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Publication Date

1977-09-01

U J - J 4 7 1 0 2 2)
Submitted to Physical Review Letters

uc-4
uc-34a
LBL-6184 c/
Preprint

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LBL-6184

ISOTOPE SHIFTS IN THE GROUND STATE OF SHALLOW,
HYDROGENIC CENTERS IN PURE GERMANIUM

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Abstract

Large isotope shifts in the ground state binding energy of a shallow acceptor A_2 ($E_V + 11.31$ meV) and a shallow donor D ($E_C - 12.34$ meV) have been observed for the first time with photoelectric spectroscopy in ultra-pure germanium. The shifts ($\Delta E^{A_2} = +21 \pm 3$ μ eV; $\Delta E^D = -51 \pm 3$ μ eV) occur when the germanium crystals are grown in pure deuterium instead of the usual, pure hydrogen atmosphere. The shallow centers are not related to elemental acceptors or donors. They are observed at concentrations $< 4 \times 10^{11}$ cm $^{-3}$. The isotope shift is a direct proof that the center A_2 and D contain hydrogen.

Using photoelectric spectroscopy (Fig. 1),¹ we have investigated a previously unexplained shallow donor D and a shallow acceptor A₂ in ultra-pure germanium. These shallow centers exhibit isotope shifts in their ground states when the germanium host crystal is grown in a pure deuterium atmosphere instead of the usual pure hydrogen atmosphere. This is the first time that an electronic isotope shift of shallow centers in semiconductors has been observed.

Photoelectric spectroscopy, closely related to photoconductivity, has recently found application in the analysis of ultra-pure semiconductors.^{2,3} The sensitivity of photoelectric spectroscopy is independent of the impurity concentration over many orders of magnitude. Signal-to-noise ratios of >500 have been reported for small samples (0.5 cm³) of ultra-pure Ge containing 10¹⁰ acceptors.⁴ For high-resolution applications, it is common to use a Fourier Transform Spectrometer (Interferometer) which has a high through-put and high energy resolution (typically $\Delta\nu \leq 10$ μ eV). The instrument used in our investigations has 7 inch, F = 1.5 optics and a set of mylar beam splitters covering a frequency range of 10 - 100 cm⁻¹ (1.2 - 120 meV). Yoshinaga filters⁵ and black polyethylene limit the frequency range and prevent aliasing of spectra. The interferometer is interfaced to a PDP 11 computer which performs a Fast Fourier Transformation of up to 2¹² points ranging between $\pm 2^{15}$. When recording single-sided interferograms, the resolution is limited by the 5 cm mirror travel to = .05 cm⁻¹ (= 8 μ eV).

Ultra-pure germanium single crystals grown in our laboratory were investigated. These crystals are extremely well characterized with

respect to residual impurities and crystallography. They are grown in a palladium diffusion purified hydrogen atmosphere (1 atm) out of a synthetic quartz crucible. The crystals typically contain between $10^9 - 10^{11} \text{ cm}^{-3}$ boron, aluminum, and phosphorus atoms identified by photoelectric spectroscopy and Hall-effect measurements. Electrically non-active impurities are oxygen ($10^{13} - 10^{14} \text{ cm}^{-3}$); silicon ($>10^{16} \text{ cm}^{-3}$) and hydrogen. Hydrogen is dissolved in Ge near the melting point at a concentration $\geq 10^{14} \text{ cm}^{-3}$ in the atomic form.⁶ A large fraction of the hydrogen is trapped in crystals of several centimeters in diameter grown at rates $>10 \text{ cm hr}^{-1}$. We estimate hydrogen concentrations of $10^{13} - 10^{14} \text{ cm}^{-3}$ in the final crystal.

In addition to the known chemical residual impurities, a number of centers producing shallow energy levels have been discovered.⁴ One acceptor (A_2) and one donor (D) are of special interest because we are able to link them to the presence of hydrogen in the Ge crystals. Hall⁷ discovered these two centers when he rapidly quenched small Ge samples. When quenching from 400°C , the concentration of A_2 and of D is $\sim 2 \times 10^{11} \text{ cm}^{-3}$ depending strongly on the cooling rate (dT/dt) and the sample's position in the original crystal. Hall speculated that the centers might be linked to the residual oxygen and silicon in his germanium crystals. The ground state energy of the centers A_2 and D have been determined to be $E_{gs}^{A_2} = 11.31 \text{ meV}$ and $E_{gs}^D = 12.34 \text{ meV}$.⁴

By growing several crystals in a pure deuterium atmosphere ($<0.03\% \text{ H}_2$), we were able to demonstrate a large isotope shift in the ground state binding energies of both A_2 and D. The upper spectrum in Fig. 2 was obtained with a rapidly quenched sample of the hydrogen containing

crystal No. 497-5.5. This sample is p-type ($N_A - N_D \approx 10^{10} \text{ cm}^{-3}$) and all the acceptor related lines are positive while the donor lines have opposite polarity. The lower spectrum has been obtained with a deuterium containing sample from crystal No. 519-4.0. The residual chemical impurities make this crystal n-type ($N_D - N_A \approx 10^{10} \text{ cm}^{-3}$) which is the reason that negative lines are produced by acceptors and positive lines by donors. The set of lines due to the donor D exhibit perfect "hydrogenic" spacing and are shifted towards lower energies in the lower spectrum by $\Delta E_{gs}^D = -51 \pm 3 \text{ } \mu\text{eV}$. This corresponds to a shift of the ground state closer to the bottom of the conduction band. An opposite shift away from the top of the valence bands $\Delta E_{gs}^{A_2} = 21 \pm 3 \text{ } \mu\text{eV}$ has been found for the acceptor A_2 .

The isotope shift in the ground state of A_2 and of D is a direct proof for the presence of hydrogen in these two centers. The microscopic structure of A_2 and D are not yet known. By varying the concentrations of the residual impurities, we have established that A_2 and D are not related to chemical residual impurities B, A1, and P as had been previously assumed.³ Experiments with crystals having strongly varying oxygen and silicon contents are in progress. Effects which could explain the observed isotope shift are the reduced mass, hyperfine interaction and Jahn-Teller distortions. A primitive reduced mass model yields a ground state shift three times too small. The hyperfine constant of free hydrogen in vacuum is 507 Gauss ($\approx 8 \text{ } \mu\text{eV}$). Shallow donors in germanium exhibit hyperfine constants which are typically one order of magnitude smaller than the one for free hydrogen.⁸ This is about fifty times too small to account for the observed shifts. Support

for Jahn-Teller distortion comes from uniaxial stress experiments which we performed on Ge-samples containing the donor D. The photoelectric spectral lines of D are exceptionally sharp and do not change their position for stresses up to $6 \times 10^9 \text{ dyn cm}^{-2}$ (high-stress regime). This situation cannot be explained with either a substitutional or a tetrahedral interstitial donor site. The spectrum appears to be due to single valley electrons whose ground state lies several meV deeper than those corresponding to the remaining three valleys. A Jahn-Teller distortion moving the donor away from a tetrahedral symmetry site can qualitatively explain the experimental results.

Previously, hydrogen was thought to be a "deep" donor in analogy with muonium in germanium.⁹ This would explain the fact that hydrogen is not electrically active. If hydrogen is molecular, it would not be electrically active either. Support for such an assumption comes from recent diffusion experiments¹⁰ which show that, at temperatures below 400°C, the diffusion constant of hydrogen is more than two orders of magnitude smaller than the values extrapolated from high-temperature experiments.⁶ Recent investigations show that hydrogen can form complexes with divacancies¹¹ and with copper.¹²

Taking into account the recent observations, we propose that the centers A_2 and D are complexes of hydrogen and other electrically non-active impurities (the most likely candidate being oxygen). We cannot exclude the possibility that the donor D is due to atomic hydrogen in which case the "deep" donor model would have to be revised.

Acknowledgments

We are indebted to P. L. Richards, University of California at Berkeley, for the use of the Fourier Transform Spectrometer facility. W. Frank, C. Kittel, G. Morton, and A. Seeger have contributed with many discussions. W. L. Hansen and G. S. Hubbard have assisted in the experiments. R. Markiewicz has helped in the preparation of the manuscript. We also want to thank F. S. Goulding for his continuous interest and support. This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

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Fig. 1 A two-step process leads to photothermal ionization, the basis of photoelectric spectroscopy.

Fig. 2 Photoelectric spectra of hydrogen grown, p-type sample 497-5.5 (H_2) and deuterium grown, n-type sample 519-4.0 (D_2). Temperature $T = 8.0^\circ K$; Al = aluminum, B = boron, P = phosphorus, $D^{H,D} =$ hydrogen, deuterium related donor $A_2^{H,D} =$ hydrogen, deuterium related acceptor. The notation of Jones and Fisher¹³ was used for the acceptor lines (B, Al).

XBL 7411-8629

Fig. 1

XBL 778.2792

Fig. 2

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

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