One-phonon ionization of neutral donors in germanium

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ABSTRACT: By phonon spectroscopy with superconducting Al tunnel-junctions we show that effective mass donors in germanium can be ionized by a one-phonon excitation.

1. INTRODUCTION

In the last decades there has been continuing interest in the problem of dynamics and interactions of carriers excited from and trapped by shallow states of semiconductors. Impact ionization or photons were used to excite the carriers from their bound states at low temperatures. For the reverse process of relaxation phonons in many cases play the dominant rôle, however, specific experimental evidence for the phonons involved as yet is missing. A problem connected with relaxation by phonons is that the deformation potential coupling may be drastically reduced by the condition of momentum conservation because the wavelength of the phonons involved is much smaller than the extent of the wave function of the shallow bound states. In particular, the deexcitation to the EMA ground state by the emission of one phonon was estimated to be small (Gummel and Lax, 1955).

Here we show by phonon spectroscopy with superconducting tunnelling junctions that one-phonon excitations from the ground state to the conduction band (CB) are measurable as phonon induced conductivity (PIC) changes in the special case of donors in Ge. For the conductivity thresholds we find somewhat smaller binding energies than evaluated from optical measurements whereas for the 1s-singlet to 1s-triplet ground state splitting as seen by elastic phonon scattering we obtain the optical values.

2. EXPERIMENTAL

The experimental setup is similar to that described by Burger and Laßmann (1986) and is shown in Fig. 1: An Al-junction as tunable phonon source is evaporated onto one of the 15 mm x 5 mm faces of the 2 mm thick samples. 100 nm thick Al-contact films are evaporated on the side opposite to the junction. It is the bias to the superconducting tunnelling junction (bath temperature typically 1 K) that determines the maximum energy of the phonons emitted by the tunnelling quasiparticles. This maximum phonon frequency is filtered by Lock-In technique if the junction bias is modulated (Eisenmenger 1976).
The side opposite to the junction was irradiated with visible light from an incandescent lamp on top of the cryostat via a glass fibre rod to pro-

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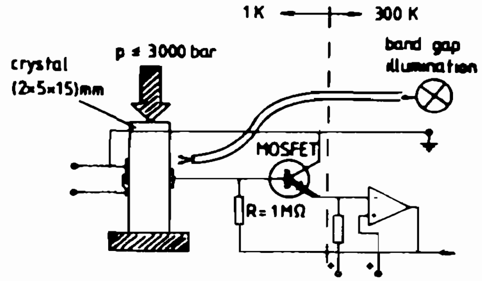

Fig. 1. Experimental setup for PIC measurements: Al-junction as tunable phonon source bandgap illumination for free carrier and D^- production, constant bias across the sample to measure the induced current. The transimpedance amplifier allows higher modulation frequencies.

duce free carriers for a finite resistance of the sample (typically 1 MΩ) to measure the phonon induced resistance changes. (Part of the electrons is trapped by the neutral donors to form D^--states (Taniguchi et al 1975) with binding energy of about 1.5 meV.) The high sample resistance allows modulation frequencies up to about 500 Hz because of the large electronic time constant. Higher modulation frequencies were 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 (SNR) and, in addition, some information on the carrier dynamics in the sample. A high upper cut-off frequency (given by $1/R_L \cdot C_L$) is conflicting with a high gain which is proportional to R_L. For $R_L = R_{sample}$ we get minimum SNR with a cut-off at about 100 kHz. Similar devices have been applied by several authors in low temperature photoconductivity (see e.g. Haller 1987). The sample was essentially kept at constant voltage. The current change was measured across the sample with the junction being one of the contacts. These evaporated Al-contacts show large contact resistances. The I-V-curves start with a linear part followed by a region of constant current where all the carriers produced by the light arrive at the contacts. Beyond this plateau the current again increases steeply due to injection from the contacts. In this region the signal becomes noisy. Alloyed ohmic contacts did not improve the SNR as compared to measuring in the plateau region with evaporated contacts.

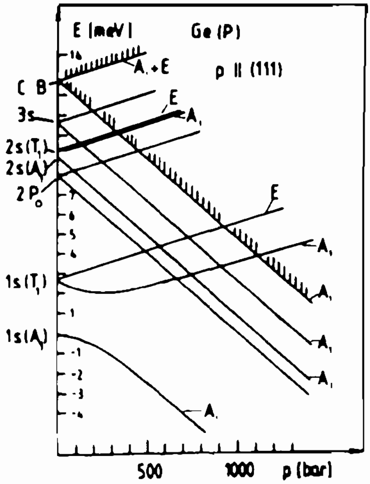

Fig. 2. Stress dependence of the energy of donor states and conduction band in Ge: decrease of binding energy, level crossings.

Uniaxial stress shifts the valleys of the CB and splits the degenerate bound states of the donors as shown in Fig. 2. As a consequence there will be a downshift of the binding energy at lower stresses and level crossings with the lowest valley(s) at higher stresses. To investigate this, stress was 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. Such contacts have the advantage of low induction wiring to the low ohmic junctions.
Another source of residual strains is the surface damage produced by polishing with .25 µm diamond grain. These strains will be more important for the highest phonon frequencies where the mean free path (mfp) is in the µm range. Two types of processes determine the phonon mfp at high frequencies and low temperatures: elastic isotope scattering $l_{is} \sim E_{ph}^{-4}$ and anharmonic decay $l_{an} \sim E_{ph}^{-5}$. Only rough estimates are possible in the high frequency range: l_{is} and l_{an} range from several 1000 µm at 2 meV (- the threshold of the D^--states) to several µm at 12 meV (- the binding energy of the D^0.) 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^0 only in a thin layer beneath the junction generating a thin space charge layer which will mainly influence the contact resistance.

3. RESULTS AND DISCUSSION

We have found phonon induced conductivity thresholds corresponding to the respective D^0-binding energies for samples containing Sb, P, and As with dopant concentrations of 2 to 6×10^{14} cm^{-3}. 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. The PIC-signal of a Ge:Sb sample is shown in Fig. 3 as a function of phonon energy: The threshold near 2 meV is due to the excitation of the Sb^- and the sharp threshold at 9.9 meV (obtained by extrapolating both the "base line" on the low energy side and the turning point tangent of the threshold to a common foot point) is attributed to the ionization of Sb^0. The feature in front of this threshold is a spectral precursor emitted by the Al-phonon source at an energy $2\Delta = 0.6$ 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.
As compared to the P^0 and As^0 thresholds the SNR for Sb^0 is rather good because the binding energy (phonon frequency) is lowest and perhaps also because the threshold coincides with a peak in the slow transverse phonon density of states. These phonons with their small group velocity should have a penetration depth even smaller than indicated above. In this thin surface layer the strains may be larger than 100 bar. As an indication for this we take the fact that the observed threshold does not depend on stress; a shift of about .3 meV would have been expected for stresses up

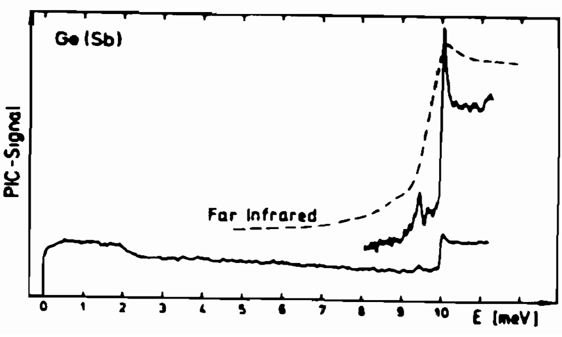

Fig. 3. PIC signal of Ge:Sb. The threshold at 2 meV belongs to Sb^-; at 9.8 meV to Sb^0. The precursor $2\Delta_{Al} = .6$ meV in front is a spectral property of the Al-junction The threshold is much sharper for PIC than for FIR. A peak in the phonon density of states may be one reason.

to 100 bar. Thus the threshold value measured here should correspond to the high stress case.
In contrast to the FIR-photoconductivity threshold at nearly the same temperature (Nagasaka and Narita 1973) the PIC thresholds are rather sharp. In the case of Sb a peak in the phonon density of states at 10 meV may be effective. There are also two "cut-off" functions that may be responsible for a steepening: The k-conservation condition reduces the interaction with phonons rapidly with increasing frequency. Also, the decreasing phonon lifetime due to spontaneous anharmonic decay will diminish the effective phonon density and thus the signal to higher energies. The photoconductivity signal below the isolated donor ionization energy (as determined by combining the measured energy differences between ground state to excited bound states from optical transitions with calculations with EMA for the excited states) down to about 9 meV has been interpreted by Nagasaka and Narita (1973) as due to donor complexes with reduced binding energies. This would then mean that the phonon interaction with these D^0-complexes is weak though, on the other hand, the broadening and shift to higher binding energies of A^+-complexes in Si is readily observed with PIC (Burger and Laßmann 1986.)
The high sensitivity for Sb is evident from the PIC signal for a Ge:As sample (Fig. 4) where the Sb concentration should be below 10^{12} cm^{-3}, the detection limit in photoluminescence measurements of the sample (Thonke 1988). The special form of the As^0-signal was reproducibly obtained with various samples. The increase of the signal after the steep step may be a sensitivity increase due to the peak in the density of states of the fast transverse acoustic phonons around 14 meV. The increase in front of the step is perhaps the effect of the strained surface layer reducing the binding energy randomly in part of the detection layer.
Whereas the SNR of the D^--signal increases for higher modulation frequencies the D^0-signal starts to diminish at about 500 Hz and was not measurable above 1.5 kHz. Since this decay shifts to somewhat higher frequencies with higher bias at the sample we believe that delay times of drifting carriers are responsible for the signal reduction, not the trapping time constants of the D^+. In the same range of modulation frequencies the phase of the D^0 shifts with respect to the D^--signal and this shift can be compensated by increasing the bias also consistent with a drift delay. Apart from the precursor there is no structure between the Sb^-- and the Sb^0-thresholds which could be attributed to scattering of phonons by transitions from the 1s to e.g. the 2s or 2p excited states since the PIC-signal has reduced spectral sensitivity far beyond the D^--threshold. (Phonothermal detection of these states is not possible at the bath

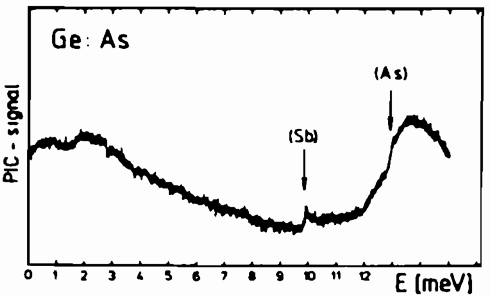

Fig. 4. PIC signal for Ge:As ($\langle As \rangle$ = $6x10^{14}$ cm^{-3}) The peak at 9.9 meV is ascribed to residual Sb^0. The form of the As^0-signal differs from that of Sb^0. Peaks in the phonon density of states around 10 and 14 meV may be one reason.

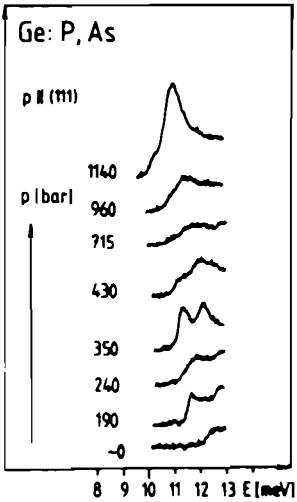

Fig. 5. Effect of level crossings on signal height.
<P> = 2.4x10^{14} cm^{-3}
<As> ~ 10^{13} cm^{-3}

temperature of 1 K since the distance from the excited states to the band is much larger than the thermal energy).
Interaction with excited ns states is, however, observable by the enhancement of the PIC signal when an excited level crosses the CB of the lowest valley under stress. This is shown in Fig. 5 for a sample containing P (2.4x10^{11} cm^{-3}) and As (~ 10^{13} cm^{-3}): In the curve for zero stress only the threshold of P^{o} at about 12 meV is visible. Under stress the threshold shifts down as expected from Fig. 2. Around 190 bar there is a first increase due to the crossing of the A_1 level of the 3s-triplet of P and at about 12.5 meV due to the crossing of the same level belonging to As. The next increase of the thresholds due to A_1 of 2s is around 350 bar and finally around 1140 bar due to the crossing of A_1 of the 1s-triplet.
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 ground state splitting is somewhat larger than the D$^-$-threshold and shows up as a small increase in the D$^-$-signal just beyond the threshold. Such an increase is expected if the phonon density becomes higher due to scattering into or trapping within the region sensitive for D$^-$-detection. 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) as mentioned in the preceding paragraph. 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 ground state splitting of the Sb donor in Ge was first observed by Dynes et al (1971) by a 1 meV fixed frequency setup with Sn junctions as emitter and detector and variing the stress.)

From the shift of the threshold (with the initial stress accounted for) we obtain the stress dependence of the binding energy as shown in Fig. 6 for the case of P. The full lines are the expected energy differences taking (i) the optically determined binding energy at zero stress, (ii) the deformation potential constants (DPC) for the ground state splitting as determined from the level crossings (see below), and (iii) the same DPC for the shift of the CBs. Our values are consistently smaller. The large discrepancy for the <100> direction is not understood. There is a slight misorientation of the stress since the number of level crossings indicates that the ground state is fully split corresponding to a nonsymmetry direction. Since, however, this direction does not deviate much from <100> as checked repeatedly with X-ray orientation and also estimated from the experiment the band shifts and level splittings and consequently the change in binding energy should be small. Extrapolating back to zero stress we obtain 12.4±.05 meV and 13.4±.1 meV for P and As, respectively (high stress value for Sb: 9.9±.05 meV). These values are between the optical values and those derived from the temperature dependence of Hall measurements (Lopez and Koenig 1968).

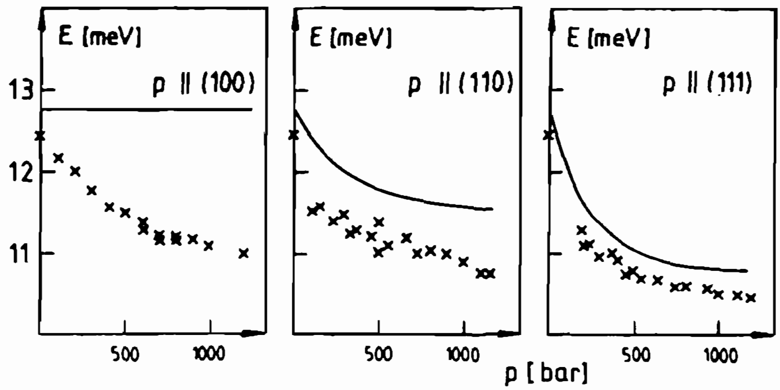

Fig. 6 Stress dependence of the PO-PIC threshold. Full lines are calculated with the optical values for the binding energies. The discrepancy for <100>-direction is discussed in the text.

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.
As regards the one-phonon ionization the donors in Ge may well be a special case because of the many valley structure of the CB supporting the k-conservation. Under similar experimental conditions we did not succeed to observe a PIC threshold for the acceptor Ga in Ge even under stresses high enough to shift the ionization energy down to about 8 meV. Also for donors in GaAs with a binding energy of nearly 6 meV we got only negative results so far. In both cases the neighbouring band extremum is at k = 0. Nevertheless, it seems promising to extend the technique to phonon-photon or phonon-phonon combination experiments to gain a direct access to the problem of phonon interaction with shallow states in semiconductors.

Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We are indebted to E.E. Haller for the supply of a P- and a Ga-doped sample and to M. Kobayashi for an As-doped sample. We are grateful to K. Thonke for his help with luminescence characterization of the donor content of the samples.

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