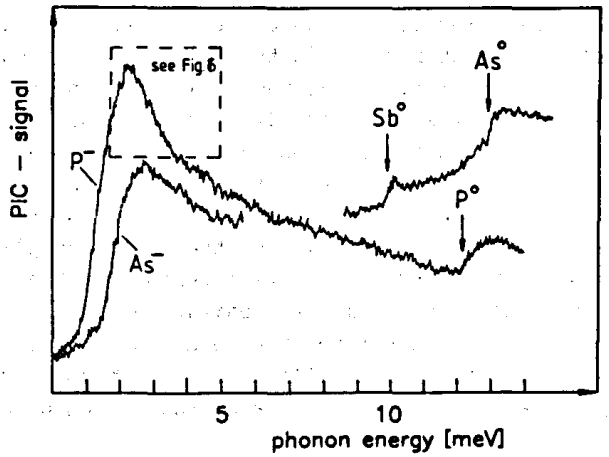

Fig. 2. PIC signal of Ge:P and Ge:P,As. The threshold at 2 meV belong to the D^-; the steps above about 10 meV to the D^o as indicated. P = $2.4\cdot10^{14}$ cm^{-3}; As = $6.0\cdot10^{14}$ cm^{-3}; Sb < 10^{12} cm^{-3}.

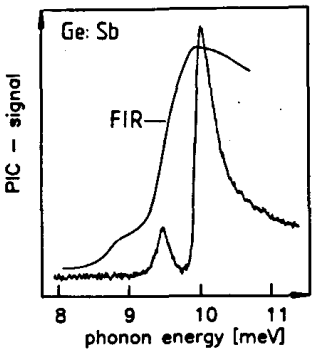

Fig. 3. PIC signal of Ge:Sb. The precursor $2\Delta_{Al}$ = .6 meV front of the rise at 9.9 meV is a spectral property of the Al-junction. The threshold for PIC is sharper than for FIR. A peak in the phonon density of states may be one reason. Sb = $3.0 \cdot 10^{14} cm^{-3}$ (PIC). Sb = $1.5 \cdot 10^{14} cm^{-3}$ (FIR) [16].

"base line" on the low energy side and the turning point tangent of the threshold to a common foot point) is much sharper than any corresponding FIR-response which appears to be sensitive to a distribution of binding energies of donor complexes somewhat below the binding energy of the isolated donor (see e.g. [16]). The optical values for the binding energy are therefore obtained from the sharp transitions to higher excited states extrapolating then to the continuum with the EMA. The optical value of 10.3 meV thus obtained for Sb is distinctly above the PIC-threshold. The feature in front of this threshold is a spectral precursor emitted by the Al-phonon source at an energy 2Δ = 0.6 meV before the main line. It can be distinguished only for sharp and prominent spectral structures on the detecting side. It proves that the gap of the Al-junction has not been reduced by the injection of quasiparticles and phonons. The sharpness and intensity of the signal is specific to Sb^0 and may be due to the slow-TA peak in the phonon density of states in Ge. This would then mean that phonons with near zero group velocity exist deep and long enough within the substrate to induce the transitions. The electronic and defect state of the contact and subsurface zone could then have a significant influence on the response. So far, correlated variations in this sense were not observed but also not systematically investigated.

One important reason for the observation of the one-step phonoionization of the donors in Ge is the many valley structure of the CB. Since the donor GS wavefunction is made up of Bloch functions of the 4 111 -valleys an effective intervalley scattering takes place in the transition taking up the large phonon wave vector. On the other hand, so far we did not succeed to obtain an ionization signal neither for the 5.8 meV Sn-donor in GaAs nor for the Ga-acceptor in Ge even if the binding energy of the latter was pulled down to 8 meV by uniaxial stress. In both cases the extrema of the corresponding bands are at k = 0.

For the donors in Ge uniaxial stress experiments confirm the picture of intervalley scattering. Uniaxial stress shifts the valleys of the CB and splits the degenerate bound states of the donors. As a consequence there will be a downshift of the binding energy and level

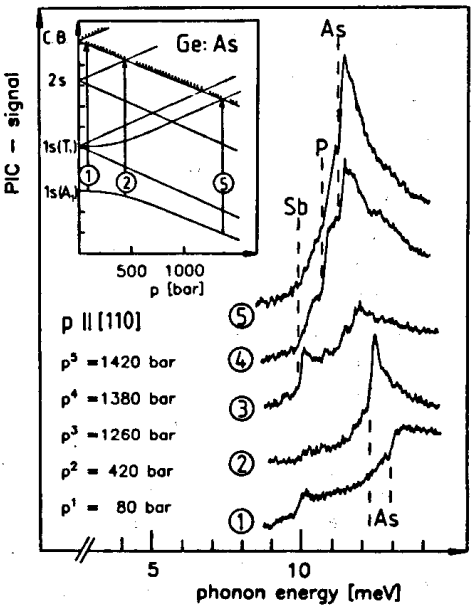

Fig. 4. Stress dependence of threshold height and position of the As-doped sample of Fig. 2 containing besides residual Sb also some P ($\cong 10^{13}cm^{-3}$). The threshold of P is visible only in curve 4 when enhanced enough by level crossing.

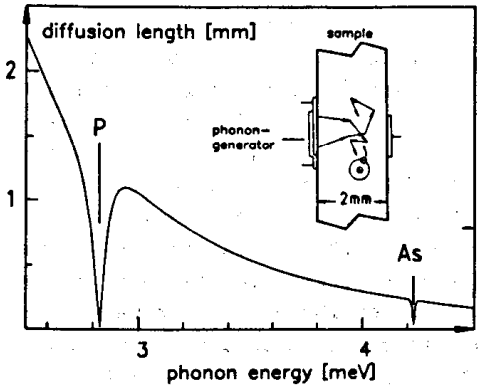

Fig. 5. Estimated diffusion length due to isotope scattering and singlet-triplet resonant scattering (As, $P \cong 5 \cdot 10^{14} cm^{-3}$, $a_B = 3.65$ nm, $v_{TA} = 3.28$ km/sec).

crossings with the lowest valley(s). The downshift is seen in the experiment as a shift of the threshold whereas the level crossings are manifest by maxima in the response.

This is shown in Fig. 4 for the As doped sample of Fig. 2 containing residual Sb ($< 10^{12}$ cm^{-3}) and P ($\sim 10^{13}$ cm^{-3}): The shift of the As threshold from 13.4 meV down to 11.3 meV as well as the variation of the threshold height according to the crossings for all three donors is clearly seen. The threshold of the P^0 is only visible for the crossing condition. In contrast to P and As the expected small shift of the threshold of Sb did not show up. This may be due to an effective pinning of the response to the steep peak of the phonon density of states.

Phonon transitions to the 1s triplet can also be observed at small stress in the case of P and As: For these donors the 1s-singlet <-> 1s-triplet GS splitting is in the energy regime of the D^--response. If by the corresponding resonant scattering the phonon density becomes higher within the zone sensitive for D^--detection, an increase of the signal is expected. An estimate for the transverse phonons shows (Fig. 5) that this extra scattering is strong at 2 meV (P) and less significant at 4 meV (As) when compared to the isotopic background. In the experiment we obtain comparable signal in-

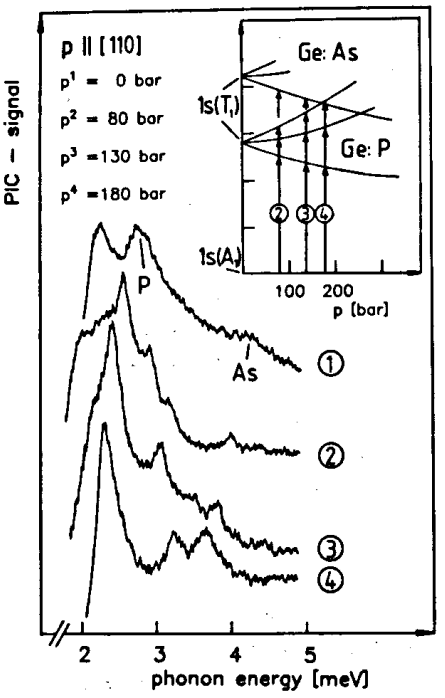

Fig. 6. Stress dependence of the D° singlet-triplet scattering superimposed on the D^{-}-signal.
$P \cong 2.4 \cdot 10^{14} cm^{-3}$,
$As \cong 10^{13} cm^{-3}$.

creases for both donors as shown in Fig. 6. At "zero" stress we find splittings of the 1s triplet differing from run to run which we attribute to residual uniaxial stress from mounting (typically 30 bar). Taking account of this initial stress we obtain from the stress dependence of this signal the ground state splitting in accordance with the optically determined values. (Phonon scattering by the GS splitting of the Sb donor in Ge was first observed by Dynes et al. [17]) by a 1 meV fixed frequency setup with Sn junctions as emitter and detector and variing the stress.)

From the threshold shift (with the initial stress accounted for) we obtain the stress dependence of the binding energy as shown in Fig. 7 for the case of P. The full lines are the expected energy differences taking (i) the optically determined binding energy at zero stress, (ii) a deformation potential constant of 16 eV for the GS splitting and the CB shifts. Our values are consistently smaller. The large discrepancy for the 100 direction is not understood. The correct orientation is ascertained directly in our experiments by the fact the GS-singlet-triplet scattering shows no splitting nor shift in this case. A slight misorientation, however, gives a fourfold structure in the level crossing expected for a nonsymmetry direction where all four valleys shift differently. Optical transitions from the GS to excited states do not show any shift nor splitting for 100 -stress. Extrapolating back to zero stress we obtain 9.9±.05 meV, 12.4±.05 meV, and

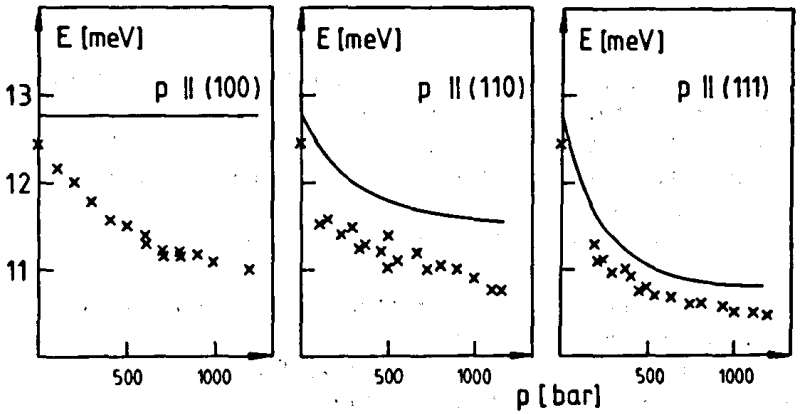

Fig. 7. Stress dependence of the P°-PIC threshold. Full lines are calculated with the optical values for the binding energies. The discrepancy for [100]-direction is discussed in the text.

13.4±.1 meV for Sb, P, and As, respectively. The difference to the optical values [18] of 10.3 meV, 12.8 meV, and 14.2 meV, respectively, apparently increases with increasing depth of the donor. Values derived from the temperature dependence of Hall measurements (Lopez and Koenig [19]) are somewhat below the PIC thresholds.
By the combination of the DPC for the band shift, the value of the ground state splitting at zero stress and the stress and threshold energy for level crossing we obtain the DPCs for the ground states of Sb, P, and As as 16.5 ± .5 eV, 16.0 ± .5 eV, and 15.7 ± .5 eV, respectively, i.e. there seems to be a small chemical shift of these constants.

4. SUMMARY

Phonoconduction spectroscopy of shallow states in semiconductors by help of superconduction Al-junctions as phonon sources with high spectral resolution is a sensitive new technique with phonon frequencies well up in the Debye range. The large k-vector of the phonons involved opens new possibilities for the investigation of electron dynamics and states in semiconductors.
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