One-Phonon Ionization of Donors in Germanium by Intervalley Scattering: Phonon Spectroscopy with Superconducting Aluminum Junctions at Debye Frequencies

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One-phonon ionization of donors in germanium via intervalley scattering by slow TA phonons at the X point of the Brillouin zone is demonstrated by the stress dependence of phonon-induced conductivity. Superconducting aluminum junctions are used as tunable quasimonochromatic phonon sources up to these extreme frequencies. The ionization probability is found to be increased when donor levels associated with stress-shifted higher valleys of the conduction band cross the lowest valley(s).

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The fast trapping of free carriers into shallow states at low temperatures in lightly doped semiconductors is an old[1,2] but as yet open problem. The capture into the impurity ground state (GS) by one-phonon emission is possible in principle for binding energies below the Debye limit, although the probability is in general small because of the difficulty to conserve momentum. So, other processes have been invoked to explain the short carrier lifetimes: the cascading down of the carrier through excited states by low-frequency phonon emission,[2-4] a one-step decay by two-phonon emission,[5] and trapping by neutral donors or acceptors in D^-, A^+ intermediate states.[6,7]

The process inverse to relaxation, the excitation of carriers from bound states by nonthermal phonons, has become accessible by phonon-induced electrical conductivity (PIC), a new spectroscopic tool,[8] using superconducting Al junctions as tunable phonon sources. At bias U the phonon spectrum emitted by the junction has a sharp limit at $eU = 2\Delta_{\mathrm{Al}}$ ($2\Delta_{\mathrm{Al}}$=superconductor gap) which by modulation (differentiation) techniques becomes effectively a quasimonochromatic line. Here we show that, in the special case of donors in Ge, one-phonon excitation is possible by the large wave-vector transfer via intervalley scattering of the carriers in the excitation process.

The experimental technique has been described earlier.[9,10] A thin Al junction is evaporated onto one of the $15 \times 5\text{-mm}^2$ faces of the 2-mm-thick samples doped with $\simeq (2-5) \times 10^{14}\ \mathrm{cm}^{-3}$ of Sb, P, or As. The face opposite to the junction is irradiated with visible light to create free carriers and thus a finite sample conductivity.

The PIC signals obtained vary with stress. This can be understood in terms of the theoretical stress dependence of the shallow donor states and the corresponding transition probabilities.

The eigenvalues and eigenfunctions are given by several authors.[11-14] The unstressed GS consists of a singlet [$1s(A_1)$, $n=0$] and a triplet [$1s(T_1)$, $n=1,2,3$] separated by the valley-orbit splitting 4Δ (Fig. 1). With increasing stress the ionization energy initially falls and then remains constant. The eigenfunctions Ψ_n are represented as a superposition of Bloch functions $\varphi_k^{(i)}(\mathbf{r})$ of the four conduction-band (CB) minima at $\mathbf{k}^{(i)}$:

$$\Psi_n(\mathbf{r}) = \sum_{i=1}^{4} \Psi_n^{(i)} = \sum_{i=1}^{4} a_n^{(i)}(p) F_n^{(i)}(\mathbf{r}) \varphi_k^{(i)}(\mathbf{r}) .$$

Here $i=1-4$ corresponds to [111], [$\bar{1}1\bar{1}$], [$1\bar{1}\bar{1}$], and [$\bar{1}\bar{1}1$], respectively. $F_n^{(i)}(\mathbf{r})$ are envelope functions and $a_n^{(i)}(p)$ are stress-dependent coefficients (see Table I).

Phonon-induced transitions may involve intravalley or intervalley scattering for small or large energy dif-

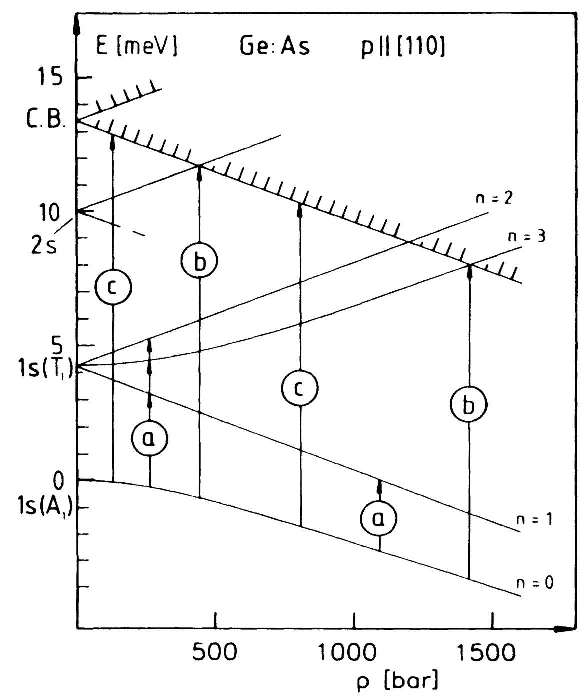

FIG. 1. Stress-induced shifts of the conduction-band minima and the GS donor levels $\Psi_n(1s)$ and $\Psi_n(2s)$ for a shear deformation potential $\Theta_u = 16$ eV (Ref. 9). Phonon-induced transitions relevant in these experiments. a, intravalley scattering within the GS multiplet: phonon trapping (see Fig. 2). b, intervalley transition to the GS triplet and also to excited states ($2s, 3s, \ldots$): level crossing (see Fig. 3). c, intervalley transition to the deepest CB valley(s): direct ionization (see Fig. 3).

TABLE I. Stress dependence of $a_n^{(i)}(p)$ (Ref. 14), given as $a_n^{(1)}$, $a_n^{(2)}$, $a_n^{(3)}$, $a_n^{(4)}$. Shear deformation potential $\Theta_u \simeq 16$ eV, valley-orbit splitting $4\Delta = 0.32$ meV (Sb), 2.83 meV (P), 4.23 meV (As), and elastic stiffness $C_{44} = 0.683 \times 10^{11}$ N/m^2. The lowest CB valleys are $i=1$ for $p \parallel [111]$ and $i=1,4$ for $p \parallel [110]$.

	$p \parallel [111]$	$p \parallel [110]$
$a_0^{(i)}$	$(1/\sqrt{6})(\sqrt{3}\,a+,\ a-,\ a-,\ a-)$	$\frac{1}{2}(a+,\ a-,\ a-,\ a+)$
$a_1^{(i)}$	$(1/\sqrt{2})(0,\ 1,\ -1,\ 0)$	$(1/\sqrt{2})(1,\ 0,\ 0,\ -1)$
$a_2^{(i)}$	$(1/\sqrt{6})(0,\ 1,\ 1,\ -2)$	$(1/\sqrt{2})(0,\ 1,\ -1,\ 0)$
$a_3^{(i)}$	$(1/\sqrt{6})(\sqrt{3}\,a-,\ -a+,\ -a+,\ -a+)$	$\frac{1}{2}(a-,\ -a+,\ -a+,\ a-)$
	$a\pm = [1 \pm (x-\frac{1}{2})(1-x+x^2)^{-1/2}]^{1/2}$	$a\pm = [1 \pm x(4+x^2)^{-1/2}]^{1/2}$
	$x = p\Theta_u/9\Delta C_{44}$	$x = p\Theta_u/6\Delta C_{44}$

ferences, respectively. Intravalley transition probabilities within the GS multiplet have been calculated by several authors,[15-18] using Hasegawa's theory[19] for the electron-lattice interaction in many-valley semiconductors (a in Fig. 1). Intervalley scattering becomes important when the stress splitting of the ground states is approximately equal to 9.95 meV, which corresponds to the energy of the phonons at the X point of the Brillouin zone whose wave vector $\mathbf{q}$ conserves the intervalley momentum.

Following Hasegawa's calculations we get the coupling parameters $C_{qt(\text{inter})}^{nm}$ (see Ref. 14) for the phonon-induced intervalley transitions between n and m:

$$c_{qt(\text{inter})}^{nm} = \sum_{i \neq j}^{4} a_n^{(i)} a_m^{(j)} f_{nm}^{(ij)} \tfrac{1}{3} \Theta_u \mathbf{e}_t \cdot [\mathbf{U}^{(i)} + \mathbf{U}^{(j)}] \cdot \mathbf{q}/|\mathbf{q}|\,,$$

$$f_{nm}^{(ij)} = \int F_n^{(i)} F_m^{(j)} e^{i\mathbf{q}\cdot\mathbf{r}} d^3 r\,.$$

The matrix $\mathbf{U}$ is given in Ref. 14. The coupling parameters for intravalley transitions, $C_{qt(\text{intra})}^{nm}$ are obtained by omitting $\mathbf{U}^{(j)}$ and setting $i=j$. The parameters $C_{qt(\text{intra})}^{0m}$ are found to decrease with increasing stress except for the transition $\Psi_0 \rightarrow \Psi_1$ induced by fast TA phonons with $p \parallel [110]$. On the other hand, there are always nonvanishing terms of $C_{qt(\text{inter})}^{0m}$, $i \neq j$.

Phonon-induced ionization from highly excited donor states to the CB has been discussed in Refs. 3 and 20. Because of the small binding energies of these states intervalley processes could be neglected. The GS binding energies of Sb, P, and As, however, are near or above the energy of the slow TA phonons at the X point. Therefore the ionization from the GS (c in Fig. 1) can only occur via intervalley processes. The corresponding matrix elements $\langle \Psi_n^{(i)} | \exp(i\mathbf{q}\cdot\mathbf{r}) | \varphi_C^{(j)} \rangle$ have been calculated by Brown and Rodriguez.[3] $\varphi_C^{(j)}$ are Coulomb wave functions of the CB electron. These calculations can be adapted for transitions to the lowest CB valley(s) under uniaxial stress by putting the stress-dependent terms $a_n^{(i)}$ in front of the integral:

$$\langle \Psi_n^{(i)} | \exp(i\mathbf{q}\cdot\mathbf{r}) | \varphi_C^{(j)} \rangle = a_n^{(i)} \langle F_n^{(i)} \varphi_k^{(i)} | \exp(i\mathbf{q}\cdot\mathbf{r}) | \varphi_C^{(j)} \rangle\,.$$

In the case of $p \parallel [111]$ only the CB valley $j=1$ and the coefficients $a_0^{2,3,4}$ (decreasing with stress) contribute. At stresses where excited donor levels cross the lowest CB (b in Fig. 1), indirect second ionization channels exist leading to an enhancement of the phonon-induced conduction signal. Though intervalley transitions to all of these split-off states are allowed, we observe the enhancement only if such a state has contributions from the lowest CB valley(s) (Table I). In the case of $p \parallel [111]$ and $p \parallel [110]$ this ionization channel is possible only for the state $n=3$.

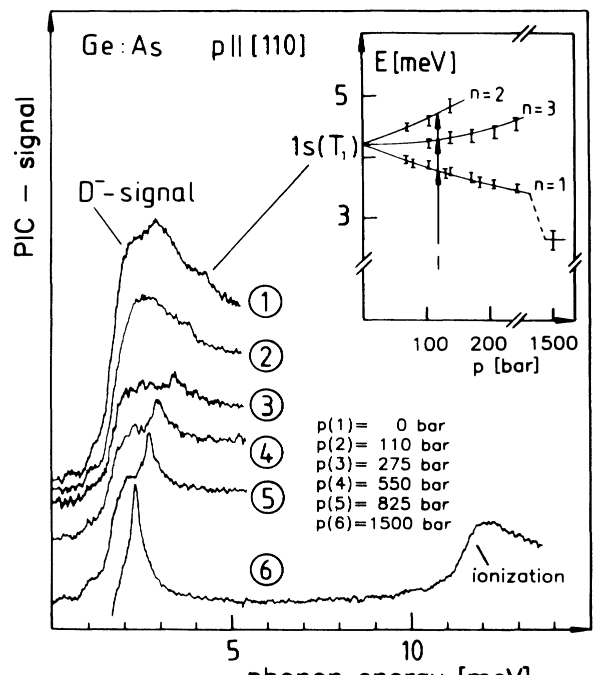

FIG. 2. As$^-$ response for different stresses. The hump at 4.2 meV in curve 1 shifting down with increasing stress to 2.3 meV in curve 6 is an enhancement of the As$^-$ signal due to resonant trapping of the phonons by $n=0 \leftrightarrow n=1$ scattering. These measuring curves have been chosen for a better overview. With longer integration times in a restricted energy range between 3 and 5 meV the transitions to $n=2$ and 3 can also be resolved. Inset: Data points in detail.

In these experiments we have found PIC signals corresponding to each of the transitions shown in Fig. 1. Intravalley transitions to the 1*s* triplet at low stresses (*a* in Fig. 1) are observed for P and As as peaks on top of the PIC signal between 2 and 5 meV (Fig. 2). The signal in this range is due to phonon-induced detachment of electrons trapped by neutral donors (D^- states). Resonant scattering of the phonons by the 1*s* triplet keeps them in the zone sensitive for D^- detection, enhancing the D^- signal at the corresponding energies. The transition energies thus obtained agree well with the optical values.[21] The stress variation of the line intensities is also qualitatively consistent with the theoretical behavior of $C_{qt(\mathrm{intra})}^{0m}$.

PIC signals attributable to one-phonon ionization from the GS of neutral Sb, P, and As donors are shown in Fig. 3 for a sample containing 5×10^{14} cm^{-3} of As and traces of P ($\simeq10^{13}$ cm^{-3}) and Sb ($\leq10^{12}$ cm^{-3}).[22] The decrease of the binding energy with uniaxial stress is evident for the As threshold. Variations of the threshold heights according to crossing or noncrossing conditions occur at different stresses for Sb and As. The position of the Sb threshold does not move under stress. We attribute this to the near coincidence of the binding energy of Sb with the narrow peak of the density of states at 9.95 meV due to the slow TA phonons at the *X* point of the Brillouin zone. This peak apparently determines largely the position, the form, and the relatively high sensitivity of the Sb response.

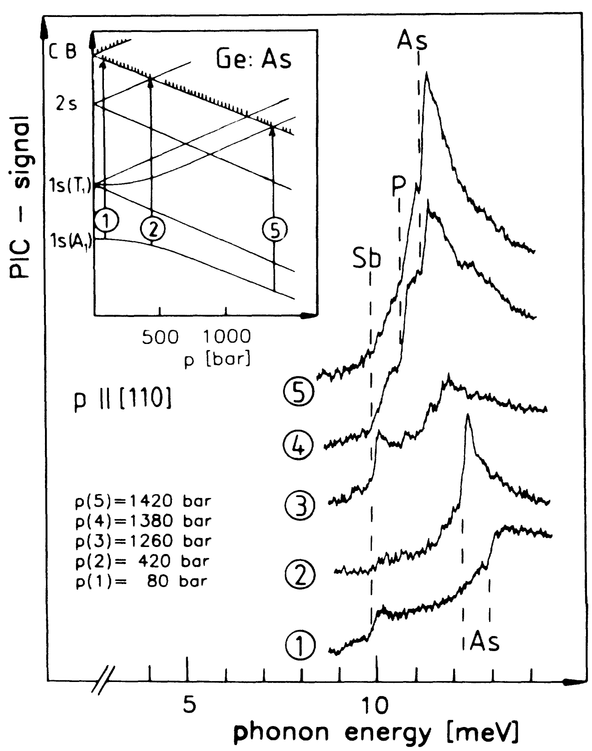

FIG. 3. PIC threshold due to ionization of the neutral donors As (5×10^{14} cm^{-3}), P ($\simeq10^{13}$ cm^{-3}), and Sb ($\leq10^{12}$ cm^{-3}) in the sample of Fig. 2. The downshift with stress of the As threshold position is evident, whereas the Sb threshold is pinned to 9.95 meV. The threshold heights increase at level-crossing conditions. The P threshold can only be seen for crossing condition in curve 4.

The ionization energies $\leq9.9\pm0.05$ meV (Sb), 12.4 ± 0.05 meV (P), and 13.4 ± 0.1 meV (As) are somewhat smaller than those determined optically but are similar to those found by temperature-dependent Hall measurements.[1] No level-crossing enhancements occur for $p\parallel[100]$ as is expected from symmetry; however, the threshold position does decrease with stress.[9,10] This is still not understood.

In contrast to the case of shallow donors in Ge, no ionization signals have been found for the 5.8-meV Sn donor in GaAs nor for the Ga acceptor in Ge even though the binding energy of the latter was shifted down to 8 meV by uniaxial stress. In both cases the extrema of the corresponding bands are at $k=0$ and the large phonon wave vector **q** cannot be taken up by intervalley processes.

The intervalley phonons, being near-zone-edge phonons, have nearly zero group velocity. So the transport will certainly be made by the longitudinal-acoustic (LA) phonons. The diffusion length of high-frequency phonons is determined by isotope scattering and anharmonic decay. From theoretical estimates we obtain several μm for these LA phonons which shows the high sensitivity of the detection. In the special case of Sb (Fig. 3) only 10^7 donors are in the sensitive region beneath the junction. To obtain reliable experimental numbers of the mean free path well-defined Al/Ge interface (contact) situations are necessary together with appropriately structured configurations.

The observation of the phonon-induced transitions might indicate that intervalley processes can contribute to the carrier lifetimes in Ge. This would be demonstrated by observing changes in the lifetime with stress when the triplet levels cross the CB.

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