Continuous high-resolution phonon spectroscopy up to 12 meV: Measurement of the A^+ binding energies in silicon

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(Received 10 September 1985)

We have measured the binding energies of Ga^+, Al^+, and In^+ centers in silicon with energy-resolved phonon-induced electrical conductivity. For Ga^+ and Al^+ we obtain the value of about 2 meV as earlier found for B^+, whereas the binding energy of In^+ is 6 meV. Spectral structures attributed to impurity interactions found for higher concentrations of In at energies up to about 12 meV demonstrate that acoustic phonons up to this energy are transmitted from the tunnel junction to the substrate.

Recently, we have demonstrated the feasibility of phonon-induced electrical conductivity (PIC) for the determination of the binding energies of shallow P^- and B^+ states in silicon by phonon spectroscopy with superconducting Al junctions.[1] Good agreement with previous far-infrared (FIR) measurements[2,3] has been obtained. In this paper we report on the application of this technique to the deeper effective mass acceptors Al, Ga, and In in silicon, showing that there is a shallow-to-deep instability for the binding energies of the A^+ series similar to that discussed for neutral centers,[4] and that phonon spectroscopy is possible with Al junctions up to energies as high as 12 meV. No multiplet structure due to the j-j coupling of the two holes has been found.

The experimental setup is as described previously.[1] However, two different contact configurations were used, measuring the conductivity change in different regions of the substrate, as indicated in Fig. 1. With the first (I), the probing electric field is confined to some tenths of mm below the contacts, that is, a sheet opposite to the phonon generator, as we know from first measurements with epitaxial layers. The second (II) probes the channel along the phonon path, i.e., also directly underneath the phonon source. In this latter case an additional distinction is possible by changing the polarity of the bias: A positive polarity of the junction electrode will prevent holes, generated by the light in a zone opposite to the junction, to produce A^+ centers near the phonon source (configuration II−); the negative polarity will do the reverse (II+). A listing of the samples is given in Table I. In the case of boron and indium a large range of concentrations is covered. All aluminum- and gallium-doped samples contain oxygen in the range of 10^{16} cm^{-3}. The FIR resonance of the interstitial oxygen is seen as an absorption line (marked by an arrow) in the PIC spectra of Al and Ga in Fig. 2. The inset shows an enlarged view of this line and is a demonstration of the resolution (here 0.03 meV) of our method which, in principle, is limited by the sharpness of the gap of the superconducting aluminum (~ 5 μeV). The boron-doped sample S80 contains an oxygen concentration of 6×10^{17} cm^{-3}.

First, we discuss the binding energies of the series B^+, Al^+, and Ga^+. Figure 2 shows the PIC signals for these impurities at low dopant concentrations (isolated A^+ centers; S80, S147, S154). For all three samples the energy value at half of the threshold height ($E_{1/2}$) scatters around 2.1 meV. In Table I we have also given the threshold values (E_0) as obtained from a linear extrapolation of the PIC values at 66% and 33% of maximum to zero signal. This extrapolation gives the same threshold for a range of smaller boron concentrations, even though the PIC rise is shifting and broadening because of the influence of complexes[3] (Fig. 1 in Ref. 1). Two things are noteworthy: (i) The binding energies $E(A^+)$ of the three elements do not scale with those of the neutral acceptors. Instead, the value

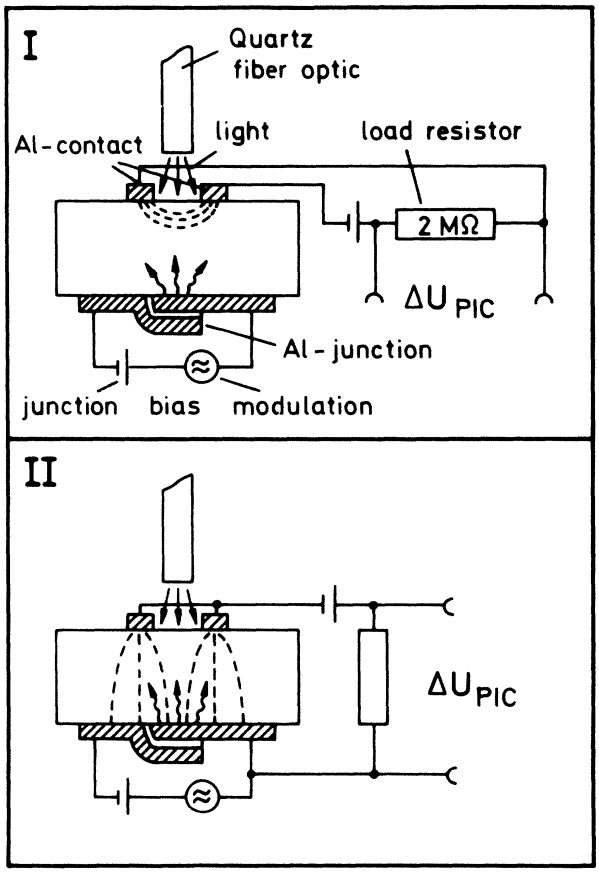

FIG. 1. Different contact configurations for PIC measurements. In case II the bias at the Al contact could be positive (II+) or negative (II−). All samples are bulk doped and the sample thickness is about 3 mm. The measuring temperature was 1.0 K.

TABLE I. Data of the measured samples. Conc. gives its concentration in 10^{15} cm^{-3}, obtained from room-temperature resistivities. In some cases the values are based on infrared measurements. $E_{1/2}$ is the energy value of half the threshold height and E_0 is extrapolated from the 33% and 66% of maximum to zero.

Sample	Dopant	Conc.	E_0 (meV)	$E_{1/2}$ (meV)
S53	B	0.005	1.83 ± 0.05	1.93 ± 0.02
S122	B	0.05	1.85 ± 0.07	2.06 ± 0.03
S83	B	0.95	1.80 ± 0.07	2.24 ± 0.03
S80	B	1.2	1.85 ± 0.07	2.13 ± 0.03
S87	B	5.4	3.3 ± 0.1	4.18 ± 0.05
S55	B	10	3.8 ± 0.1	4.87 ± 0.05
S154	Ga	0.95	1.69 ± 0.05	1.94 ± 0.02
S157	Ga	3.2	1.55 ± 0.07	2.38 ± 0.03
S150	Al	0.78	1.63 ± 0.1	2.05 ± 0.04
S148	Al	0.82	1.45 ± 0.1	1.96 ± 0.05
S147	Al	1.5	1.64 ± 0.07	2.10 ± 0.03
S137	In	≃ 2.0	5.90 ± 0.2	6.30 ± 0.05
S136	In	≃ 4.0	5.90 ± 0.1	6.30 ± 0.05
S96	In	≃ 5.0	5.80 ± 0.1	6.25 ± 0.05
S162	In	7.5	5.75 ± 0.1	6.25 ± 0.05
S160	In	28	5.40 ± 0.1	6.05 ± 0.05
S161	In	28	5.50 ± 0.1	6.35 ± 0.05
S123	In	≃ 25	5.50 ± 0.1	7.35 ± 0.05
S103	In	≃ 40	5.50 ± 0.1	8.60 ± 0.05

of 2.1 meV fits rather well to the hydrogenic model relation $E(A^+)/E(A^0) = 0.055$[2] if one takes 36 meV (Ref. 5) as the effective mass value for $E(A^0)$, that is, the larger Bohr radius of the state is correlated with a reduced influence of a central-cell deviation from the ideal situation, as it is in the case for the excited states of the neutral centers. (ii) Due to the j-j coupling of the two holes one might expect ground-state splittings in the meV range. Such splittings are discussed theoretically[6] and found experimentally[7] for acceptor bound excitons, where it is frequently assumed that this system can be viewed as an A^+ state surrounded by the electron with negligible influence on the hole-hole splittings. If this model is correct we would expect excited states at 0.09 and 0.16 meV for B^+, at 1.2 and 1.5 meV for Al^+, and at 1.4 and 1.8 meV for Ga^+.[8] At our measuring temperature of 1 K we should be able to resolve the direct excitation from the B^+ triplet state, whereas the thermal occupation of the Al^+ and Ga^+ excited states is much too small for direct excitation from these states. However, in the case of Ga the distance from these excited levels to the band should be small enough to allow a combined detection scheme: The center is transferred into the excited state by the quasimonochromatic phonons, and subsequent excitation of the hole into the band by thermal phonons

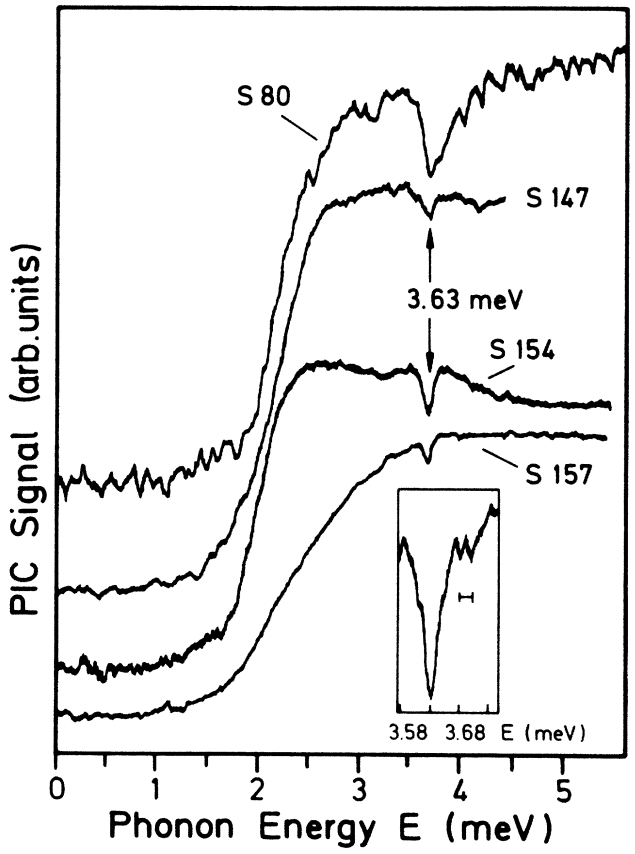

FIG. 2. PIC signals for B (S80), Al (S147), and Ga (S154, S157) doped samples. The abosrption line marked by an arrow is due to interstitial oxygen. The inset shows an enlarged view of this line. Only S157 is taken in configuration II+ which, to our experience, always gives less noisy signals.

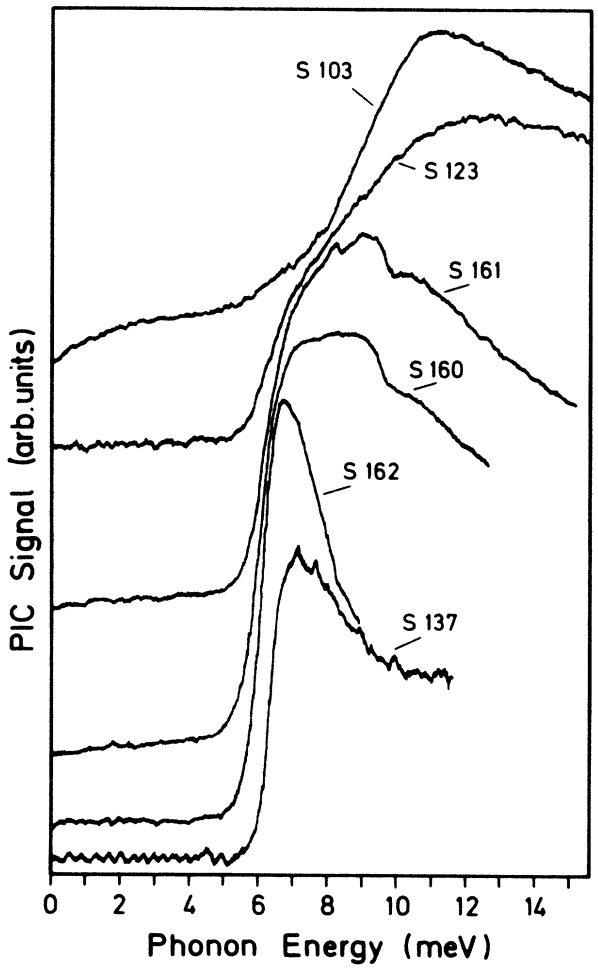

FIG. 3. PIC signal for various In-doped samples (parameter, see Table I). The In concentration increases from S137 to S103. The contact configuration is II+ except for S137 (configuration I).

($3.8k_BT \simeq 0.3$ meV at 1 K) leads to a conductivity change. One would, however, expect well resolved lines instead of thresholds. Thus, it appears that the A^+ state does not show the splittings observed for the bound exciton.

We turn now to the deep acceptor In [$E(\mathrm{In}^0)+155.4$ meV]. Figure 3 shows the PIC signals for a series of concentrations. Up to 5×10^{15} cm^{-3} we find a constant threshold at 5.8 meV. Thus, for the A^+ centers we have a similar shallow-to-deep instability of the binding energy with increasing electronegativity of the central cell as is discussed for the neutral centers.[4] Because of the larger Bohr radii associated with the A^+ centers, the turning point of the instability is shifted to larger values of the electronegativity. In this context the presented results may help to verify the consistency of the theoretical models. Again, no structure is found in the PIC signals at these low concentrations. From luminescence one would expect excited states 3.1 and 6.3 meV above the A^+ ground state. At higher In concentrations the threshold is shifting to somewhat smaller energies and broadening with growing additional structures on the high-energy side. These maxima have some similarities with those observed in FIR photoconductivity[2] of B^+ and P^- in silicon at higher concentrations. They may be associated to complexes with maxima in the density of states at certain binding energies, whereas the shift of the threshold may be due to an In^+-In^+ interaction analogous to that for neutral centers.[9]

From these results it is clear that thin Al junctions emit to a sufficient extent the primary phonon spectrum as determined by the junction bias up to energies of at least 12 meV, so that continuous high-resolution phonon spectroscopy is possible beyond the Debye frequency of many materials. Compared to Sn or Pb or other superconductors as phonon generators, aluminum is distinguished by its high Debye temperature, its small electron-phonon interaction preventing inelastic decay of the primary high-frequency phonons by Cooper-pair breaking, and finally, by the possibility of depositing Al as very thin continuous films (8 nm) without special technical expenditure. The very small spectral density of the high-frequency phonons necessitates sensitive and frequency selective detecting mechanisms such as the described phonon-induced conductivity.

As regards the interesting question of the mean free path of these high-frequency phonons, the PIC signals observed with the different contact configurations allow some qualitative statements: For lower concentrations of In the threshold at 6 meV can be found for all three contact possibilities, but with different signal strength. For higher concentrations (S161, S123, S103 in Fig. 3) the PIC signal is only obtained in configuration II+, which favors the phonon probing directly under the junction (for D^- centers we find configuration II− to be optimum). This shows that in silicon phonons of 6 meV travel a distance of the order of 3 mm, whereas this distance is much shorter for phonon energies of about 10 meV; however, in this case the higher bulk In doping may be of influence. More confined contact geometries in combination with doped layers may help to sort out and determine the elastic (e.g., isotope scattering) and inelastic (e.g., phonon-phonon interaction) mean free paths of these very high-frequency phonons, which is not possible in the present situation.

Fruitful discussions with W. Eisenmenger, R. Sauer, F. Weber, A. Ambrosy, and S. Burger are gratefully acknowledged. W. Zulehner from Wacker Chemitronic kindly supplied us with well characterized samples. Some of the In-doped samples were obtained from W. Keller (Siemens). We want to thank also K. Thonke for checking the Al and Ga concentrations and G. Untereiner for polishing the samples.

[1]W. Burger and K. Lassmann, Phys. Rev. Lett. **53**, 2035 (1984).
[2]E. M. Gershenzon, A. P. Mel'nikov, R. I. Rabinovich, and N. A. Serebryakova, Usp. Fiz. Nauk **132**, 353 (1980) [Sov. Phys. Usp. **23**, 684 (1980)].
[3]P. Norton, J. Appl. Phys. **47**, 308 (1976).
[4]P. Vogl, in *Advances in Solid State Physics XXI*, edited by P. Treusch (Vieweg, Braunschweig, 1981), p. 191.
[5]D. Schechter, J. Phys. Chem. Solids **23**, 237 (1962).
[6]D. S. Pan, Solid State Commun. **37**, 375 (1981).
[7]K. R. Elliott, G. C. Osbourn, D. L. Smith, and T. C. Gill, Phys. Rev. B **17**, 1808 (1978).
[8]M. L. W. Thewald, Can. J. Phys. **55**, 1463 (1977).
[9]K. Nagasaka and S. Narita, J. Phys. Soc. Jpn. **35**, 797 (1973).