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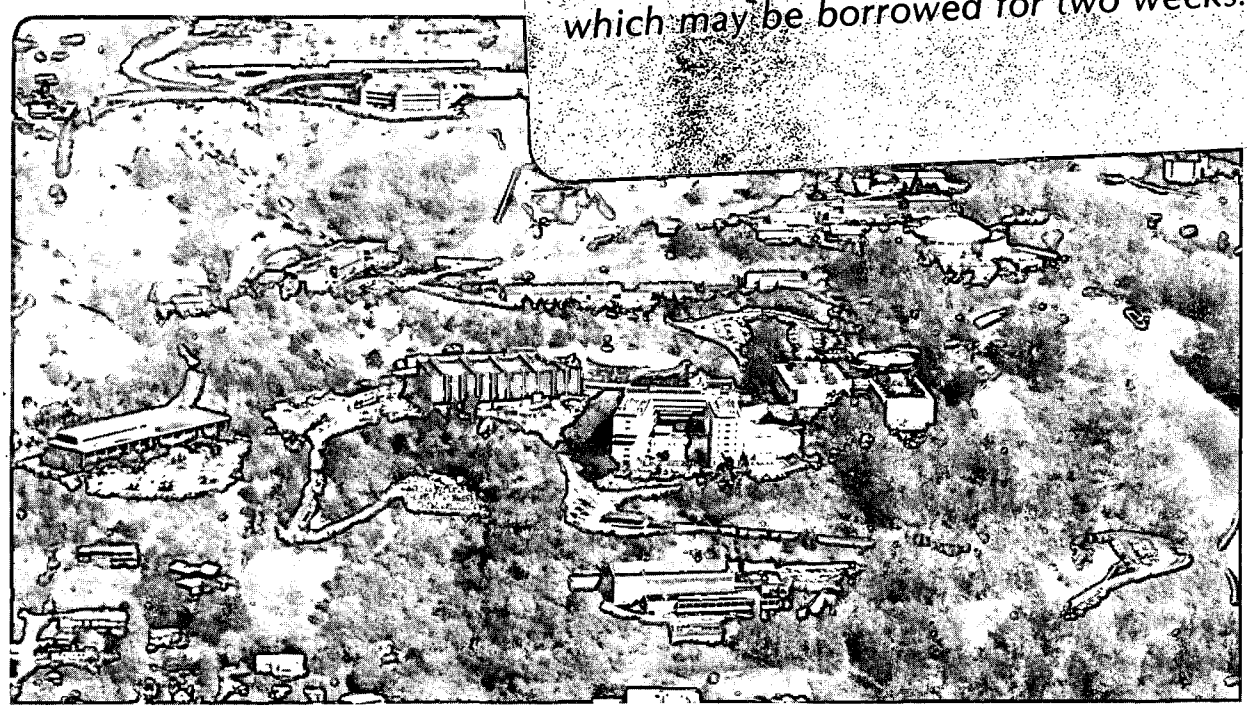

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Hydrogen-Related Impurity Complexes in Germanium and Silicon

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ABSTRACT

The properties of a number of hydrogen-related complexes in crystalline Ge and Si are reviewed. Hydrogen is shown to form electrically active as well as neutral complexes with native defects and impurities in germanium, silicon and several III-V compound semiconductors. Most of the electrically active centers form shallow levels in the bandgap. The complexes form when hydrogen binds to substitutional impurities such as C, O, Si, Be, Zn, Cu in the case of Ge. A shallow Be-H acceptor complex has been found in Si. The unusual electronic groundstate configurations of these complexes can be explained for some centers with a model involving tunneling hydrogen and for the rest of the centers with a trigonally distorted impurity complex. The structure and composition of several complexes has been determined using infrared piezospectroscopic techniques, substitution of hydrogen with deuterium or tritium, and crystal-growth-related impurity arguments. Hydrogen has been shown to fully passivate impurities leading to neutral complexes. Such centers are less well understood because they lack properties which could be observed with high sensitivity and resolution. Local vibrational mode spectroscopy may elucidate the structure of some neutral complexes.

1. INTRODUCTION

Hydrogen is currently attracting much interest on the part of scientists and engineers working with semiconductors. What are the reasons for this surge in interest? On the one hand, no electrical activity of isolated hydrogen in silicon, germanium, and other semiconductors has been found in spite of significant experimental

efforts. On the other hand, hydrogen has recently been found to interact with a very large number of native defects as well as impurities in many semiconductors. The reasons for this unusual behavior are not well understood, but the following three experimental facts are of great help in the formulation of a consistent picture of the physics and chemistry of hydrogen in semiconductors. First, it is well established that hydrogen is a rapidly diffusing, interstitial impurity in Ge [1] and Si [2]. At high temperatures, where the thermal energy exceeds the binding energies between hydrogen and defects or impurities, accurate, reproducible diffusion and solubility data have been obtained for germanium and silicon. Second, the solubility of hydrogen in germanium and silicon is surprisingly small, reaching $\sim 10^{15} cm^{-3}$ near the melting point [3]. Again, this low solubility indicates that hydrogen does not interact (e.g. bind) strongly with the perfect semiconductor lattice. Third, this small solubility or reactivity with the perfect lattice is sharply contrasted by a very strong tendency of hydrogen to form impurity complexes [4]. This rich spectrum of reactions has led to a host of experimental results, some of which are very well understood while others are still most confusing.

The major driving force in the discovery and understanding of hydrogen-related complexes was the development of ultra-pure germanium used for large-volume gamma-ray detectors [5]. Single crystals of up to several kg weight and net-impurity concentrations $\lesssim 10^{10} cm^{-3}$ (one electrically active impurity in 4×10^{12} Ge atoms!) are usually grown in a pure hydrogen atmosphere [6]. Attempts to use different ambients have never led to useful crystals. Detectors made from such crystals exhibit imperfect charge collection which leads to asymmetric and broadened gamma-ray peaks.

The high sensitivity of the net dopant concentration of the ultra-pure crystals to quite moderate heat treatments ($T < 450°C$) was explained, after an intensive search, with a number of hydrogen-related impurity complexes which form shallow energy levels in the bandgap. Systematic studies in ultra-pure germanium have prompted the discovery of over twenty different electrically active complexes. The discussion

of the structure and composition of these complexes constitutes a major part of this review. Earlier reviews [4,7,8] contain complementary information on crystal growth, shallow level impurity complexes without hydrogen, and a number of special characterization techniques. Space limitations do not permit the presentation of all this information here.

More recently, hydrogen has generated a large amount of interest in the silicon-research-oriented community. This interest is based on the discovery that both shallow and deep level centers in silicon can be passivated by exposure to a variety of environments containing atomic hydrogen. Hydrogen plasmas [9], electrolytic dissociation of phosphoric acid [10], and polishing with ammonia- or amine-containing syton [11] all lead to passivation of all elemental group III acceptors and several deep levels in silicon. Researchers at Siemens were perhaps the first to observe this effect when they discovered that p-Si wafers showed a decrease in minority carrier lifetime after exposure to atomic hydrogen during etching or electrolysis [12]. This lifetime change disappeared rapidly after annealing for 30 min at the moderate temperature of 450°C. The more recent studies with amine- or ammonia-containing syton are most surprising insofar that passivation of acceptors throughout 1 cm thick Si slabs was observed after only tens of hours of polishing at room temperature. In our opinion, it is likely that not only hydrogen but also native defects such as interstitial Si play a role in this special kind of passivation.

The fact that shallow acceptors and some deep level impurities are fully passivated through hydrogenation makes it difficult to study the passivation process as well as the final structure and composition of neutral complexes with sensitive and high resolution methods. Only relatively insensitive techniques such as secondary ion mass spectroscopy (SIMS) and local vibrational mode spectroscopy (LVMS) can be applied to these studies. In sharp contrast one has been able to use high resolution infrared spectroscopic techniques to investigate the electronic states of the large number of electrically active impurity complexes in germanium. The recent study of the partially-hydrogen-passivated double acceptor beryllium in silicon [13] gives hope that

more electrically active centers, short of full passivation, can be generated and studied in this technically most important semiconductor.

The importance of the role of theory can hardly be overestimated for the development of a consistent picture of all the hydrogen-related effects. Whereas theoretical models accurately describe the electronic structure of tunneling hydrogen centers [14] and of trigonally distorted impurity complexes [15] in germanium and in silicon, only rather qualitative models have been proposed for the description of the neutral complexes. We assume that the results obtained from partially-passivated complexes can be used in the interpretation of the fully-passivated centers. Recent cluster calculations have led to very interesting results for hydrogen bound to a boron acceptor in silicon [16]. Contrary to the model which proposes that boron assumes a three-fold coordinated lattice position and a hydrogen atom passivates the nearby dangling silicon bond, these calculations indicate that the hydrogen forms a partially ionic and partially covalent bond with the boron acceptor. Such a picture quite naturally relates to the well-known and understood lithium-acceptor pairing mechanism [17].

An introduction to hydrogen-related effects in semiconductors would be incomplete without at least a mention of a very interesting group of experiments using the low mass hydrogen analogues muonium and pionium. These mesonic atoms can be created by injecting energetic positive muons or pions which are abundantly created at a number of meson factories [18] into semiconductors. Though the lifetimes of these mesons are short [$\tau_\mu = 2.2\ \mu s$, $\tau_\pi = 26$ ns], they are sufficiently long to lead to fully thermalized hydrogen-like atoms. The results of experiments with μ^+ have recently been reviewed [19] while the π^+ experiments have just been started [20]. We hope to obtain some definite answers regarding the lattice sites of hydrogen atoms in the pure semiconductor lattice. This would be of great value because hydrogen may assume such positions, at least transiently, during diffusion or during drift in an electric field as a proton while it does not seem to remain isolated in equilibrium. The limited space does not permit an extensive discussion of these experiments here but

the interested reader is advised to follow the results obtained with these techniques.

2. EXPERIMENTAL TECHNIQUES

2.1 Standard Methods

Most of the hydrogen-related shallow acceptors and donors have been discovered and studied in ultra-pure germanium single crystals. Typical concentrations of electrically active centers in such crystals are of the order of 10^{10} cm^{-3} which corresponds to one acceptor (or donor) for every 4×10^{12} Ge atoms! The extreme purity reduces the vast range of semiconductor characterization techniques to a relatively small number which are sufficiently sensitive. Measurements based on space charge effects, free carrier transport, and photoconductivity belong to this group. A special form of the latter technique which combines the energy resolution of infrared spectroscopy with the sensitivity of photoconductivity deserves a more detailed discussion which can be found in Chapter 2.3.

Space charge techniques based on capacitance-voltage measurements, both in the DC and pulsed regime, have been extensively used, mostly for the study of deep levels in ultra-pure crystals. We will not give further consideration to these techniques in this review because they are typically not well suited for the study of shallow levels.

The determination of the free carrier concentration as a function of temperature using Hall effect, either in the classical or in the van der Pauw [21] geometry, gives a direct and quantitative measure of the net-acceptor $(N_A - N_D)$ or donor $(N_D - N_A)$ concentration in a semiconductor sample. The Hall voltages are typically large (tens of millivolts) and easily measurable because they are inversely proportional to the free carrier concentration which is very small. The logarithm of the free carrier concentration as a function of the inverse absolute temperature represents an Arrhenius plot displaying three distinct regimes. An example of such a plot for a dislocation-free and a dislocated ultra-pure Ge sample is displayed in Fig. 1. At

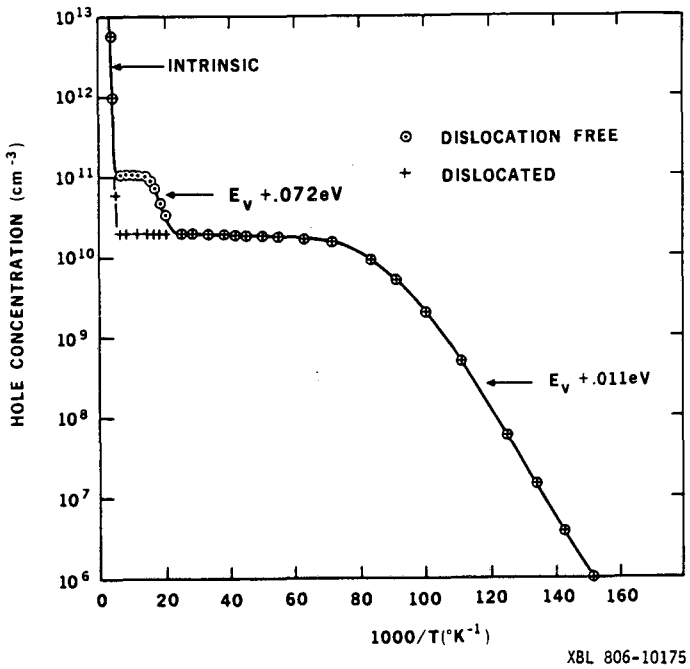

Fig. 1. Arrhenius plot of the free hole concentration p (log p versus 1000/T). The dislocation-free sample contains an acceptor level at E_V + 72 meV and shallow acceptors.

high temperatures ($T \gtrsim 200$ K), we observe the intrinsic carrier regime. The slope of the curve is proportional to one half of the band gap energy of Ge (Eg ≃ 700 meV). The constant carrier concentration extends from 200 K to about 14 K. This long flat plateau corresponding to $|N_A - N_D|$ is very typical for ultra-pure crystals. Below 14 K we observe the shallow level freeze-out regime. The slope in this regime corresponds to the ionization energy of the shallow levels. The difference between the dislocation-free and the dislocated Ge samples which were cut from the same, partially-dislocated single crystal slice is a deep acceptor level at E_V + 72 meV which freezes out at around 60 K. This acceptor has been ascribed to a divacancy-hydrogen complex [22]. For a quick determination of $|N_A - N_D|$ and in the absence of deep levels, it is sufficient to perform a Hall effect measurement at one temperature within the constant concentration regime, most conveniently at liquid nitrogen temperature (T = 77 K).

Excellent ohmic contacts which do not freeze out at low temperatures are an important requirement for all electrical measurements. They deserve special mention because the very pure crystals are easily contaminated during high temperature treatments which are sometimes used in contact formation. The contact formation technique which is

most reproducible, which does not lead to mechanical stresses, and which does not require excessively high temperatures is ion implantation. A low energy implant (25 to 50 keV) of 10^{14} to 10^{15} boron or phosphorus ions per cm^2 into a polish-etched, defect-free Ge surface followed by thermal annealing for one hour at 350°C in an inert atmosphere (N_2 or Ar) leads to degenerately-doped (metallic) contact layers which are p- or n-type respectively. Metallization with a few hundred Å of Pd for good adhesion followed by ~ 2000 Å of Au completes the formation of contacts on germanium. The contact formation recipe for Si differs only in the annealing temperature which has to be increased to the 600 to 800°C range. Ion implanted contacts are very shallow (~ few hundred Å) reducing the introduction of strain and making it very easy to form specific patterns which may be required by a certain measurement technique (e.g. van der Pauw Hall effect).

A less desirable but nevertheless often useful group of low temperature contact formation techniques are based on alloying. Gold doped with small amounts of Ga or Sb is evaporated on a clean defect-free surface of a Ge or Si crystal. Upon heating to the eutectic temperature T_E, a liquid phase forms. Further heating to ~ T_E + 100°C leads to a semiconductor-material-rich liquid phase. During slow cooling, the semiconductor atoms grow back epitaxially on the underlying material, incorporating Ga or Sb at the solubility limit. This regrown layer is heavily doped and forms a low energy barrier for majority carriers moving between the pure semiconductor and the metal. In certain cases, one does not require an intermediate solvent such as Au in the case just described. For example, it is possible to form p-type contacts directly by alloying with pure In. Standard diffusion techniques are usually less desirable for the formation of contacts on pure semiconductors because of the high temperature and the long time requirements.

2.2 Electronic States of Shallow, Hydrogenic Levels

The information one can obtain about the shallow levels from variable temperature Hall effect is not accurate enough to allow for the distinction between group III acceptors or between group V donors.

Especially in Ge but also to a large degree in Si, the shallow impurity levels lie within a very narrow energy range and their binding energies do not deviate much from the values predicted by the effective mass theory (EMT) for donors [23] or for acceptors [24,25]. Clearly, a high resolution spectroscopic technique is required to study shallow centers. In order to comprehend fully the potential of a high resolution technique, we briefly recall the main properties of shallow levels in Ge and Si. An excellent review on this topic has been written by Ramdas and Rodriguez [26].

The effective mass theory describes shallow levels in terms of the hydrogenic model. An electron is bound to the positive donor core (e.g. $P^+ + e^-$) or a hole to a negative acceptor core (e.g., $B^- + h^+$). In the simplest approximation, the binding energy E and the Bohr radius r are given by:

$$E = -\frac{e^4 m^*}{2\varepsilon^2 \varepsilon_0^2 \hbar^2}, \quad r = \frac{\varepsilon \varepsilon_0 \hbar^2}{e^2 m^*} \qquad (1),(2)$$

where ε is the relative dielectric constant, ε_0 is the permittivity of vacuum, m^* is the effective mass of the bound electron or hole, e is the charge of the electron, and $\hbar$ is Planck's constant divided by 2π. Values for germanium are $E_{Donor} = 9.81$ meV and $E_{Acceptor} = 11.2$ meV, and for silicon they are $E_{Donor} = 31.27$ meV and $E_{Acceptor} = 33.9$ meV. In view of the fact that the multivalley nature of donors and the valence band degeneracy and split-off band for acceptors have been neglected, it is surprising how well these values approximate the experimentally observed values. The major exception is the Si isocoric acceptor aluminum with an experimentally determined value of $E_{Al} = 70.18$ meV [26]. The calculations of Baldereschi and Lipari [27] which take the Si split-off valence band and wavevector dependent dielectric screening into account, yield a value $E_{Acceptor} = 70.5$ meV. This excellent agreement shows that the effective mass formalism describes shallow acceptors and donors very well indeed.

Equation 2 gives good estimates of the Bohr radii. We obtain r_{Bohr} (Ge) ≈ 80 Å and r_{Bohr} (Si) ≈ 35 Å. The large radii lead to wavefunction overlap already at low impurity concentrations. The consequence is the broadening of bound hole or electron states. In ultrapure crystals which constitute the main focus of this review, one can usually neglect wavefunction overlap.

The effective mass theory can be extended to describe bound excited states besides the ground state discussed above. The recent calculations for shallow donors by Broeckx, et al. [28] give excited states binding energy values which agree to within 0.02 meV with experimentally determined results for p-like quantum states up to quantum number 6. This extremely good agreement is due in part to the vanishing amplitude of p-wave functions at the impurity core. The s-like states are strongly affected by the impurity core. A consequence of this is the splitting of the (1s) ground state level by the intervalley coupling in multivalley semiconductors. In Ge we observe a (1s) singlet and a (1s) triplet while in Si a (1s) singlet, a (1s) doublet, and a (1s) triplet are found. The triplet and doublet states exhibit energies very close to the values obtained by EMT while the singlet states suffer large impurity-specific shifts which can be of the order of the EMT ground state energy [26].

The bound excited states of shallow acceptors are well described by the calculations of Baldereschi and Lipari [27]. The theoretical and experimental values for Ge agree within 0.01 meV and are summarized in Fig. 2. The agreement for silicon is not quite as perfect (~ 0.2 meV) but can still be considered very good.

2.3 Photothermal Ionization Spectroscopy (PTIS)

The electronic states spectrum of shallow levels was explored in the 1970's by the Purdue group using far infrared absorption spectroscopy. For Ge, acceptor spectra were reported by Jones and Fisher [29] and donor spectra by Reuszer and Fisher [30]. The crystals used for these early studies contained shallow levels at a concentration close to 10^{14} cm^{-3}. The linear absorption coefficients for photons with ground-state-to-bound-excited-state energies are of the order of a few

inverse cm at these concentrations. Reducing the concentration by four orders of magnitude leads to absorption coefficients which are too small to result in detectable absorption peaks. Recent absorption measurements [31] have shown that the linear absorption coefficients at the maximum of the various absorption peaks decrease less than linearly with the impurity concentration because the peaks become sharper due to the decrease in wave function overlap. Still, at concentrations close to 10^{10} cm^{-3}, a much more sensitive technique is required.

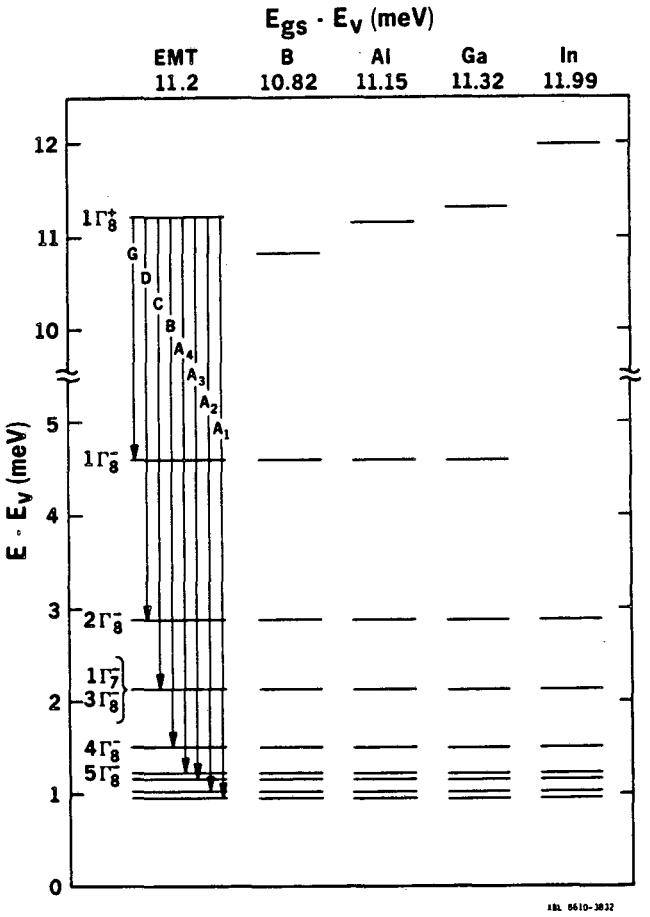

Fig. 2. The energy levels for the ground state and lowest lying odd-parity excited states of Group III acceptors in Ge.

Lifshits and Nad [32] discovered sharp peaks in photoconductivity spectra of pure n-type Ge samples. The peaks were located precisely at photon energies corresponding to ground-state-to-bound-excited-state transitions of impurity-bound electrons. No increase in photoconductivity should occur at photon energies short of the full ionization energy. The process leading to the peaks was interpreted correctly in terms of a two-step ionization event. The donor electron is excited from the ground-to-bound-excited state by absorption of a photon (Fig.

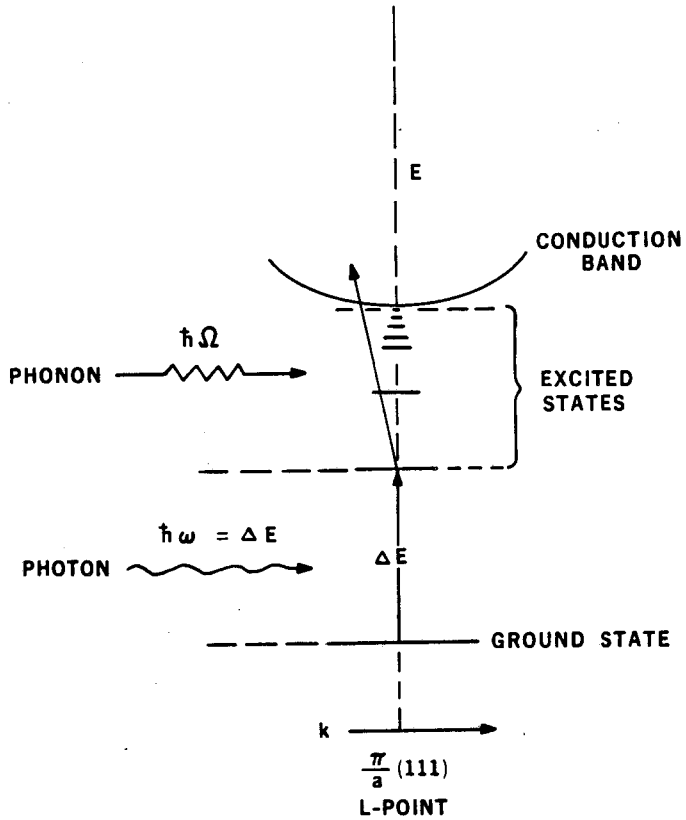

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Fig. 3. The two-step absorption process which leads to photothermal ionization.

3). The lifetime in the excited state is sufficiently long for a phonon to transport, with finite probability, the electron into the conduction band. This in turn leads to an increase in conductivity. Kogan [33] showed that the sensitivity of this two-step ionization spectroscopy, called photothermal ionization spectroscopy, is to first order independent of the impurity concentration. A simplified argument for this can be found in the fact that both the dark current as well as the PTIS signal depend linearly on the impurity concentration leading to a concentration-independent ratio. A more detailed study by van den Steeg, et al. [34] taking into account sample impedance, electronic noise, amplifier properties, and optical parameters predicts that as little as 10^5 cm^{-3} shallow levels can be detected and identified in ultra-pure samples. This limit is and will probably remain for some time below impurity concentrations in real crystals.

The PTIS spectrum depends on the temperature of the crystal. At very low temperatures, the phonon population is too low for a second ionization step to occur with finite probability. We observe the well-

known photoconductivity spectrum of an extrinsic photoconductor (Fig. 4a). As temperature increases, we begin to observe PTIS lines first close to the continuum and then further away (Figs. 4b and c). The warmer the crystal is, the larger is the concentration of phonons which can lead to the second ionization step required for PTIS. When the temperature reaches a point at which direct thermal ionization from the ground state into the band occurs, we begin to reduce rapidly the number of neutral centers, and the PTIS signal as well as the photoconductive continuum disappear. The crystal is in the constant free-carrier regime shown in Fig. 1. The optimum temperature ranges for PTIS of Ge and Si are 5 - 8 K and 15 - 20 K respectively.

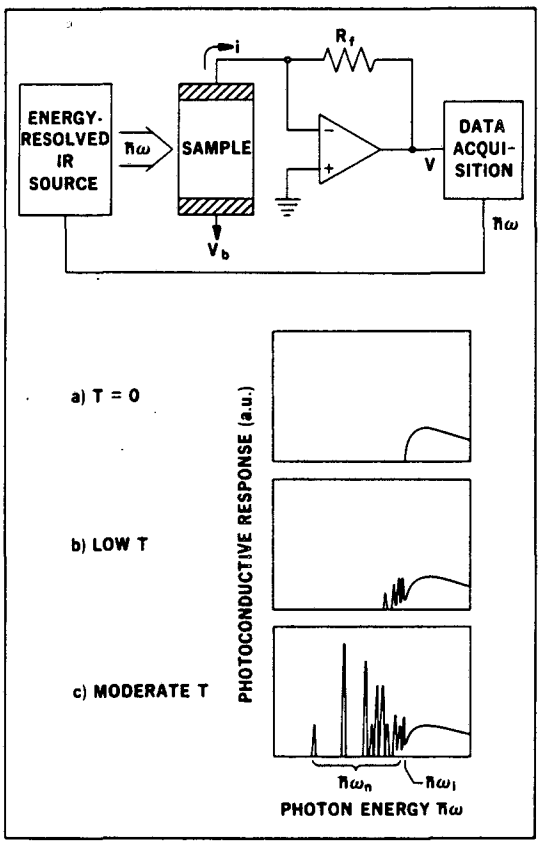

Fig. 4. Photothermal ionization spectroscopy (schematic). Typical spectra recorded at (a) T = 0, (b) low T, and (c) moderate T.

The excellent sensitivity of PTIS can be combined with the high spectral resolution capability of modern infrared Fourier transform spectrometers. An example of a spectrum obtained with a p-type ultrapure Ge crystal containing the acceptors B, Al, and A(D,C), a deuterium-carbon complex, is shown in Fig. 5. The narrowest lines are

~ 11 μeV wide at half height and are fully resolved. Residual strains, Stark effect due to ionized acceptors and donors, and phonons contribute to this linewidth. The largest peaks are about 250 times the root mean square value of the noise. The fact that the continuum onset is barely discernible in the spectrum illustrates the large values of the dipole transition matrix elements for the ground-state-to-bound-excited-state transitions as compared to ground-state-to-band transitions. This situation rapidly inverts with increasing depth of the energy levels. It is quite difficult to obtain a line spectrum of the neutral copper acceptor which is located at E_V + 44 meV, approximately four times as deep as shallow hydrogenic acceptors. PTIS is clearly a shallow level technique.

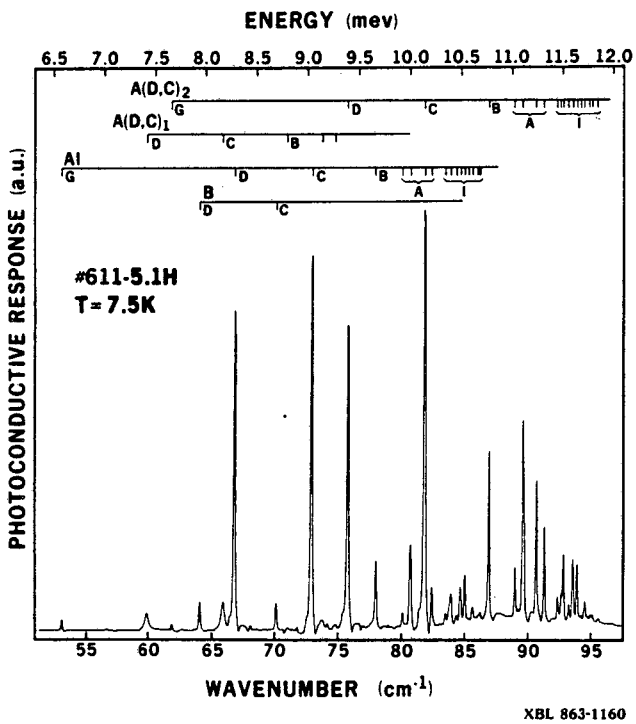

Fig. 5. PTI spectrum of a p-type, ultra-pure Ge sample. The sample contains the acceptors B, Al and A(D,C), in a total concentration of 6×10^{10} cm^{-3}. The narrowest lines are 0.09 cm^{-1} = 11 μeV wide.

3. HYDROGEN-RELATED COMPLEXES

3.1 The Centers A(H,Si), A(H,C), A(V_2H), and D(H,O)

Hall [35] discovered a shallow acceptor which appeared to convert into a shallow donor around room temperature upon rapidly quenching small single crystal pieces of ultra-pure Ge from 425°C. Both centers

could be annealed out and regenerated with a new quenching cycle. Only crystals grown in a hydrogen atmosphere from a melt contained in a silica crucible showed the novel centers. The presence of hydrogen in the two centers was unambiguously verified using PTIS and the substitution of hydrogen with deuterium. Both centers showed an isotope-related shift in their ground state energies. The acceptor hole-binding energy increased with deuterium by 21 μeV while the donor electron-binding energy decreased by 51 μeV [36]. Experiments with crystals grown in a mixed $D_2 + H_2$ atmosphere showed that each center contained precisely one hydrogen atom. The additional materials-related arguments led to the assignment of a H,Si complex to the rapid quench acceptor A(H,Si), and of a H,O complex to the rapid quench donor D(H,O).

PTIS studies as a function of temperature and of uniaxial stress revealed a number of unusual properties of A(H,Si) [37] and D(H,O) [38]. The acceptor gives rise to two series of hydrogenically-spaced lines originating from a groundstate manifold consisting of at least two components split by $\Delta E = 1.07$ meV. Under uniaxial stress, the lines split significantly less than the elemental acceptor lines. In a recent high resolution study, Kahn [39] showed that the A(H,Si) lines split under <111> stresses into two lines with a 3:1 intensity ratio and a 1:3 energy shift ratio. Crystals grown from a melt contained in a graphite crucible also contain hydrogen-related acceptor complexes which were assigned, in full analogy to the A(H,Si) centers, to a H,C complex. The A(H,C) acceptor behaves like A(H,Si) in every respect but with a groundstate manifold split by $\Delta E = 1.98$ meV. The recent findings have led Kahn [15] to propose that the two centers are complexes which are trigonally distorted along the <111> directions. The observed uniaxial stress splitting is due to the difference in orientation of the acceptors oriented randomly along the four <111> directions. Three quarters are aligned along the off-stress axes and 1/4 lies along the stress direction. This orientational splitting is very different from the splitting of a degenerate level under an external (or internal) symmetry-breaking perturbation. The static trigonal distortion, on the

other hand, is assumed to be the cause for the existence of the two ground state components. It is modeled with an "internal uniaxial stress" parallel to a <111> axis of the acceptor complex. This model serves the sole purpose of obtaining the matrix elements of a perturbation Hamiltonian and is not meant to describe a real physical internal stress. The description of A(H,Si) and A(H,C) with trigonally distorted complexes distributed evenly among the four <111> orientations could be tested by attempting to align the complexes along or away from the uniaxial stress orientation at high temperature followed by cooling under applied stress. Such experiments are currently underway.

The model by Kahn can be viewed as a limiting case of a more general model which has been proposed by Falicov [14]. This model describes the hydrogen-containing complexes in terms of a heavy substitutional impurity which binds a hydrogen atom in its vicinity. The rapid tunneling of the hydrogen between four equivalent real space positions leads to the recovery of full tetrahedral symmetry and to a rich ground state multiplet. The tunneling hydrogen model has recently been used to describe successfully the properties of an acceptor in silicon consisting of the double acceptor beryllium and hydrogen. It will be discussed in some more detail in the following section (3.2).

The donor D(H,O) again has most unusual groundstate properties. The lines of this donor do not shift within the instrumental resolution under uniaxial stress in the [111] direction up to a stress value of about 2×10^8 dyne cm^{-2}. At this stress value a new hydrogenically-spaced series of lines appears shifted by 2.78 meV to lower energies. The zero stress spectrum vanishes at higher stress values (Fig. 6). Stress along the other main crystallographic directions has a similar effect though the values at which the new spectrum appears are different.

Figure 7 shows a schematic picture of the D(H,O) donor. A substitutional OH^+ core tunnels between four equivalent positions. We can no longer assume a donor electron bound in a static Coulomb field. The combined nuclear and electronic energy spectrum must be taken into account. The abrupt change of the ground state energy at a certain

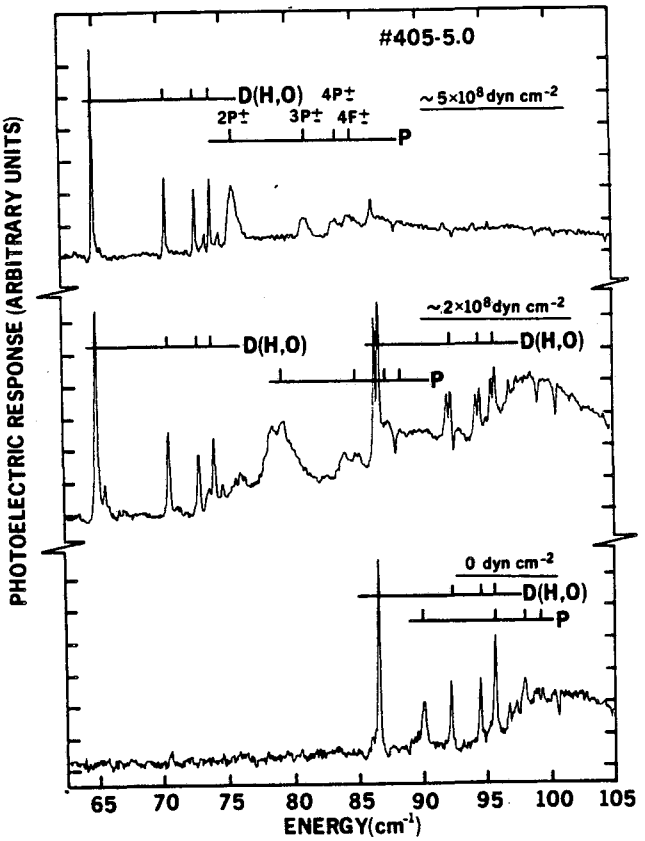

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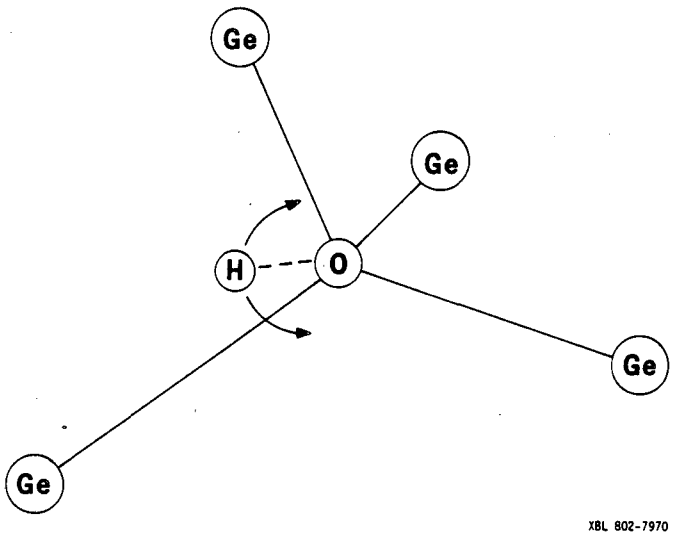
Fig. 6. Three PTI spectra of an n-type Ge sample containing phosphorus donors (P) and the D(H,O) donor at different [111] uniaxial compressional stress values.

value indicates a symmetry change from s- to p-like. The group theoretical treatment of the combined electronic-nuclear system has been performed by Joos, et al. [38]. Their results are presented in Fig. 8. At zero stress the ground state is a fully degenerate quadruplet ($\Gamma_1 + \Gamma_5$) which splits into a triplet increasing in energy parallel to the three rising off-axis valleys, and a singlet (Λ_1) following parallel to the decreasing valley in the stress direction. At the critical stress, a (Λ_3) state crosses the (Λ_1) state and becomes the ground state. The photon-induced transitions occur now at energies which are lower by ΔE_i.

An interesting hydrogen-related acceptor has been discovered in dislocation-free, hydrogen-grown crystals. Its energy level lies at E_v + 72 meV and is too deep to allow PTIS studies. As in the cases of A(H,Si) and D(H,O), one can vary the concentration of this acceptor reversibly by appropriate thermal treatments. Systematic annealing studies [22] have led to the conclusion that the center contains

Fig. 7. Schematic representation of the OH donor complex in a germanium vacancy.



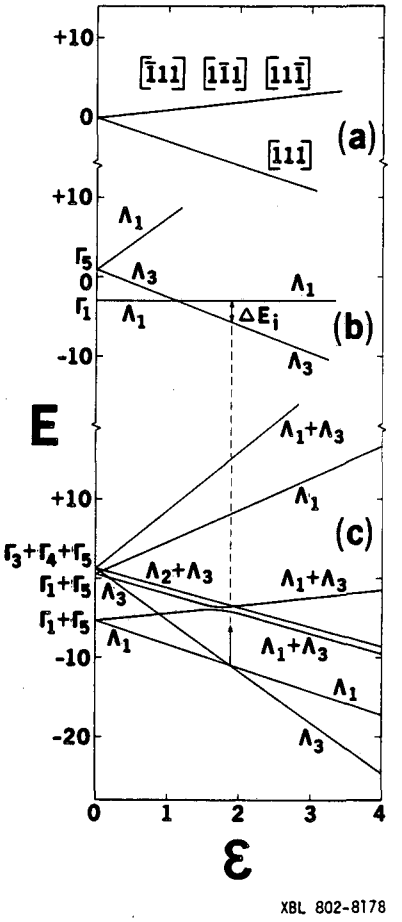


Fig. 8. Stress dependence of the various energies for the D(H,O). (a) The behavior of the four conduction-band valleys. (b) The stress dependence of the nuclear states only. (c) The energy of the fully interacting system. The stress is applied along [111]. All energies in arbitrary units. The ionization energy of the complex donor is obtained by subtracting the groundstate 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_i gives the shift in the spectra observed between the low stress and the high stress cases of Fig. 6.

hydrogen and most likely a divacancy, i.e., $A(V_2H)$. Monovacancies were excluded because of their very high mobility, and higher order vacancy complexes would most likely result in a number of different centers with more than one energy level and complicated annealing behavior. The acceptor $A(V_2H)$ has been studied with Hall effect (see Fig. 1) and deep level transient spectroscopy [40]. No symmetry information could be obtained so far and some clever experiments are required to arrive at a better understanding. The most important practical aspect of $A(V_2H)$ is that it is an efficient hole trap in gamma radiation detectors, yielding dislocation-free, hydrogen-grown Ge crystals useless for radiation detector fabrication.

3.2 The Centers A(Be,H), A(Zn,H), and A(Cu,H_2)

The double acceptors formed by substitutional Be and Zn have been thoroughly studied in Ge by far infrared spectroscopy [41] and photoluminescence [42,43]. Both centers exhibit ground state splitting due to hole-hole interaction. All energy levels are accurately known. The triple acceptor Cu has been known for a long time [44]. The shallowest energy level of natural substitutional Cu has been studied with infrared spectroscopy [45]. The deeper levels are known from Hall effect measurements.

In Ge crystals which we doped in the melt with Be or Zn and which are grown in a hydrogen or deuterium atmosphere, McMurray, et al. [46] discovered new hydrogenic shallow acceptors with unusual ground states. Upon outdiffusion of the hydrogen at temperatures around 600°C, the shallow levels disappear. It was proposed that the partially-hydrogen-passivated double acceptor complexes A(Be,H) and A(Zn,H) form. The A(Be,H) acceptor has two ground state components split by 0.5 meV. Uniaxial stress in the <111> direction splits each line of the two hydrogenic series into two components with 3:1 intensity ratios and 1:3 shifts (Fig. 9). The trigonally distorted impurity complex model has been successfully used to explain the properties of the A(Be,H) center. Only one series of lines has been found for A(Zn,H). These lines also split in a 3:1 ratio and it is assumed that the second groundstate component simply lies too high to be significantly populated at typical PTIS temperatures. This explains the absence of the second line series and suggests that A(Zn,H) is also a trigonally distorted complex. In contrast to the A(H,Si) and A(H,C) acceptors in which hydrogen appears as H^-, hydrogen effectively substitutes in the A(Be,H) and A(Zn,H) centers one hole, screening the doubly charged impurity core by precisely one charge. An intuitively appealing model for a Be-H complex is the united atom model [47]. The Be-H complex can be replaced by a boron nucleus which of course forms a well-known EMT-like acceptor. It would be interesting to learn if cluster calculations which were performed by Assali and Leite [16] for

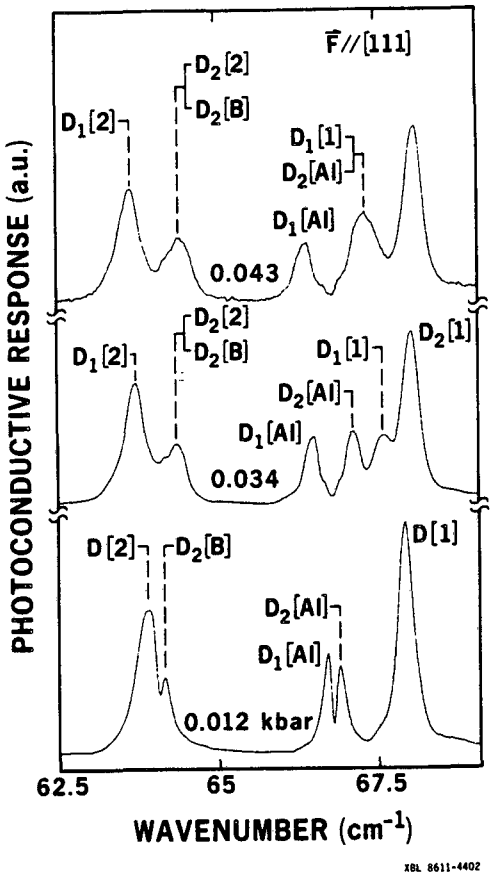


Fig. 9. PTI spectra of the D-transitions of $A(Be,H)_1$ and $A(Be,H)_2$, as well as B and Al, under [111] stress. In square brackets, the numbers "1" and "2" refer to $A(Be,H)_1$ and $A(Be,H)_2$, respectively. These spectra were recorded at 6.0 K.

fully passivated B-H- complexes in Si would yield useful results for Be-H centers as well.

Contrary to the static trigonally distorted A(Be,H) centers in germanium, Muro and Sievers [13] have found a dynamic Be-H acceptor in Si which displays properties due to tunneling hydrogen. They have explored the combined electronic-nuclear hole energy spectrum and have found all five ground state components predicted by Falicov's model. The nuclear motion splits each p-like excited state into two components. A large isotope shift occurs upon the substitution of H with D. To our knowledge, this is the first dynamic acceptor in Si.

Copper, a substitutional triple acceptor, has been known to form complexes with hydrogen [48]. Kahn, et al. [49] recently showed that this complex contains two hydrogen atoms. The character of the ground state of the single acceptor $A(Cu,H_2)$ changes from a most complicated manifold, containing at least eleven but probably more components, to a very simple single groundstate level upon substitution of at least one

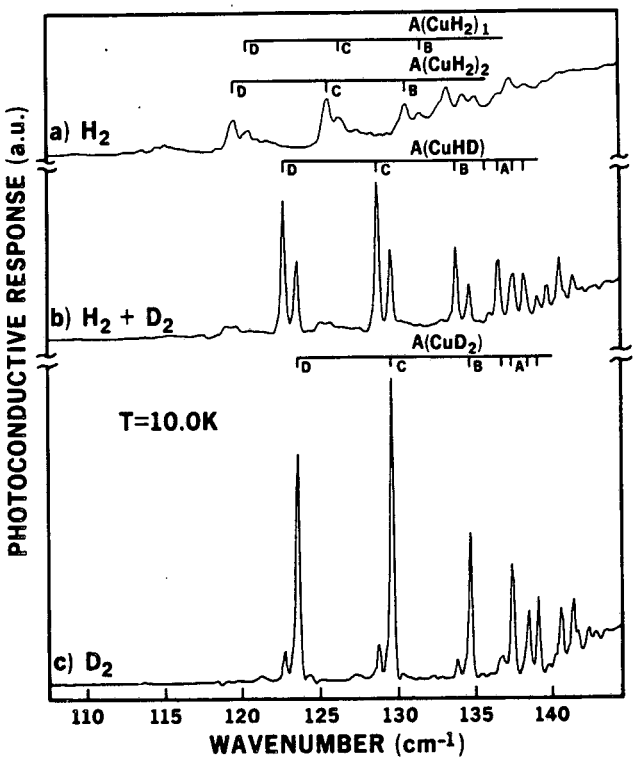


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Fig. 10. PTI spectra of the copper-dihydrogen acceptors that appear in samples which were grown under atmospheres of different hydrogen isotopes. (a) Pure H_2, showing the complex spectrum of $A(CuH_2)$; (b) a 1:1 mixture of H_2 and D_2, showing $A(CuH_2)$, A(CuHD), and $A(CuD_2)$ in a 1:2:1 ratio; (c) nearly pure D_2, showing $A(CuD_2)$ and a trace of A(CuHD).

of the hydrogen atoms by its heavier isotopes D or T. This is clearly shown by the three spectra in Fig. 10. The presence of three groups of hydrogenic series of lines in the mixed-gas-grown crystal is direct proof for the participation of two hydrogen atoms in the formation of these complexes. Kahn [15] and Kahn, et al. [49] have performed extensive studies of the acceptors $A(Cu,H_2)$, A(Cu,D,H), $A(Cu,D_2)$, A(Cu,H,T), and $A(Cu,T_2)$. They found the groundstate energy to depend linearly on the reduced mass of the two hydrogen isotopes with the exception of the $A(Cu,H_2)$ center. This dependence points to dynamic effects, i.e., motion of the hydrogen atoms. The differences between the groundstate structures of the $A(Cu,H_2)$ acceptor and the other centers containing heavier isotopes have been elucidated by the Devonshire model [50]. This model, originally developed for molecular impurities (e.g., CN) in alkalihalide crystals, predicts how the energy states of a rigid rotor are affected by a crystal potential which hinders the rotation. A sufficiently large potential or a small rotor

inertia can reduce rotation to libration. The rotor can still tunnel between potential minima. While the rotational energy levels are widely spaced, the librational levels are bunched to a small energy range. Using the Devonshire model, Kahn was able to explain qualitatively the differences between the various A(Cu,X,Y) acceptors.

3.3 Fully Passivated Centers

The literature on hydrogen passivation of shallow and deep level defects has become voluminous in the past few years. Though the effects of exposure of a semiconductor to atomic hydrogen in a gas discharge [9], in an electrolytic cell [10], or in a polishing process [11] are spectacular, leading in some cases to the disappearance of practically all the dopants (e.g., 99.99% of the shallow boron acceptors in Si can be passivated), the passivation process and the complexes which are formed are not well understood. The main reason for the poor understanding is the fact that neutral complexes cannot be investigated with sufficiently sensitive and high resolution tools.

We restrict this review to a brief summary of experimental findings and mention first attempts at theoretical treatments of what appears to be going on. Observations of hydrogen-related effects in silicon date back as far as 1960. Seibt and Zerbst at Siemens reported on lifetime decreases caused by exposure of p-type Si wafers to atomic hydrogen [12] though this information never appeared in the published literature. Haller, et al. [48] studied the formation of Cu-related complexes in Ge and proposed the formation of electrically active complexes as well as neutral Cu-H_3 complexes. Sah, et al. [51] observed hydrogen-related passivation of the p-type Si adjacent to the oxide in MOS devices. Pankove, et al. [9] used a gas discharge H-plasma to show passivation of shallow acceptors in Si. A large number of experiments on H passivation of deep levels in Si, Ge, and GaAs were performed by Pearton, et al. [10,52,53]. The quantitative studies of Johnson [54], and of Johnson and Moyer [55] indicated that the hydrogen concentration in p-type Si depends on the local acceptor concentration, an effect which has been observed for interstitial lithium donors [17]. This impurity concentration correlation supports H-acceptor pairing in

contrast to simple compensation of acceptors by donors. Additional reasons which strongly support passivation by pairing can be found in the foregoing section on partially-passivated multivalent acceptors and from the absence of any observations which would indicate that an interstitial hydrogen donor level exists in the bandgap. Recently, Pantelides [56] has attempted to present a unified picture of all the hydrogen-related experimental observations. He concludes that if atomic hydrogen produces a donor level in the lower half of the bandgap, all the experimental data can be explained satisfactorily. If hydrogen were indeed a deep donor, one would expect to observe unique electron paramagnetic resonance (EPR) spectra of the unpaired electrons. The absence of any EPR signals may indicate that the above assumption is not correct. It is likely that hydrogen molecule (H_2) formation fully dominates at moderate and low temperatures which would explain the absence of EPR signals. Diffusion studies by Hall [57] in pure germanium clearly showed a strong deviation of the diffusivity at low temperataures from the values predicted by high temperature studies [1]. Formation of H_2 was cited as the most probable cause.

Theoretical treatments of the possible structure of H-acceptor pairs have been performed by DeLeo, et al. [58], and Assali and Leite [16]. The former group based their calculation on a model of a threefold coordinated acceptor and a H-passivated Si bond. The predicted vibrational frequency of the Si-H bond is in good agreement with experimental observations. Unfortunately there exist no experimental data on the possible changes of the acceptor local vibrational mode. Such data would be most useful because they could either confirm or contradict the proposed trigonal symmetry of the passivated acceptor. Furthermore, a significant change in the LMV frequency would be expected. The model of Assali and Leite is based on H being bound to the acceptor. Such a picture is quite similar to the well-known acceptor-lithium pairs with the important difference that the latter are assumed to be bound purely ionically. It becomes clear that much progress is required before we can claim to understand H passivation.

4. CONCLUSIONS

We have shown that the simplest atom, hydrogen can form a large number of complexes with impurities and defects in Si and Ge. The complexes which lead to energy levels in the bandgap are reasonably well understood while the neutral complexes require further studies. From the work in pure Ge, a systematic behavior of hydrogen can be derived. Acceptors are passivated by H^+ ions while isoelectronic impurities such as Si and C bind a H^- ion. In the case of the OH donor, H also appears to play the role of a H^- ion bound to the doubly-charged positive oxygen impurity ($O^{2+} + H^-$).

The unusual electronic structure of the shallow level complexes can be understood for some cases by invoking a tunneling hydrogen atom. The rapid tunneling recovers full tetrahedral symmetry of the combined electronic-nuclear state. Several complexes can be modeled with trigonally distorted centers distributed randomly along all four <111> directions. We close this review by listing a number of only partially answered questions [59,60]:

1) Why do H and C as well as H and Si, electrically inactive impurities, form shallow acceptors?
2) What is the precise nature of the binding forces?
3) Why do H and O form a shallow donor?
4) Oxygen is assumed to occupy a bond-centered position. Why is OH^+ at a T_d site?
5) OH^+ does not form as free molecular ion. Why is it stable in a Ge matrix?
6) What is the nature of the binding forces in OH^+?
7) What is the structure of electrically-inactive H-acceptor complexes and what are the binding forces?

We hope to have shown that hydrogen-related complexes present a number of exciting challenges for theory as well as for experiment. This field of studies is rapidly progressing because of strong fundamental and applied science interests.

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REFERENCES

[1] Frank, R. C. and Thomas, J. E., J. Phys. Chem. Solids 16, 144 (1960).

[2] van Wieringen, A. and Warmoltz, N., Physica XXII, 849 (1956).

[3] Hansen, W. L., Haller, E. E. and Luke, P. N., IEEE Trans. Nucl. Sci. NS-29, No. 1, 738 (1982).

[4] Haller, E. E., Festkörperprobleme (Advances in Solid State Physics) 26, 203, P. Grosse (ed.), Vieweg, Braunschweig, 1986.

[5] Haller, E. E. and Goulding, F. S., Handbook on Semiconductors, Vol. 4, Ch. 6C, 799, C. Hilsum (ed.), North Holland, 1981.

[6] Hansen, W. L. and Haller, E. E., Proc. Mat. Res. Soc. Symp. Vol. 16, 1, E. E. Haller, H. W. Kraner, and W. A. Higginbotham (eds.), Elsevier Sci. Publ., 1983.

[7] Haller, E. E., Hansen, W. L. and Goulding, F. S., Advances in Physics 30, 93 (1981).

[8] Haller, E. E., Mat. Res. Soc. Symp. Proc. 46, 495; N. M. Johnson, S. G. Bishop and G. D. Watkins (eds.), Mat. Res. Soc., 1985.

[9] Pankove, J. I., Carlson, D. E., Berkeyheiser, J. E. and Wance, R. O., Phys. Rev. Lett. 51, 2224 (1983).

[10] Pearton, S. J., Hansen, W. L., Haller, E. E. and Kahn, J. M., J. Appl. Phys. 55, 1221 (1984).

[11] Schnegg, A., Grundner, M. and Jacob, H., J. Elec. Chem. Soc. 133, No. 3, 100C (1986), abs. 141.

[12] Seibt, H. and Zerbst, M., unpublished Siemens report (1960).

[13] Muro, K. and Sievers, A. J., Phys. Rev. Lett. 57, 897 (1986).

[14] For a brief overview, see: Falicov, L. M. and Haller, E. E., Sol. State Commun. 53, 1121 (1985).

[15] Kahn, J. M., Ph.D. Thesis, University of Calif., Berkeley, Nov. 1986, Lawrence Berkeley Laboratory Report LBL-22652.

[16] Assali, L. V. C. and Leite, J., Phys. Rev. Lett. 55, 980 (1985).

[17] Reiss, H., Fuller, C. S. and Morin, F. J., Bell Syst. Tech. J. 35, 535 (1956).

[18] LAMPF, Los Alamos; TRIUMF, Vancouver; and SIN, Zurich.

[19] Schenck, A., Muon Spin Spectroscopy, Adam Hilger, Bristol, 1985.

[20] Flik, G., Bradbury, J., Cooke, W., Heffner, R., Leon, M., Paciotti, M., Schillaci, M., Maier, K., Rempp, H., Reidy, J., Boekema, C. and Daniel, H., Phys. Rev. Lett. 57, 563 (1986); see also: Hyperfine Interactions 32, 595 (1986).

[21] van der Pauw, L. J., Phillips Res. Rept. 13, 1 (1958).

[22] Haller, E. E., Hubbard, G. S., Hansen, W. L. and Seeger, A., Inst. Phys. Conf. Series 31, 309 (1977).

[23] Faulkner, R. A., Phys. Rev. 184, 713 (1969).

[24] Kittel, C. and Mitchell, A. H., Phys. Rev. 96, 1488 (1954).

[25] Luttinger, J. M. and Kohn, W., Phys. Rev. 97, 869 (1955).

[26] Ramdas, A. K. and Rodriguez, S., Rep. Prog. Phys. 44, 1297 (1981).

[27] Baldereschi, A. and Lipari, N. O., Proc. 13th Intl. Conf. Semicon., 595, F. G. Fumi (ed.), Marves, Rome, 1976.

[28] Broeckx, J., Clauws, P. and Verni, K. J., J. Phys. C. 19, 511 (1986).

[29] Jones, R. L. and Fisher, P., J. Phys. Chem. Solids 26, 1125 (1965).

[30] Reuszer, J. H. and Fisher, P., Phys. Rev. 135, A1125 (1964).

[31] Haller, E. E., McMurray, R. E., Jr., Haegel, N. M. and Falicov, L. M., Proc. 17th Intl. Conf. Phys. Semicon., 679, J. D. Chadi and W. A. Harrison (eds.), Springer, N.Y., 1985.

[32] Lifshits, T. M. and Nad, F. Ya., Dokl. Akad. Nauk. USSR 162, 801 (1965); for an extensive review, see: Kogan, Sh. M. and Lifshits, T. M., Phys. Stat. Sol. (a) 39, 11 (1977).

[33] Kogan, Sh. M., Fiz. Tekh. Poluprov. 7, 1231 (1973).

[34] van den Steeg, M. J. H., Jongbloets, H. W. H. M. and Wyder, P., Phys. Rev. Lett. 50, 1234 (1983); also: Phys. Rev. B30, 3374 (1984).

[35] Hall, R. N., Inst. Phys. Conf. Ser. 23, 190 (1975); see also: IEEE Trans. Nucl. Sci. NS-21, No. 1, 260 (1974).

[36] Haller, E. E., Phys. Rev. Lett. 40, 584 (1978).

[37] Haller, E. E., Joos, B. and Falicov, L. M., Phys. Rev. B21, 4729 (1980).

[38] Joos, B., Haller, E. E. and Falicov, L. M., Phys. Rev. B22, 832 (1980).

[39] Kahn, J. M., Phys. Rev. B, to be published.

[40] Haller, E. E., Po-Yee Li, P., Hubbard, G. S. and Hansen, W. L., IEEE Trans. Nucl. Sci. NS-26, No. 1, 265 (1979).

[41] Cross, J. W., La Brec, C. R., Rodriguez, S., Ramdas, A. K. and Haller, E. E., Phys. Rev. B32, 7992 (1985).

[42] Thewalt, M. L. W., Lightowlers, E. C. and Haller, E. E., Sol. State Commun. 54, 1043 (1985).

[43] Sauer, R. and Weber, J., J. Phys. C: Solid State Physics 17, 1421 (1984).

[44] Hall, R. N. and Racette, J. H., J. Appl. Phys. 35, 379 (1964).

[45] Salib, E. H., Fisher, P. and Simmonds, P. E., Phys. Rev. B32, 2424 (1985).

[46] McMurray, R. E., Jr., Haegel, N. M., Kahn, J. M. and Haller, E. E., Sol. State Commun. 61, 27 (1987).

[47] Harrison, W. A., Electronic Structure and Properties of Solids (Freeman, San Francisco, 1980) p. 20.

[48] Haller, E. E., Hubbard, G. S. and Hansen, W. L., IEEE Trans. Nucl. Sci. NS-24, No. 1, 48 (1977).

[49] Kahn, J. M., Falicov, L. M. and Haller, E. E., Phys. Rev. Lett. 57, 2077 (1986).

[50] Devonshire, A. F., Proc. Roy. Soc. (London), A153, 601 (1936).

[51] Sah, C. T., Sun, J. Y. C. and Tzon, J. J. T., Appl. Phys. Lett. 43, 204 (1983); see also: J. Appl. Phys. 54, 5864 (1983).

[52] Pearton, S. J., Kahn, J. M. and Haller, E. E., J. Elect. Mat. 12, No. 6, 1003 (1983).

[53] Pearton, S. J., Tavendale, A. J., Kahn, J. M. and Haller, E. E., IEEE Trans. Nucl. Sci. NS-31, No. 1, 326 (1984).

[54] Johnson, N. M., Phys. Rev. B31, 5525 (1985).

[55] Johnson, N. M. and Moyer, M. D., Appl. Phys. Lett. 46, 787 (1985).

[56] Pantelides, S. T., Proc. 14th Intl. Conf. on Defects in Semicon., Mat. Sci. Forum Vol. 10-12, Pt. 2, 573 (1986).

[57] Hall, R. N., Proc. 13th Intl. Conf. on Defects in Semicon., L. C. Kimerling and J. M. Parsey, Jr. (eds.) AIME Publ. 14a, 759 (1985); see also: IEEE Trans. Nucl. Sci. NS-31, No. 1, 320 (1984).

[58] De Leo, G. G. and Fowler, W. B., Phys. Rev. Lett. 56, 402 (1986).

[59] Oliva, J. and Falicov, L. M., Phys. Rev. B28, 7366 (1983).

[60] Oliva, J., Phys. Rev. B29, 6846 (1984).

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