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DEFECT IDENTIFICATION IN HIGH-PURITY SEMICONDUCTORS

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ABSTRACT

The elemental semiconductors silicon and germanium can be purified to electrically active impurity concentrations as low as $10^{10}$ cm$^{-3}$. Highly sensitive, energy dispersive analytical techniques have been developed to identify and measure the concentration of the residual elemental impurities. The application of these techniques to very pure materials has also resulted in the discovery of a large number of new levels which are due to impurity/defect complexes. Photothermal ionization spectroscopy using uniaxial stress or a magnetic field, electron paramagnetic resonance, and doping experiments using stable and radioactive elements have been used in combination to identify the composition and the structure of some of the new centers.

INTRODUCTION

This paper reviews some of the experimental methods which have been developed and used in the determination of the concentration and the species of residual impurities and native defects in very pure germanium and, to a lesser degree, silicon. A large number of impurity and defect complexes have been discovered in these pure semiconductors. The structure and composition of some of these novel centers will be discussed.

The designations "pure" or "ultra-pure" are relative and can best be defined by a brief description of semiconductor devices which require unusually low levels of electrically active centers.

The development of large volume (up to $\sim 200$ cm$^3$) p-i-n diodes for nuclear radiation detection [1,2] was the primary driving force in the development of germanium with net-impurity concentrations of the order of $10^{10}$ cm$^{-3}$. One may ask why ultra-purity is required when only the net doping concentration is relevant. This is indeed a very appropriate question in view of the fact that for more than 15 years (and still today for extremely large p-i-n coaxial diodes) detectors were fabricated by using the well-known lithium drifting technique. The major reason for the development of pure material is the very poor stability of the lithium compensation at room temperature. Unlike Li-drifted material, ultra-pure crystals are stable at room temperature, allowing for extensive preparation time which may be needed for complicated multidetector systems. In addition, they also contain extremely low concentrations of deep levels when properly handled. This is responsible for the excellent charge collection over large distances contributing to high energy resolution of these devices.

The development of ultra-pure silicon dates back as far as 1959 when Hoffman et al [3] achieved resistivities approaching $\geq 100$ k$\Omega$cm. An important application of high-purity silicon was demonstrated in 1974 when the first high power silicon-controlled rectifiers (SCR) were fabricated from ultra-pure silicon which was neutron transmutation doped (NTD)[4]. NTD silicon is very homogeneously doped because the thermal neutron flux through a crystal is homogeneous and the residual doping impurity striations are several orders of magnitude below the NTD-generated phosphorus concentration. Today the NTD technique is fully commercialized however the supply of ultra-pure silicon and thermal neutrons has remained tenuous at times.

Far infrared extrinsic photoconductors require extraordinary control
of the residual impurities which are not intentionally added to give photoconduction. The residual minority impurities directly control the lifetime of the photogenerated charge carriers. The signal amplitude is proportional to the lifetime [5]. High performance photoconductors require very low levels of residual impurities, often $10^4$ times lower than the "optically active" dopant. Ultrapurification followed by a "pure" doping process is used to grow single crystals of silicon and germanium for photoconductor applications [6].

The development of ultra-pure semiconductors has not only yielded a number of useful, high performance devices, but it also has led to many interesting questions regarding the limits of purification of materials and to the discovery of a large number of new impurity and defect complexes. These novel centers could not have been found and studied in less pure materials.

An especially appealing aspect of ultra-pure semiconductors is the absence of impurity interactions. The wave functions of bound excited states of shallow impurities which extend over thousands of unit cells do not overlap in such crystals. This results in very sharp states with long lifetimes. At this moment, the experimental results [7] still outpace even the most sophisticated calculations using advanced effective mass theory models [8].

EXPERIMENTAL METHODS

The low concentrations of shallow and deep levels in ultra-pure silicon and germanium require sensitive and, if possible, highly resolving measurement techniques. A number of these are described in detail by other authors' papers printed in these proceedings. Junction spectroscopies, electron paramagnetic resonance methods, and optical spectroscopies have been covered in review papers. We deem repetition of the explanation of these techniques unnecessary, despite the fact that all of them have been used for studies involving ultra-pure semiconductors. We will restrict ourselves to the description of methods which have not been discussed and which are uniquely suited for the study of ultra-pure materials.

A very important aspect of the identification of novel centers in pure semiconductors is the necessity of combining the results of several analytical techniques in an effort to determine the structure as well as the composition of these centers.

Photothermal Ionization Spectroscopy (PTIS)

PTIS has played the single most important role in the study of shallow levels in pure semiconductors. This well established technique was discovered [9] and later reviewed [10] by L.M. Lifshits and his collaborators at the Institute of Radioengineering in Moscow. The basic principle governing PTIS is illustrated in Fig. 1. As in the case of optical absorption spectroscopy, electrons (holes) are excited from the ground state of a donor (acceptor) to a bound excited state. Instead of observing the reduction of photon flux at photon energies corresponding precisely to such transitions, one measures the flow of free carriers produced by photoexcitation followed by phonon excitation from the bound excited state into the corresponding band. The basic difference between the two methods is schematically illustrated in Fig. 2. One very important condition for successful PTIS is the availability of low noise ohmic contacts at low temperatures. Ion implantation followed by proper annealing can produce excellent contacts for all silicon and germanium samples which exhibit one type of conduction throughout the whole volume. Difficulties arise when highly compensated samples containing n- and p-type regions are studied. Illuminations with DC-band edge light ($E_{\text{photon}} > E_{\text{gap}}$) can in some cases lead to acceptable photoconductivity measurements.
Fig. 1. PTIS involves two excitation steps.

Fig. 2. A. Standard absorption set up versus B. PTIS.

Fig. 3. Photo conductivity interferogram of a p-type Ge sample at T=6K.

The photon energy range of interest for shallow levels in silicon and germanium (5 to 200meV) lies in the far infrared (40 to 1600cm$^{-1}$) where interferometers perform better than grating spectrometers. Interferograms have to be Fourier transformed, a task which is becoming faster and cheaper with the ever increasing computing power of mini- and microcomputers. A typical 4096 point photoconductivity interferogram of a pure, p-type germanium sample (#611-5.1) containing mostly aluminum and the acceptor complex $A(D,C)$ [$D$ = deuterium, $C$ = carbon] is shown in Fig. 3. Fourier transforma-
tion yields a spectrum, the information containing part of which is reproduced in Fig. 4. The full width at half maximum (FWHM) of the C line of A(D,C) is 0.12 cm\(^{-1}\) or 15\(\mu\)eV. The instrumental resolution was estimated to be better by a factor of \(\sim 4\) based on the mirror travel of the interferometer and taking the effects of the source aperture (7mm) and focal length (20cm) into account [11]. The small splitting of the Al lines indicates that a residual stress, probably from the sample mounting, was present. This stress splits the ground state and lightly broadens the width of all the bound states. It is assumed that the residual stress is the resolution limiting factor. The lines of A(D,C) are not split, a noteworthy feature which we will discuss in the section on novel centers and the role of hydrogen. In order to obtain quantitative information on the total net acceptor concentration, a van der Pauw Hall effect measurement was performed which yielded \(N_A - N_D = 5.7 \times 10^{10}\) cm\(^{-3}\). We estimate the compensation \(k = N_D / N_A\) to be of the order of 0.1. Samples with \(N_A - N_D\) as low as \(10^9\) cm\(^{-3}\) and a sample volume < 0.1 cm\(^3\) have successfully been measured with signal to noise ratios (highest line to RMS noise) better than 100 at 1 sec integration time.

In an interesting recent application of PTIS to the search for fractional charge atoms, van de Steeg et al [12] have estimated that approximately \(10^7\) cm\(^{-3}\) group III element impurities with 2/3 or 1/3 charge could be detected if present in p-type germanium with \(N_A - N_D = 10^{11}\) cm\(^{-3}\), \(k = 0.5\), and 10 s integration time. For an experiment using a far infrared tunable laser source and band edge illumination they predict that \(< 10^5\) cm\(^{-3}\) fractional charge impurities (i.e., one fractional for every \(10^{19}\) atoms!) should be detectable.

![Fig. 4 Fourier transform spectrum of the interferogram in Fig. 3.](image-url)
Radioactive Tracer Techniques

The release of a large amount of energy in the decay of an atomic nucleus makes it possible to accurately measure and time individual decay events. It seems natural to use the highly developed semiconductor nuclear radiation detectors in the effort to determine the concentration and distribution of electrically neutral impurities with low solubility. Such experiments have been performed using radioactive carbon (\(^{14}\)C) which was incorporated during crystal growth in silicon [13] and germanium [14]. Tritium (\(^{3}\)H), the radioactive form of hydrogen, has been incorporated in ultra-pure germanium in order to determine the absolute concentration of hydrogen in these crystals and to study its diffusion behavior [15].

In standard autoradiography the nuclear radiation exposes x-ray film. Using this method, it has been shown that the segregation coefficient of carbon in germanium depends on the crystallographic orientation of the crystal growth plane [14]. Fig. 5 shows autoradiographs which display the variation in segregation coefficient. They also illustrate that hydrogen atmosphere grown crystals contain carbon clusters, revealed by dark spots of varying size. Nitrogen atmosphere grown crystals by comparison contain very few clusters. This phenomena is not understood at the present time. The experiment can detect carbon concentrations as low as \(10^{12}\) cm\(^{-3}\) using x-ray film and exposure times of the order of one month. Experiments in silicon also show the crystal orientation dependent segregation [13]. The advantage of autoradiography is the good sensitivity and spatial resolution which can reach a few \(\mu\)m.

If one can sacrifice the spatial resolution, the lower detection limit can be improved by many orders of magnitude. Sufficiently pure Ge or Si crystals containing radioactive tracer elements can be used to make large volume radiation detectors which are self counting. A decaying \(^{14}\)C nucleus emits an electron (beta-particle) with a characteristic probability versus energy distribution. The maximum energy for this decay is \(E_{\text{max}} = 156\) keV while the most probable energy is 25 keV. The range of electrons with such energies is less than 10 \(\mu\)m in germanium. A detector with dimensions of several centimeters approximates an "infinite" volume with negligible

![Autoradiograph of a \(^{14}\)C doped, nitrogen atmosphere grown Ge crystal slice ||(113). The arrows indicate the facets on the outer crystal surface. The darker areas adjacent to the facets show higher carbon content. A few carbon clusters are producing the dark spots.](image-url)
surface effects. Fig. 6 shows schematically an autodetection system which has been used to determine the total carbon concentration in ultra-pure germanium [14]. The guard ring was used to eliminate "dead" volume near the bare surface. By using the signals from the guard ring in coincidence with signals from the central volume it was possible to accurately limit the sensitive central area. A typical $^{14}$C beta spectrum is displayed in Fig. 7. The spectral shape follows precisely the theoretical curve predicted by Fermi [16]. This experiment not only gives the absolute carbon concentration in germanium ($\sim 10^{14}$ cm$^{-3}$), but it has also put an end to speculations that the $^{14}$C decay kinetics deviates from Fermi's prediction because of the existence of "preformed" helium nuclei in the $^{14}$C nucleus [17]. These speculations originated from the earlier experimental observation that the $\beta$-energy distribution deviated from Fermi's standard distribution. In view of the result displayed in Fig. 7, we assume that the earlier results were distorted and suffered from "thick" detector window effects.

![Internal $^{14}$C detection scheme](image)

Fig. 6. Internal $^{14}$C detection scheme

The lower detection limit for radiotracers is given by the radiation background. A special low level radiation facility was used for these experiments. A lower detection limit of $10^{8}$ carbon per cm$^3$ was estimated for the internal detection method. We feel that this internal detection technique could be used to answer many questions which depend on absolute concentrations of impurities and not only on electrically active fractions.

**NOVEL SHALLOW CENTERS: COMPOSITION AND STRUCTURE**

During the early phase of the development of ultra-pure germanium a number of shallow levels were discovered which were not due to simple elemental impurities [18,19]. The concentration of these new levels was so high after certain heating or cooling cycles involving moderate temperatures ($< 450^\circ$C) as to render the crystals useless. The new centers had to be understood in order to avoid their generation or to eliminate them completely. Variable temperature Hall effect together with isochronal and isothermal annealing, PTIS with and without uniaxial stress or a
magnetic field, impurity doping and isotopic substitution were used in combination to identify several of the new centers. Over the past ten years the family of these new centers has steadily grown and it seems that many more can be generated using the current knowledge on composition and structure of the novel centers. Table I summarizes the pertinent information. For further details the reader is referred to the original literature cited in the table. The centers listed in Table I have many of the following characteristics in common. These are:

- The centers consist of a substitutional impurity which binds an interstitial hydrogen or lithium ion.
- The centers are well described by the effective mass theory, i.e., the bound excited states are dominated by the semiconductor band structure and are as such identical to the excited states of elemental acceptors or donors respectively.
- The ground state of the novel centers consists in most cases of a manifold with stress insensitive components. This property stands in sharp contrast to the ground states of group III or group V impurities which all have stress sensitive ground states.
- In centers consisting of hydrogen, lithium and a IIIrd or lower column group impurity, the interstitial impurity appears to donate its electron thereby reducing the number of missing binding electrons by one (e.g. double acceptor +H+ single acceptor); somewhat naively expressed one can assign the proton the role of a very "heavy" hole.
- In centers consisting of hydrogen and a IVth or higher column group impurity, the hydrogen atom appears to stabilize a second 1s electron in its lowest orbit. This reduces the number of excess valence electrons by one (e.g. double donor +H+ single donor, neutral impurity +H+ single acceptor).
- Upon the substitution of hydrogen with deuterium, one observes an isotope shift in the ground state of some centers.

These unusual experimental observations have led to a host of questions. Probably the most important one is: what kind of impurity complex structure would lead to an electronic structure exhibiting the unusual features? In the limited space available it is not possible to bring together all the detailed arguments which have led to a simple but very powerful model. We will elucidate this model with the shallow acceptor A(H,Si). This impurity complex appears always and only in crystals containing silicon and hydrogen of the order of $10^{14}$ cm$^{-3}$ [7,18,19,20].

Isotope substitution (H$\rightarrow$D) leads to a small but easily measurable isotope shift of 21μeV. The application of stress along any orientation does not split the ground state though a large stress will split the bound excited states in the expected way. PTIS spectra recorded at a number of different temperatures show a second ground state component which can be thermally populated because it lies only 1.07 meV higher. The tunneling hydrogen model (Fig. 8) which has been proposed by Falicov [20,32] can be used to explain the special properties of the center. The model assumes that the interstitial hydrogen tunnels between four equivalent interstitial tetrahedral sites. The nuclear motion affects the electronic states of the bound hole (the Born-Oppenheimer approximation becomes invalid). The unperturbed hole ground state is of $\Gamma_8$ type due to the degeneracy of the valence band top. The product of the four old $\Gamma_8$ state and the four equivalent nuclear states leads to a sixteenfold ground state manifold with one $\Gamma_6$, one $\Gamma_7$, and three $\Gamma_8$ components. The tunneling of the hydrogen restores the full tetrahedral symmetry of the center, a necessary condition for any model which can explain the stress results. The former two states are Kramers (or spin) doublets which are insensitive to uniaxial stress. It is assumed that these are the two lowest lying ground state components (Fig. 9). The $\Gamma_8$ states have so far not been found. This is not too surprising because the probability for thermal population decreases exponentially with increasing energy level separation. If the separation becomes larger than -2.5 meV, the center
<table>
<thead>
<tr>
<th>Center</th>
<th>Other Symbols</th>
<th>Compos.</th>
<th>Method(s) of Generation/Annihilation</th>
<th>Ground State Energies (meV)***</th>
<th>Comments</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(H,Si)</td>
<td>A_{1,2}</td>
<td>H_{1,2}Si</td>
<td>Rapid quench from T≥400°C of H_{2}-atmosphere, silica-crucible-grown crystals; anneals at ~25°C to form D(O,H), Si-doped crystals do not show conversion to D(O,H)</td>
<td>( E_V + 10.59 )</td>
<td>split ground state, stress insensitive, isotope shift</td>
<td>([7,18, 20,29])</td>
</tr>
<tr>
<td>A(H,C)</td>
<td>A_{6,6'}</td>
<td>H_{1,2}C</td>
<td>Rapid quench from T≥500°C of H_{2}-atmosphere, graphite-crucible-grown crystals; anneals at ~200°C</td>
<td>( E_V + 10.30 )</td>
<td>split ground state, stress insensitive</td>
<td>([7,18, 20])</td>
</tr>
<tr>
<td>A(C,N) _ {\text{S}}</td>
<td>A_{3,5}</td>
<td>(C,N)_{1}</td>
<td>Present in N_{2}-atmosphere, graphite-crucible-grown crystals, diffusion from a KCN rich surface; anneals at ~400°C with a time constant of ~100hr</td>
<td>( E_V + 10.22 )</td>
<td>split ground state, stress insensitive</td>
<td>([7,21, 22])</td>
</tr>
<tr>
<td>A(C,N) _ {\text{I}}</td>
<td>A_{4}</td>
<td>(C,N)_{1}</td>
<td>As A(C,N)<em>{S}; A(C,N)</em>{S} and A(C,N)_{I} can be interconverted reversibly</td>
<td>( E_V + 10.77 )</td>
<td>normal ground state</td>
<td>([7,21, 22])</td>
</tr>
<tr>
<td>A(Be,H)</td>
<td>--</td>
<td>Be_{3},H_{1}</td>
<td>Present in Be-doped, H_{2}-atmosphere-grown crystals; anneals at T≥550°C</td>
<td>( E_V + 10.29 )</td>
<td>split ground state, stress insensitive</td>
<td>([23])</td>
</tr>
<tr>
<td>A(Zn,H)</td>
<td>--</td>
<td>Zn_{5},H_{1}</td>
<td>Present in Zn-doped, H_{2}-atmosphere-grown crystals; anneals at T≥650°C</td>
<td>( E_V + 12.53 )</td>
<td>stress insensitive, a shallower component hasn't been found</td>
<td>([23])</td>
</tr>
<tr>
<td>A(Cu,H_{2})</td>
<td>--</td>
<td>Cu_{5},2H_{1}</td>
<td>Copper diffusion in H_{2}-atmosphere-grown crystals</td>
<td>( E_V + 16.41 )</td>
<td>several sets of broad lines</td>
<td>([24, 25])</td>
</tr>
<tr>
<td>A(Cu,D,H)</td>
<td>--</td>
<td>Cu_{5},H_{1},D_{1}</td>
<td>Copper diffusion in H_{2}-D_{2}-atmosphere-grown crystals</td>
<td>( E_V + 18.10 )</td>
<td>stress insensitive, one set of sharp lines</td>
<td>([26])</td>
</tr>
<tr>
<td>Symbol</td>
<td>Chemical Formula</td>
<td>Description</td>
<td>Energy (meV)</td>
<td>Notes</td>
<td></td>
<td></td>
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<td>--------</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>A(Cu,D₂)</td>
<td>Cu₅,2D₁</td>
<td>Copper diffusion in D₂-atmosphere-grown crystals</td>
<td>Eᵥ + 18.20</td>
<td>stress insensitive, one set of sharp lines [26]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A(Cu,L₁₂)</td>
<td>Cu₅,2L₁</td>
<td>Copper and lithium diffusion</td>
<td>Eᵥ + 25.30</td>
<td>one set of lines each, assignment may be reversed [25]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A(Cu,L₁,H)</td>
<td>Cu₅,L₁,H₁</td>
<td>Copper and lithium diffusion in H₂-atmosphere-grown crystals</td>
<td>Eᵥ + 20.41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A₇</td>
<td>unknown</td>
<td>Observed in very few &quot;as-grown&quot; crystals; no obvious impurity correlation</td>
<td>Eᵥ + 11.01</td>
<td>[7]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A(V₂,H)</td>
<td>V₂,H₁ or VO,H₁</td>
<td>Divacancy-hydrogen center found always and only in dislocation-free, H₂-atmosphere, silica-grown crystals; equilibrium concentration can be reversibly changed up to 450°C</td>
<td>Eᵥ + 80</td>
<td>Hall effect, DLTS [7,27]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D(O,H)</td>
<td>D,C O₅,H₁</td>
<td>Rapid quench from 400°C followed by annealing at ~90°C of H₂-atmosphere, silica-crucible-grown crystals; anneals at ~120°C</td>
<td>Eᵥ - 12.50</td>
<td>spectrum is stress insensitive up to ~2x10⁸ dyne cm⁻² above which a new, shallower spectrum appears; isotope shift upon substitution of H with D [7,18, 28,29]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D(O,L₁)</td>
<td>S,A O₅,L₁</td>
<td>Lithium diffusion in H₂-atmosphere, silica-crucible-grown crystals</td>
<td>Eᵥ - 9.46</td>
<td>broad Eᵥ - 10.03</td>
<td>broad Eᵥ - 10.50</td>
<td>sharp EPR + PTIS studies [30,31]</td>
</tr>
</tbody>
</table>

* A = acceptor; D = donor
** S = substitutional; I = interstitial
*** The ground state energy of the acceptors has been determined by adding the theoretical value [8] of the D-line excited state (= 2.88 meV) to the energy of the D transition. The ground state energy of the donors was obtained by adding 1.76 meV [36] to the 1s-2p transition energy.
will thermally ionize before an appreciable fraction of the upper ground state component is occupied. Optical pumping with a tunable far infrared laser may lead to the discovery of the three $I_g$ states.

![Diagram](image)

**Fig. 8.**

There exists no direct proof that the tunneling model is correct. It is, however, the simplest model which can explain the experimental features of this new center and all the other centers which show a stress insensitive ground state.

**DISCUSSION AND CONCLUSIONS**

The study of ultra-pure semiconductors, mostly germanium, has led to the discovery that electrically neutral impurities such as silicon, oxygen, hydrogen, etc. can combine to form electrically active centers. Electrically active impurities also bind hydrogen or lithium forming an impurity complex which is shallower than the isolated impurity. A model based on tunneling hydrogen or lithium can explain the structure and many of the unusual electronic properties of most of the hydrogen or lithium related complexes. Though there exists no direct proof for the correctness of this model, its simplicity and predictive power are very appealing.

There still exists a host of unanswered questions which are of general interest:
- What is the nature of the binding forces which retain hydrogen in the vicinity of isovalent impurities silicon and carbon or of any other kind of impurity?
- Hydrogen seems to contribute a binding electron to substitutional impurities of the IIIrd and lower groups of the periodic table but it binds a second electron in complexes involving group IV or high group impurities. What is the cause for this systematic behavior which suggests an energy minimization principle?
- What kind of a physical model can explain quantitatively the observed isotope shifts?
• Why should the \( \Gamma_6 \) and \( \Gamma_7 \) states be the lowest components in the ground state manifold? It is important to recognize that in a case where one of the \( \Gamma_8 \) states would be the lowest component, we could not recognize any unusual stress behavior!

• Can the findings for germanium be generalized? Do such complexes exist in silicon or III-V compound semiconductors and if so, at what concentrations? The neutralization of boron in silicon [33] by hydrogen follows the same pattern. Furthermore, the neutralization of several deep level species [34,35] by hydrogen seems to fit the pattern observed in germanium if one allows an appropriate number of hydrogen atoms to bind to a deep level impurity.

In conclusion, we can state that the study of ultra-pure semiconductors has yielded the most accurate data on the electronic state spectra of elemental and complex shallow acceptors and donors. A large number of centers with unusual structures and electronic properties has been found. Hydrogen and to a lesser degree lithium play dominant roles in these novel centers. Some general trends begin to emerge regarding the exchange of electrons between hydrogen and the particular impurity to which hydrogen is bound.

The extreme purity of the crystals has simplified many experiments, has permitted the observation of very highly excited acceptor and donor states, and has led to the discovery of interesting novel centers.

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