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Publication Date

1984-08-01

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August 1984

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DYNAMIC IMPURITIES IN ULTRAPURE SEMICONDUCTORS

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Theoretical and experimental results are presented which shed light on a series of unusual shallow level impurities in ultrapure germanium. These impurities, both donors and acceptors, (1) show hydrogenic spectra with signatures identical to all other shallow impurities; (2) exhibit unusual dependence in their spectra to applied uniaxial stresses; (3) display a clear isotope effect (hydrogen to deuterium) in the electronic spectrum when the crystal growing conditions are changed -- a clear violation of the Born-Oppenheimer approximation. They are dynamic impurities consisting of a two-atom center in a fully tetrahedral environment, in which coherent nuclear motion is coupled to the electronic degrees of freedom. Experimental data, together with group-theoretical analysis, permit a complete description of these systems.

INTRODUCTION

Ultrapure germanium single crystals, with net-acceptor or net-donor concentrations of less than 10^{11} per cubic centimeter, are probably the purest substance produced by man¹. Their existence, coupled to accurate experimental techniques, has led to the discovery of novel impurity complexes with very unusual properties.

In particular Photothermal Ionization Spectroscopy (PTIS), with its extremely high resolution and sensitivity², has permitted the study of electronic effects of the order of tens of a micro electron volt. PTIS is a photoconductivity technique based on the absorption of a photon from an infrared source and the subsequent absorption of a lattice photon which transports the electron (hole) into the conduction (valence) band, where it becomes a free carrier.

An important feature of shallow-level impurity spectra is the fact that the spacing between the lines of the "hydrogenic" series is a property of either the conduction or the valence band of germanium, and not of the chemical nature of the center. The latter only influences the ground-state energy, and makes the "hydrogenic" donor or acceptor set appear at different energies in the spectrum¹.

The new impurity centers discussed here are identified by their donor (D) or acceptor (A) character, followed by their chemical composition. In particular we are concerned with A(H,C), A(H,Si) and D(H,O), although several other complexes have been studied and analyzed: D(Li,O), A(C,N), A(H,Zn), A(H,Cu), etc.

ACCEPTORS

The acceptors A(H,C) and A(H,Si) exhibit spectra³ with the well known signature of all shallow-level acceptors. The spectra have however unusual characteristics which make them unique.

1. As shown in Figure 1 the lines due to these centers do not split under uniaxial stress, as is the case for all elemental acceptors, e.g. Al. This fact by itself is paradoxical, and difficult if not impossible to explain.
2. Each center gives rise to two sets of acceptor lines [originally considered two different impurities and labelled A1 and A2 for A(H,Si) and A6 and A6' for A(H,C)]. These two sets are separated by 1.07 meV (8.63 cm^{-1}) in

the case of A(H,Si), and of 1.98 meV in the case of A(H,C). In each case the relative strength of each set can be altered with temperature (Figure 2). The ratio of the intensities of corresponding members of the pair of sets -- the ratio of intensities of the D line of A(H,Si)1 and the D line of A(H,Si)2 for example -- follows a Boltzmann function as a function of temperature. The sum of the intensities of corresponding lines (the D lines for example) of A(H,Si)1 and A(H,Si)2, divided by the intensity of the same line (the D line) of a residual elemental impurity (e.g. Al) is, on the other hand, independent of temperature (see Figure 3). This fact clearly indicates that the two related spectral series come from the same center, and that the 1s electronic state is split into a manifold, with energy separations of the order of one meV.

3. The spectrum of A(H,Si) is only found in germanium crystals grown in a hydrogen atmosphere from a melt contained in silica. The A(H,C) appears only in germanium crystals grown in graphite crucibles in a hydrogen atmosphere. There is an isotope shift in A(H,Si) when the atmosphere is changed to pure deuterium gas. The value of the shift for A(H,Si)-A(D,Si) is 0.021 meV. In a mixture of hydrogen and deuterium two and only two isotopic lines are observed. The observations above clearly point out to two important facts: only one hydrogen atom is involved in each center; and there is a clear violation of the Born-Oppenheimer approximation, since a change in nuclear mass has a measurable influence in the electronic and optical properties.

The facts described above directly suggest the model of Figure 4. Because the ground state does not split with stress, the symmetry must be other than the usual Γ_8 of the top of the valence band: Γ_8 splits under any uniaxial stress. The center must however have full tetrahedral symmetry, otherwise the inequivalent lattice positions would again split under a general uniaxial stress.

Symmetry arguments³ restrict the ground state to be of the Γ_6 or Γ_7 types, i.e. require an extra degree of freedom which interacts with the electronic wave function and produces a ground state of the total system of multiplicity two, a Kramer doublet. The isotope shift, discussed above, points clearly toward a degree of freedom which involves directly the motion of the hydrogen atom, i.e. a dynamic impurity.

The model of Figure 4 yields a ground-state manifold of sixteen states: a direct product of four electronic Γ_8 states, and the four equivalent, tetrahedral tunneling sites of hydrogen in the vicinity of substitutional carbon or silicon. A direct analysis of the (16x16) matrix of the Hamiltonian for these states³ yields essentially three unknown parameters, a nuclear tunneling matrix element t , and two mixed electronic-nuclear energies, V_0 and V_1 which go beyond the Born-Oppenheimer approximation. Although these elements cannot be directly calculated, the fact that the ground state is a doublet gives a very restricted range over which they can vary. The observed double spectra, A(H,Si)1 and A(H,Si)2 in one case and A(H,C)1 and A(H,C)2 in the other, give unequivocally the absolute value of V_1 , which is equal to three quarters of the series separation: 0.80 meV for A(H,Si) and 1.48 meV for A(H,C).

DONORS

The donor D(H,O) is obtained from germanium samples containing A(H,Si) when they are annealed slightly above room temperature. This new impurity center has the characteristic signature of all donors in germanium, but presents also very unusual characteristics.

1. As shown in Figure 5, D(H,O) shows an isotope effect when the crystal is grown in a deuterium, rather than in a hydrogen atmosphere. The D(H,O)-D(D,O) shift is 0.051 meV. The PTIS measurements of Figure 5 establish that only a single hydrogen atom is involved in the complex. This donor, as the acceptors above, violates the Born-Oppenheimer approximation.
2. Experiments using silicon doping suppress the formation of D(H,O).
3. The stress behavior of D(H,O) is unusual and unexpected (see Figure 6). The line frequencies are stress independent up to a certain stress amplitude, where they suddenly reduce sharply in intensity and a new set of lines, also with the characteristic donor signature, appears at lower frequencies. This sudden change in ground-state electronic energy occurs for stresses in any direction, and indicates a symmetry change from an s-like unstressed ground state to a p-like stressed one.

The experimental facts above point once again to a complex center, consisting of oxygen and a single hydrogen atom. The center must have tetrahedral symmetry and be dynamic in character. A schematic representation of a model

that satisfies these conditions is shown in Figure 7. It consists of an OH^+ group, a substitutional complex in the Ge lattice that rotates (tunnels) among its four equivalent orientations.

A group-theoretical analysis of the complete electronic-nuclear system can be easily carried out⁴. A (16x16) matrix Hamiltonian can be set up in all its generality, and its matrix elements reduced by symmetry considerations. In spite of the fact that more than seven parameters are involved, experiment determines the necessary number of conditions on their sign and order of magnitude. The resulting electronic, nuclear and total energy spectra as a function of an applied [111] stress are shown in Figure 8.

GENERAL CONSIDERATIONS

The electronic structure of these dynamic complexes poses some basic problems of great interest:

1. Why H and C (or Si), two electrically inactive impurities in Ge, combine to make an active shallow acceptor?
2. What are the binding forces for these complexes?
3. Why the stable configurations are HC^- and HSi^- and not the neutral species?
4. Why H and O, inactive impurities in pure Ge combine to yield a shallow donor?
5. Why the OH^+ species only exists in a tetrahedral environment in Ge?
6. Why the OH^+ , unknown as a free standing species, exists in the Ge matrix?
7. What are the mechanisms for conversion from A(H,Si) to D(H,O) ?

These questions have at this time some preliminary answers, based mostly on conjecture and supported by experimental evidence and some calculations^{5,6}. In particular:

- The OH^+ species has, as a unit, four outer-shell electrons similar to the Group IV elements, Ge in particular. It therefore is a likely candidate for a substitutional center. The fact that contains two elements, neither of which is stable as a substitutional impurity, explains the necessity of annealing: the two elements and a vacancy must all "find each other".
- Most of the hydrogen in germanium is either bound to defects or in molecular H_2 form.
- Hydrogen as an atomic impurity in Ge is qualitatively similar to free standing atomic hydrogen, with a single electron (an unpaired spin) occupying the H-1s state.

- When trapped in the vicinity of another atom the H-1s orbital tends to become doubly occupied (two paired electrons with zero net spin).
- If the trapping atom is either neutral C or neutral Si, the extra electron becomes a negative charge for the whole complex, hence the existence of A(H,C) and A(H,Si).
- If the trapping species is a "four-electron" oxygen, i.e. the O^{++} ion, the resulting complex is the singly charged D(H,O).

In conclusion, the study of these novel and unusual shallow impurities has resulted in an exploration of new chemical species and unexpected physical processes of considerable scientific interest.

ACKNOWLEDGMENTS

We would like to acknowledge the help, support and collaboration of F.S. Goulding, N. Haegel, W.L. Hansen, G.S. Hubbard, B. Joos, R. McMurray, J. Oliva, and P.L. Richards.

This work was supported at the Lawrence Berkeley Laboratory by the Department of Energy under Contract Number DE-AC03-76SF00098.

REFERENCES

1. E.E. Haller, W.L. Hansen and F.S. Goulding, Adv. Phys. 30, 93 (1981) and references therein.
2. Sh. M. Kogan and T.M. Lifshits, phys. stat. sol. (a) 39, 11 (1977).
3. E.E. Haller, B. Joos, and L.M. Falicov, Phys. Rev. B 21, 4729 (1980).
4. B. Joos, E.E. Haller, and L.M. Falicov, Phys. Rev. B 22, 832 (1980).
5. J. Oliva and L.M. Falicov, Phys. Rev. B 28, 7366 (1983).
6. J. Oliva, Phys. Rev. B 29, 6846 (1984).

FIGURE CAPTIONS

Figure 1: Uniaxial-stress spectra of a sample containing A(H,C), gallium, aluminum, and boron. The lines of all the elemental acceptors split, the lines of A(H,C) do not.

Figure 2: PTIS of a sample containing A(H,Si) and aluminum acceptors at two different temperatures.

Figure 3: The ratio of the intensities of the C lines in the two series of A(H,Si) (circles) and the D lines in the same series (plus signs) are proportional to a Boltzmann factor $\exp(1.07 \text{ meV/kT})$. The ratio of the sum of the intensities of the C lines of the A(H,Si) to the intensity of the aluminum acceptor C line is temperature independent (squares). The same holds true for the D lines (x's).

Figure 4: Schematic representation of the silicon-hydrogen impurity complex.

Figure 5: PTIS of samples from three crystals grown in pure hydrogen, pure deuterium, and a 1:1 mixture of the two gases. The donors D(H,O) and D(D,O) exhibit an isotope shift of 0.051 meV in their ground state. The mixed-gas grown crystal shows only two lines, indicating that only one H or D atom is part of the donor complex.

Figure 6: PTIS of a sample containing P and D(H,O) donors, with compressional stresses along [111].

Figure 7: Schematic representation of the OH complex in a germanium vacancy.

Figure 8: Stress dependence of the various energies for the D(H,O). (a) The behavior of the four conduction-band valleys. (b) The stress dependence of the nuclear states only. (c) The energy of the fully interacting system. The stress is applied along [111]. All energies in arbitrary units. The ionization energy of the complex donor is obtained by subtracting the ground-state energy (c) at a given stress from the sum of the [111] valley energy (a) and the nuclear energy (b) of the same Λ symmetry. The energy difference ΔE_1 gives the shift in the spectra observed between the low stress and the high stress cases of Figure 6.

XBL 7911-12835

Figure 1

Figure 2

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Figure 3

XBL 796-10139

XBL 798-11028

Figure 4

XBL 788-10100

Figure 5

XBL 7710-6740B

Figure 6

XBL 802-7970

Figure 7

XBL 802-8178

Figure 8

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