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A NEW METHOD TO DETERMINE THE CHEMICAL COMPOSITION AND STRUCTURE OF NON-ELEMENTAL ACCEPTOR AND DONOR CENTERS IN ULTRA-PURE GERMANIUM

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Whereas, the position of all lines due to elemental impurities coincide perfectly (B, Al, P) a large isotope shift is observed in the D-donor and the A₂-acceptor spectra. The donor D moves by $-51 \pm 3 \text{ eV}$ closer to the conduction band edge and the acceptor A₂ ground-state energy increases by $+21 \pm 3 \text{ eV}$. These isotope shifts are the most direct proof for the presence of hydrogen (and deuterium) in A₂ and D.

It is of interest to explore the possible causes of the observed isotope shift. Deuterium has twice the mass and twice the nuclear spin of hydrogen. Using a simple hydrogen model for the description of a donor in Ge, one can estimate the effect of the mass on the ground-state binding energy $E_{gs}$:

$$E_{gs} = e^2m^* \frac{1}{2e^2h^2}$$

$e =$ charge of the electron, $m^*$ = effective mass of the electron, $c =$ dielectric constant of Ge ($c = 16$) and $h =$ Planck’s constant divided by $2\pi$. The effective mass of the electron, $m^*$, differs from the mass of a free electron due to the presence of a periodic lattice and due to the finite mass of the donor nucleus. The latter effect leads to the reduced mass $m_r$:

$$\frac{1}{m_r} = \frac{1}{m_e} + \frac{1}{m_N}$$

$m_e =$ electron mass, $m_N =$ mass of nucleus. The influence of the reduced mass effect is largest when we assume that the A₂/D pair consists only of hydrogen or deuterium. Using equations (1) and (2) one can estimate the change in binding energy $\Delta E_{gs}$:

$$\Delta E_{gs} = E_{gs}^H - E_{gs} = E_{gs}^H - E_{gs}D = E_{gs}^H \left(1 - \frac{m_e}{m_D} \right) \left(1 - \frac{m_e}{m_D} \right)$$

$$\equiv E_{gs}^H \left(1 - \frac{1}{4000} \right) \equiv 3 \text{ eV}$$

where H and D designate hydrogen and deuterium, respectively. The estimated value is far too small to account for the observed effect.

The change in binding energy due to the interaction of the nuclear spin with the electron spin is also far too small (-50 times) to account for the observed values. A third possibility is a static or dynamic Jahn-Teller distortion. In such a model one would assume that the donor atom is not located at a highly symmetric position but is pushed to a lower symmetric site (JTD) or that it oscillates between more than one stable position (dynamic JTD). In either case more has to be known about the detailed structure of the donor before quantitative estimates about the isotope shift can be made. This leads to the second important part of the analysis of these unknown impurity centers.

**Structure of Impurity Centers**

The structure of substitutional elemental acceptors and donors has tetrahedal symmetry, the same as the germanium atoms. This situation is reflected in the ground state of donors and acceptors. For reasons of simplicity, we restrict ourselves to donors in the following text.

The electron which is bound to a donor can be compared to the electron of a hydrogen atom. At low temperatures, the electron occupies the lowest lying state, the ground state, in which it is most strongly bound to the positively charged nucleus. Above the ground state lies a series of bound excited states. At a certain energy above the ground state, the electron becomes unbound, i.e., it enters the continuum. The periodicity and dielectric constant $c$ of a crystal lattice hosting a donor atom modifies the energies of the ground and the excited states. ⁹

In pure germanium the ground state is fourfold degenerate. The continuum corresponds to the four conduction band minima along the [111] directions. The presence of a donor "core" splits the fourfold degenerate ground state into a triplet (T) and a singlet (S) state. The energy difference is called chemical split $4\Delta$. However, all the bound excited states remain fourfold degenerate.

Fig. 2 Dependence of the energies of the ground- and excited-states and the conduction band minima (valleys) on uniaxial compression applied along the [111] direction. Whereas, the four valleys and the excited states show perfectly linear dependences, the ground-state components exhibits quadratic terms resulting in changes in energy differences between ground- and excited-states. These changes cause the shift of the lines in photoelectric spectra under uniaxial compression. At the temperatures used in photoelectric spectroscopy (~7°K) only the lowest lying S-state is populated.
If a uniaxial stress is applied to the germanium crystal, the energies of the band edges and of the ground and excited states are changed. The fourfold lattice symmetry is broken and this affects the degeneracy of the donor states in the way illustrated in Fig. 2. The case of compressional stress along the [111] axis is presented. The [111] valley falls proportional to the stress three times as fast as the remaining three valleys and three components of each bound excited state rise in energy. The triplet (T) component of the ground state splits into a doublet (D) and a singlet (S) both of which move parallel to the rising valleys in the high stress limit. At low stress, the lowest lying singlet (S) moves closer to its corresponding [111] valley and asymptotically reaches, in the high stress limit, the same stress dependence. The changes in the photoelectric infrared spectrum of a substitutional donor under stress can directly be deduced from Fig. 2. At zero stress, a series of lines corresponding to the transition between the ground state and excited states is observed. The value of 46 is large enough (46(P) = 2.82 meV) that only the singlet level of the ground state is populated at the temperatures used for photoelectric spectroscopy (T-8°K). That means that only one set of infrared lines appear in the spectrum. When stress is applied this set of lines will move to lower energies because the ground-state singlet moves closer to the conduction band valley minimum. All elemental donors follow exactly the described pattern which proves that they are substitutional.

The spectrum of the hydrogen related donor D does not follow the pattern described above. From spectra recorded at various values of stress (Fig. 3), we obtained the situation displayed in Fig. 4. The position of the lines does not change at all under stress. At a stress of 2.1 x 10^8 dyn cm^-2 (0.981 x 10^6 dyn = 1 kg force) the intensity of the lines reduces rapidly and new set of lines appear at 2.7 meV lower energy. No further changes occur up to very large stresses.

Preliminary group theoretical considerations lead to the conclusion that the donor has a symmetry axis along a [111] direction and does not occupy a substitutional site. It follows that D is interstitial, located at a low symmetry site. This is the case of a static Jahn-Teller distortion. A more detailed
which has not been solved satisfactorily up to the other unknown centers and also to the case of lithium hydrogen. We assume that at can be successfully used to determine composition and germanium. The same technique will be applied to structure of unknown acceptor and donor centers in experimental observation better than Model 2 (or any demonstrated that isotope effects and uniaxial stress interstitial hydrogen donor. 

This configuration becomes unstable and one hydrogen becomes interstitial. In analogy to lithium, donor D anneals through the formation of molecular hydrogen. This ·reaction would be of second order hydrogen becomes interstitial. In analogy to lithium, donor D anneals through the formation of molecular hydrogen. This ·reaction would be of second order 

exactly as observed by Hall.

2) In a second model, we identify A₂ with an oxygen-hydrogen molecule. The molecule captures a hydrogen molecule forming OH₂, the donor D. At 160°C This configuration becomes unstable and one hydrogen atom is split off producing a neutral water molecule and an electrically inactive hydrogen atom. The latter reaction of the second model is of first order and does not agree with the experimental observations. Experiments with Ge crystals containing strongly varying amounts of oxygen are in progress, and they should show if oxygen is involved in the formation of A₂ and D.

At this time, we feel that since Model 1 fits experimental observation better than Model 2 (or any previous model), we have discovered an atomic interstitial hydrogen donor.

Using the A₂/D pair as an example, we have demonstrated that isotope effects and uniaxial stress can be successfully used to determine composition and structure of unknown acceptor and donor centers in germanium. The same technique will be applied to other unknown centers and also to the case of lithium which has not been solved satisfactorily up to the present time.

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References
