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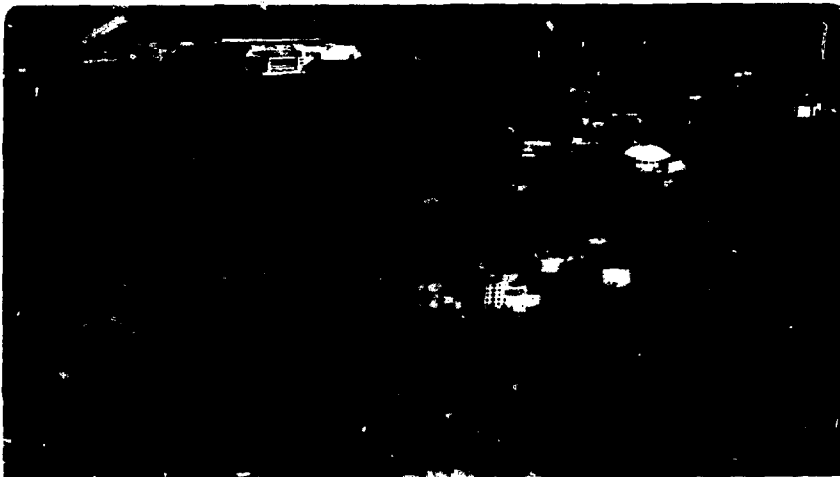
**HYDROGEN CONCENTRATION AND DISTRIBUTION IN HIGH-
PURITY GERMANIUM CRYSTALS**

W.L. Hansen, E.E. Haller, and P.N. Luke

October 1981

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Abstract

High-purity germanium crystals used for making nuclear radiation detectors are usually grown in a hydrogen ambient from a melt contained in a high-purity silica crucible. The benefits and problems encountered in using a hydrogen ambient are reviewed. A hydrogen concentration of about $2 \times 10^{15} \text{cm}^{-3}$ has been determined by growing crystals in hydrogen spiked with tritium and counting the tritium β -decays in detectors made from these crystals. Annealing studies show that the hydrogen is strongly bound, either to defects or as H_2 with a dissociation energy $> 3 \text{eV}$. This is lowered to 1.8eV when copper is present. Etching defects in dislocation-free crystals grown in hydrogen have been found by etch stripping to have a density of about $1 \times 10^7 \text{cm}^{-3}$ and are estimated to contain 10^4H atoms each.

Introduction

The ambient selected for growing high-purity germanium crystals must satisfy a variety of conditions: 1) it must be of high purity so that it does not contribute electrically-active centers to the crystal, 2) it must not interact with the crystal growth materials to liberate impurities, 3) it must provide some mechanism for suppression of impurities contributed by crystal grower parts, 4) it should not combine with vacancies, interstitials or dislocations to give electrically-active centers, 5) it should allow the establishment of the proper thermal environment for growing crystals of high structural perfection and 6) it should be compatible with heating by radio frequency induction. The ambients which have been considered are vacuum, inert gases, nitrogen and hydrogen.

Vacuum

A vacuum environment seems to meet all the criteria listed above. In our diffusion-pumped vacuum system, the residual "impurity" concentration is much higher than in inert gases and hydrogen. The impurities consist almost entirely of H_2O , CO , H_2 and C_2H_4 . The H_2 and C_2H_4 should not affect purity and the H_2O and CO can only form GeO . GeO has a very high vapor pressure at the melting point of germanium and so will deposit on the cooler parts of the crystal grower in vacuum, thus being removed from the system. The reaction of oxygen with the quartz may lead to SiO_x precipitates.

Vacuum-grown crystals have generally exhibited low purity and trapping occurs in detectors made from such crystals. These impurities are most likely the result of bombardment of the cooler parts of the crystal grower (seed rod, seals, crucible support, vacuum plumbing) by residual hot gas atoms.

Inert Gases and Nitrogen

Ambients with flowing gas at NTP have an advantage over vacuum because of simplicity in maintaining a high-purity environment. Cooler parts of the crystal grower may out-gas. But the flowing gas carries

away the products. Inert gases can be purified to a very high degree using reactive getters. Boil-off helium can be used as well. Nitrogen can only be purified with great difficulty because it reacts with strong getters such as titanium, barium, etc.

Germanium crystals grown from silica crucibles in inert gases or nitrogen at NTP always contain high concentrations of oxygen ($> 10^{14} \text{cm}^{-3}$) because GeO evaporation is effectively prevented by the gas. This residual oxygen is always accompanied by charge trapping in detectors¹ and gives "smooth pits"² when crystals are etched with preferential chemical etchants. The charge trapping has been attributed to SiO_2 precipitates.² No discrete energy levels in the bandgap have been found which can be associated with smooth pits.

A further disadvantage of inert gases is that radio frequency induction heating cannot be used with high-purity inert gases because of their low breakdown voltage. Nitrogen and hydrogen, on the other hand have sufficiently high breakdown voltages to allow RF heating.

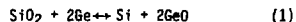
Hydrogen

Hydrogen is the only gas which has been successfully used for high-purity Ge crystal growth. Its behavior as an ambient for crystal growing is complicated. In spite of the complications, the advantages are such that all commercial detector grade germanium is grown exclusively in hydrogen.

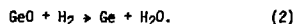
Hydrogen as a Growth Ambient

Hydrogen gas has a very high thermal conductivity and low viscosity so that thermal convection greatly disturbs the one-dimensional thermal gradient desired for growing highly perfect crystals. One way to lower convective effects is to lower the thermal gradients. This means that large diameter crystals ($> 4 \text{cm}$ dia.) must be grown at very low rates ($1-3 \text{cm/hr}^{-1}$) to prevent twinning, mosaic and dendritic growth. Small thermal gradients lead to the development of surface facets which cause crystal growth to be very unstable.

The concentration of oxygen in crystals grown in hydrogen from silica crucibles is low ($\approx 5 \times 10^{13} \text{cm}^{-3}$) because the reaction:



is forced strongly to the left by the competing reaction:



When germanium is in equilibrium with its melt in hydrogen, the solubility of hydrogen is much higher in the melt than in the solid. This is shown by the observation that when a partially frozen mass of germanium is rapidly cooled, the newly frozen parts are filled with bubbles. These observations together with the known low solubility of hydrogen in

germanium means that Henry's law¹⁵ is obeyed so that the segregation coefficient, C_2/C_1 , is less than one. A segregation coefficient much different from one means that the impurity concentration in the crystal will be sensitive to the pull rate.

The solubility of hydrogen in germanium at its melting point extrapolated from permeation measurements at lower temperatures is $4 \times 10^{14} \text{ cm}^{-3}$ and the heat of solution is 53 kcal/g. atom (2.30 eV). Thermodynamic analyses^{4,5,6} indicate that systems with such low solubilities or high heats of solution have a solubility which is strongly retrograde near the melting point. However, the data of Frank and Thomas³ only 20°C below the melting point show no retrograde effect. There is thus the conflict that a system which would be expected to be retrograde does not behave in this manner. All other elements that are weakly soluble in germanium are retrograde, including Li which is an interstitial impurity like hydrogen.

Because of this conflict, no reasonable estimate can be made for the expected hydrogen concentration in crystals grown at normal rates. The small segregation coefficient and the data of Frank and Thomas suggest that the hydrogen concentration should be greater than $4 \times 10^{14} \text{ cm}^{-3}$ while the thermodynamic data predicts retrograde solubility and a concentration less than $4 \times 10^{14} \text{ cm}^{-3}$.

As the crystal grows, the newly grown material progressively cools as it moves further away from the melt/solid interface. Since the hydrogen solubility is lower at lower temperatures, the growing crystal becomes progressively more supersaturated with hydrogen. The excess hydrogen in the bulk probably precipitates on defects while, at the same time, hydrogen diffuses out from the surface to maintain the solubility limit at the given temperature, e.g., about $3 \times 10^{13} \text{ cm}^{-3}$ at 800°C. In this dynamic process, the degree of hydrogen supersaturation increases with time and the diffusion constant decreases. The seed end of the crystal is subject to significant hydrogen diffusion for much longer times than the tail end. For our typical growing conditions (12 cm/hr), a crude estimate of the hydrogen depletion at the surface gives an integral diffusion length of about 2 mm at the head and about 1/2 mm at the tail.

Electrical Effects of Hydrogen

Electrical activity related to hydrogen in semi-conductors was first discovered in high-purity germanium.⁷ When dislocation-free germanium crystals are grown in hydrogen, an acceptor with an activation energy $E_v + 0.08 \text{ eV}$ ⁹ appears at a concentration of 1 to $5 \times 10^{11} \text{ cm}^{-3}$. This center is believed to be the divacancy hydrogen complex V_2H . It usually dominates the electrical activity in ultra-pure dislocation-free crystals.⁸

Other hydrogen-related centers which have been found are: $A(H, Si)$ at $E_v + 0.1 \text{ eV}$; $A(H, C)$ at $E_v + 0.1 \text{ eV}$; $A(H, Cu)$ at $E_v + 0.17 \text{ eV}$ and $D(H, O)$ at $E_c - 0.1 \text{ eV}$.⁹

All of the hydrogen-related centers found to date are weakly bound complexes whose concentration can be greatly modified by heating or quenching in the temperature range 0-400°C. As a consequence, detector fabrication processes (lithium diffusion, implantation annealing) can modify the concentration of electrically active centers.

The phenomenon of "coring"¹⁰ is another important problem which may be related to hydrogen. Germanium

crystals grown in hydrogen out of silica tend to be p type at the head and n type at the tail (never the reverse) due to non-segregating aluminum acceptors and segregating phosphorus donors. Hall effect measurements on slices from such crystals often show a p-type outer region and an n-type inner region (coring). In extreme cases, the crystal is in effect covered with a thin p-type skin. The phenomenon of coring is often found in crystals grown in hydrogen out of silica and can be removed by annealing for times and temperatures which do not remove all the hydrogen.¹¹ Coring could be explained if the crystal contains hydrogen in two forms—one form which is weakly bound, diffuses at the rate of atomic hydrogen³ and is responsible for the acceptor compensation and another form which is molecular¹³ or strongly bound to defects. The hydrogen which is probably bound to shallow acceptors (acceptor compensation) would dissociate before the hydrogen which is more strongly bound in the centers (H, Si) , (H, C) , (H, O) and (V_2H) or other even more strongly binding centers. The presence of hydrogen with different activation energies of diffusion can be tested by isochronal annealing.

Hydrogen Concentration—Experimental

The total hydrogen concentration has been determined using the self-counting detector technique¹⁶ and the radioactive hydrogen isotope tritium. Germanium crystals have been grown in a hydrogen ambient containing a known fraction of T_2 and the total concentration of hydrogen is found from the counting rate of tritium decays in detectors made from these crystals. Tritium decays according to the following reaction:

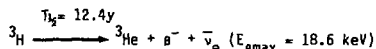


Figure 1 is a schematic of the apparatus used in growing ${}^3\text{H}$ -doped crystals. A Czochralski crystal puller was assembled with a recirculating hydrogen purifier and a generation and recovery system for the ${}^3\text{H}$. In order to minimize the total ${}^3\text{H}$ inventory, the interior volume was made to be less than one liter. The ${}^3\text{H}$, ${}^3\text{H}$ generation-recovery was achieved by absorbing the gas mixture on a uranium pellet contained in a welded stainless steel thimble. The gas was recirculated and purified during growth using a stainless steel bellows pump and liquid nitrogen cooled trap packed with stainless steel wool. The total gas content absorbed on the uranium pellet was $2000 \text{ cm}^3 \text{ H}_2 + 3.85 \text{ cm}^3 \text{ T}_2$ (10 Curies) at NTP. In order to minimize contamination of the Ge melt by silicon and oxygen, the silica crucible was coated with Si_3N_4 deposited from a chemical vapor (from NH_3 and SiH_4).

The crystal growing process involves the following steps: 1) add the high-purity germanium charge to the crucible (usually 800 g to 1 kg), 2) evacuate the entire apparatus including the loaded uranium cell to 10^{-7} torr, 3) heat the germanium under vacuum to 800°C to remove GeO and H_2O , 4) close off the vacuum and heat the thimble until the internal H_2 pressure is 8 psi—about 450°C, 5) cool the trap with LN_2 , start the pump and melt the charge, 6) lower the furnace to the growth position—the pressure is now 1 atm—grow the crystal, 7) immediately after the melt is depleted from crystal growth, shut off heater. The crystal cools to 300°C in about 15 min, 8) at 300°C, open the valve to the uranium thimble to recover the gas mixture. The pressure will return only to about 10^{-5} torr due to ${}^3\text{H}$ decay, plus outgassing of the system during growth. The uranium pellet source can be used almost indefinitely (12.4 y half-life). Close to 100%

gas transfer efficiency can be achieved since with each use, the ^3H decay product ^3He is pumped off.

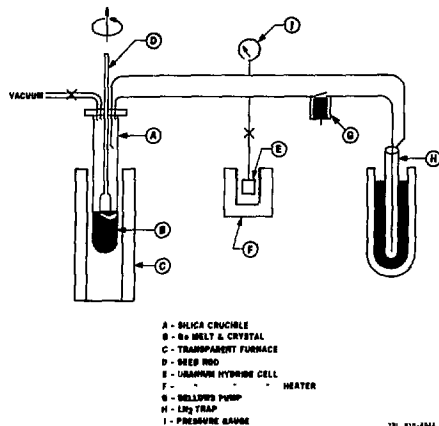


Fig. 1. Apparatus used to grow tritium-doped crystals. The silica crucible is coated with CVD Si_3N_4 and the total internal volume of the system is less than one liter.

Detectors are made from the ^3H -doped crystals using lithium diffused n^+ and boron implanted p^+ contacts.¹⁷ The free surfaces are passivated with amorphous Ge:H to suppress surface channels.¹² There is an uncertainty in the event rate near zero energy due to system noise in the continuum spectrum of ^3H .¹⁸ This uncertainty is removed by fitting the obtained spectrum to the Fermi distribution for beta decay. Integration over the fitted Fermi distribution from zero to 18.6KeV leads to the ^3H concentration. The total hydrogen concentration is obtained from the tritium concentration by multiplying by the growth ambient dilution factor (2000 ± 3.85)/3.85. The dominant errors in this analysis method are the original volume of tritium used ($3.85 \pm 0.1\text{cm}^3$) and the measurement of the detector active volume ($\pm 5\%$).

Hydrogen Concentration—Results

As described earlier, the hydrogen concentration is expected to be a function of the location in the crystal since out-diffusion begins immediately on crystallization. Figure 2 shows the hydrogen concentration measured by the self-counting detector technique for various locations in a crystal grown at about 3cm hr^{-1} . Using the concentration in the sample from the center of the tail end of the crystal as representative of the concentration immediately after growth, this value ($1.9 \times 10^{15}\text{cm}^{-3}$) is to be compared with the extrapolated value of Frank and Thomas³ of $4 \times 10^{14}\text{cm}^{-3}$. Our result could be compatible with Frank and Thomas assuming supersaturation and by choosing quite reasonable parameters for our growing condition, i.e. $C_1 = 10^{16}\text{cm}^{-3}$, C_5/C_1 (static) = 0.04 and C_5/C_1 (effective) = 0.2, where C_1 is the hydrogen concentration in the melt and C_5 the concentration in the solid in equilibrium with the melt.

The outdiffusion length is quite insensitive to the temperature history of the grown crystal still in contact

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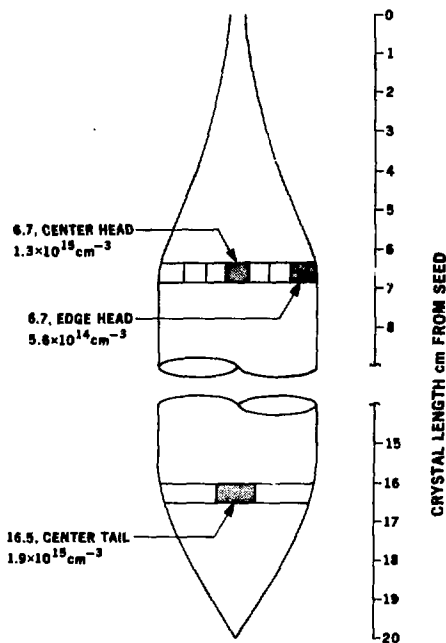
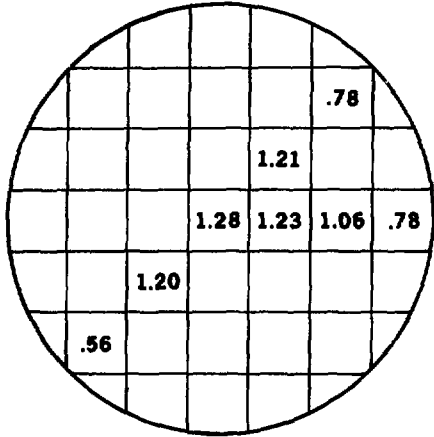


Fig. 2. Location of samples taken from tritium-grown crystal.

with the melt because of the low activation energy for diffusion of $8.7\text{kcal/g.atom.} (.38\text{eV})^2$ and changes only from 4.6×10^{-5} to $6.5 \times 10^{-5}\text{cm}^2\text{s}^{-1}$ between 800 and 900°C. The time that a certain crystal section remains hot after growth, then, gives a good estimate of the out diffusion. The sample from the center of the head was exposed to the crystal grower temperature for about 6 hrs. (3cm/hr^{-1} growth rate) which gives a diffusion length for hydrogen of about 1cm if the average temperature was about 800°C. The crystal is 37mm dia. at the location where the center head sample was taken and the hydrogen loss compared to the tail sample is 30%—a result consistent with the 1cm diffusion length.

The hydrogen concentration at the crystal surface is directly determined by the crystal temperature after growth because it is nearly in equilibrium with the hydrogen ambient. A reasonable estimate for the temperature of the crystal during growth would be about 800°C, for which condition the equilibrium surface concentration is $4 \times 10^{13}\text{cm}^{-3}$. This estimate is to be compared with the hydrogen concentration found in a near-surface sample (5mm wide) of $5.6 \times 10^{14}\text{cm}^{-3}$. Although the temperature history of the growing crystal is not known, the hydrogen concentrations obtained are consistent with reasonable estimates of this temperature. The radial distribution of hydrogen at the head end is shown in more detail in Fig. 3.

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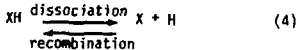
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Fig. 3. Radial distribution of hydrogen as measured with detectors made on a slice near the head end of a tritium-grown crystal. The numbers are hydrogen concentration $\times 10^{15} \text{cm}^{-3}$.

Hydrogen Binding and Out-Diffusion

Frank and Thomas³ showed that above 800°C hydrogen diffuses in germanium as an atom. From a study of the annealing behavior of the quench-induced donor $D(\text{H}_2\text{O})$, Hall¹³ suggested that at temperatures near 400°C hydrogen is either bound to a defect or diffuses as a molecule. Instead of relying on a secondary reaction [$D(\text{H}_2\text{O})$ annealing], we have been able to measure the hydrogen directly after heating tritium-spiked crystal samples to various temperatures and then make detectors from the samples.

The dissociation of a hydrogen complex can be analyzed by first considering the equilibrium:



where X is any defect or even hydrogen. If the atomic hydrogen has a high diffusion coefficient at a temperature where significant dissociation begins then the process becomes irreversible because of hydrogen out-diffusion. That this is the case for the present experiment can be shown by examining the equation for the diffusion from a slab¹⁴:

$$\frac{N}{N_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp(-[2n+1]^2 y) \quad (5)$$

where $y = \frac{t D_0}{(2w)^2}$

N_0 is the initial concentration, N the final concentration, D is the diffusion coefficient, $2w$ is the slab thickness and t is time. Using $D=5.8 \times 10^{-6} \text{cm}^2/\text{s}$ at 440°C extrapolated from the data of Frank and Thomas, it is found that only about 10^{-8} atom fraction of hydrogen remains in a slab of 1.5mm after two hours as a result of atomic hydrogen diffusion.

Therefore reaction 4 is essentially irreversible at the dissociation temperatures and we can express the change in hydrogen content N with time as:

$$\frac{dN}{dt} = -kN \quad (6)$$

where $k = \nu \exp(-E_D/kT)$, with E_D the activation energy of dissociation and ν the attempt frequency so that:

$$\frac{dN}{N} = -\nu \exp(-E_D/kT) dt. \quad (7)$$

Integration leads to:

$$\ln N = -\nu t \exp(-E_D/kT). \quad (8)$$

Expressing the hydrogen concentration in terms of the ratio of the initial, N_0 , and final, N , concentration:

$$\frac{N}{N_0} = \exp[-\nu t \exp(-E_D/kT)] \quad (9)$$

solving for E_D ,

$$E_D = kT \ln \left[\frac{1}{\nu t} \ln \left(\frac{N_0}{N} \right) \right] \quad (10)$$

In order to test for the presence of bound hydrogen, several samples of dimensions $1.5 \times 10 \times 10 \text{mm}$ were cut from the center of a tritium-grown crystal. All of the samples had a net shallow acceptor concentration ($N_A - N_D$) of $1.1 \times 10^{11} \text{cm}^{-3}$ and a total hydrogen concentration of $1.3 \times 10^{15} \text{cm}^{-3}$. Each piece was etched and cleaned in acidic peroxide (6:1:1; $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{HCl}$) and heated for two hours in a silica furnace tube in nitrogen at different temperatures. After the heat treatment, each piece was fabricated into a radiation detector by diffusing lithium into one side (at temperatures well below the annealing temperature) and implanting boron (10^{14}cm^{-2} at 25keV) on the opposite side.

Capacity-voltage measurements were taken on each device in order to measure the net acceptor concentration and detector depleted volume; the hydrogen concentration was found from the tritium decay rate. The result of such a set of measurements is shown in Fig. 4.

The hydrogen concentration data points of Fig. 4 are fit to the theoretical expression for simple dissociation (Eq. 9) by using the dissociation energy, $E_D=1.8\text{eV}$ and the attempt frequency, $\nu=10^{12}\text{s}^{-1}$. This result is to be compared to that from quench induced donor $D(\text{H}_2\text{O})$ decay of $E_D=1.4\text{eV}$ at $\nu=10^{15}\text{s}^{-1}$.¹³ It is clear from the higher dissociation temperatures of Fig. 6 that the dissociation energy is higher than the 1.4eV of Ref. 13 but the attempt frequency of $\nu=10^{12}\text{s}^{-1}$ needed to fit the data is unreasonably low for a simple center at such a high temperature. This suggests that the disappearance of hydrogen involves a more complicated process than simple dissociation.

The apparent coupling of the decrease of the hydrogen concentration to the increase in net acceptor concentration suggests a more complex process. Deep-level transient spectroscopy (DLTS) shows that essentially all the acceptor increase is due to copper

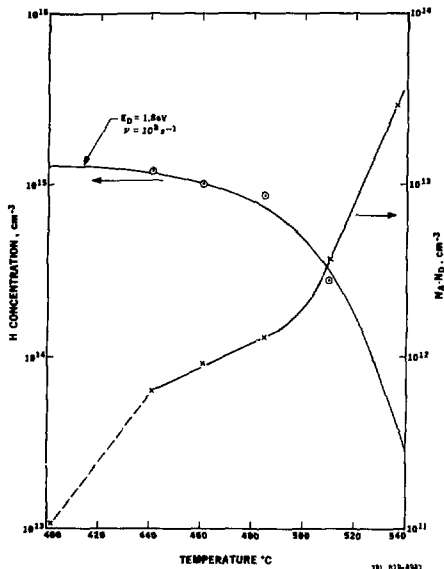
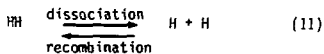
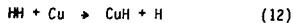


Fig. 4. Hydrogen and net acceptor concentration after heating tritium-doped samples. The dotted segment indicates the unheated N_A-N_p . The theoretical curve is fitted using $N_D=1.3 \times 10^{15} \text{ cm}^{-3}$ (from unheated crystal), $t=2 \text{ hrs.}$, $\nu=10^8 \text{ s}^{-1}$ and $E_D=1.82 \text{ eV}$. The rise in N_A-N_p with heating is due to Cu contamination.

contamination. From these observations it is concluded that the dissociation energy of the simple hydrogen complex is even higher than 1.8eV and has been lowered through some process mediated by copper. The process of Eq. 4 could be re-written as:



and with copper changed to a two-step process:



so that a single high energy process (11) is changed into two lower energy processes with the measured $E_D=1.8 \text{ eV}$ being characteristic of either (12) or (13). The fact that the CuH complex¹⁹ is still seen with DLTS in our samples at temperatures above 500°C suggests that reaction (13) may be dominating under our conditions. An explanation for the low value of $E_D=1.4 \text{ eV}$ found by Hall¹³ could be due to different experimental conditions—Hall used lower temperatures and longer times—so that reaction (12) became controlling.

These ideas were tested using experimental conditions which exclude copper. The measurements on samples like those of Fig. 6 were repeated using active

copper gettering. This was accomplished by sputtering on both sides of the samples 400Å Pd followed by 2µm Au before they were placed in the annealing furnace. The Pd served as a wetting agent; both the Pd and Au were of commercial purity (99.99%). After annealing, the Au-Ge eutectic was lapped off and the samples were made into radiation detectors. During annealing the Au-Ge eutectic "beads up" due to its high surface tension and does not cover the samples uniformly so that the sample is not encapsulated but is simply in contact in many spots with a liquid phase.

Figure 5 shows the result of the active getter annealing. The experimental points are best fit by $E_D=3.0 \text{ eV}$ and $\nu=10^{14} \text{ s}^{-1}$. Again it is seen that the disappearance of hydrogen is coupled to the rise in acceptor concentration but in this case DLTS shows that it is not due to copper. The rise in acceptor concentration is due to another deep impurity which has not as yet been identified. The hydrogen concentration as a function of annealing temperature for both the gettered and ungettered samples are plotted together on the same temperature scale in Fig. 6.

Preliminary analyses of the gold-gettered samples using C-T, DLTS^{4, 21} and PTIS²⁰ show two new levels—one at $E_D=0.017 \text{ eV}$ and the other at $E_D=0.032 \text{ eV}$. The sample heated to 540°C has a concentration of the 32meV level of $2.9 \times 10^{10} \text{ cm}^{-3}$ while the concentration of the 17meV level cannot be resolved from the shallower acceptor concentration of $1.6 \times 10^{11} \text{ cm}^{-3}$. However, the 17meV center is seen clearly with PTIS and is a complex, non-hydrogenic acceptor. It does not correspond to the two known Cu-H levels.³ For the sample heated to 575°C, the 17meV concentration is $5.0 \times 10^{11} \text{ cm}^{-3}$ (calculated by difference assuming the shallower concentration has not changed) and 32meV is $2.7 \times 10^{11} \text{ cm}^{-3}$.

Thus, when the copper is removed, the hydrogen binding center still does not dissociate directly but is mediated by another fast diffusing impurity which comes in at a higher temperature. The dissociation energy of the hydrogen binding center is therefore probably greater than 3.0eV. Of the known hydrogen complexes— CuH , V_2H , SiH , OH —all have much lower dissociation energies. A possible candidate to be considered is H_2 . Free H_2 has a dissociation energy of 4.5eV.

Hydrogen Precipitation

Crystals grown in hydrogen are highly supersaturated at ambient temperatures and it is to be expected that precipitation will occur in a manner analogous to the well-known lithium and copper precipitation. It has been observed that dislocation etching gives larger pits under equal conditions for hydrogen-grown crystals than for nitrogen, as though an additional strain is associated with hydrogen precipitational dislocations. Dislocation-free crystals grown in hydrogen have a homogeneous distribution preferentially of etchable defects which are not observed for hydrogen-grown dislocated crystals. These defects always have associated with them the presence of the V_2H center ($E_D=0.08 \text{ eV}$), are fewer and larger at the head end of a crystal and are more numerous and smaller at the tail. Chemical stripping and counting from a slice from the center of such a crystal shows that the density of the precipitates is about $1 \times 10^{10} \text{ cm}^{-3}$. Together with the now known hydrogen concentration, this density means that each precipitate contains on the average 10^8 hydrogen atoms if precipitation is nearly complete.

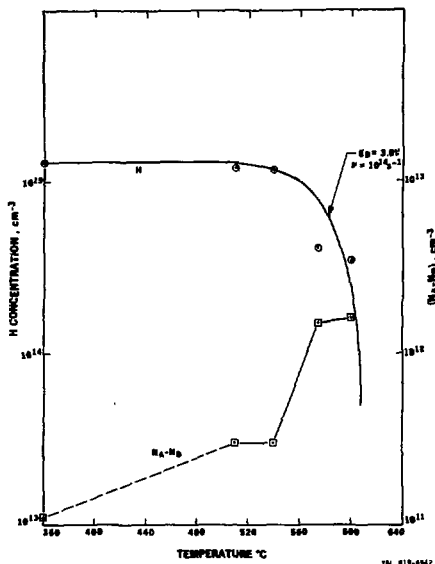


Fig. 5. Hydrogen and net acceptor concentration after heating gold-gettered samples. The theoretical curve is fitted using $N_D = 1.3 \times 10^{15}$, $t = 2$ hrs., $\nu = 10^{14} \text{ s}^{-1}$ and $E_D = 3.0 \text{ eV}$. The dotted segment indicates the unheated $N_A - N_D$. The rise in $N_A - N_D$ at high temperatures is not due to Cu.

To test whether the hydrogen incorporation kinetics are different in dislocated and dislocation-free crystals, a crystal was grown in tritium-spiked hydrogen from which a slice was obtained which was half dislocated and half dislocation free. The dislocated half had a hydrogen concentration of $1.4 \times 10^{15} \text{ cm}^{-3}$ and the dislocation-free half $1.5 \times 10^{15} \text{ cm}^{-3}$. Therefore dislocations do not modify the hydrogen incorporation kinetics.

Hydrogen Concentration in Precipitates

The defects which give rise to etch pits in dislocation-free hydrogen-grown germanium crystals are expected to result from hydrogen precipitation. However, it is not known whether these defects actually contain hydrogen or not. If they do contain hydrogen, the hydrogen can form an interstitial precipitate or can be trapped in a void or a bubble.

Evidence to resolve the structure of the pits can be obtained from the high temperature stability of the defects. If dislocation-free hydrogen-grown crystals are heated to a temperature and for a time sufficient to out-diffuse all the hydrogen, the local strain field should collapse for the case of an interstitial precipitate and the etch pits should disappear. If the local strain which is decorated by the chemical etchant is due to an internal surface, the etch defect may not be annealed out even at high temperatures.

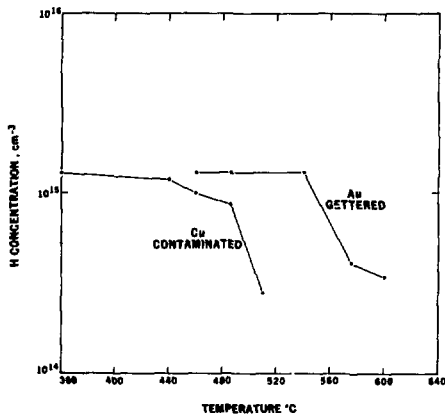


Fig. 6. Hydrogen concentration in heated samples showing effect of Au gettering on Cu contamination and dissociation temperatures of hydrogen binding centers.

Several 1mm and 1cm thick hydrogen-grown dislocation-free slices were heated to increasingly higher temperatures and then re-etched. No significant changes were observed until the samples were heated to over 900°C . Above 900°C the etch pits were different from slice to slice. In some, all the pits disappeared after 30 min., in others the pits became much smaller and needed prolonged heating (six hours) before the pits disappeared. Most commonly, the pits became smaller but disappeared in map-like areas before finally leaving after prolonged heating. Heated thick slices were sectioned and showed no apparent gradient from the interior to the surface except for the part of the sample which was the crystal surface during growth. The surface was depleted of pits to a depth of 3 to 4mm after 30min. at 900°C .

The foregoing suggests that the etch defects are due to bubbles filled with hydrogen and that the internal surface left after hydrogen out-diffusion contains most of the lattice strain. It is, of course, highly probable these results are strongly influenced or even dominated by copper contamination. It would be very difficult to exclude copper at such high temperatures.

Experiments are in progress to measure the hydrogen content of the precipitates using autoradiography with nuclear emulsions on tritium-grown crystals and using the $d(^3\text{He}, p)^4\text{He}$ reaction on deuterium-grown crystals.

Discussion

The accuracy of the measurement of the total hydrogen concentration in germanium crystals by the self-counting detector technique using the β -decay of tritium is limited almost entirely by simple measurements (such as the detector volume and tritium dilution ratio) and thus is not open to gross systematic or interpretive errors. The close agreement between the present results and the predictions of Frank and Thomas³ from hydrogen permeation studies suggests that

hydrogen probably does not exhibit retrograde solubility near the melting point. This last observation, if true, indicates a unique property of hydrogen in that all the other impurities in germanium which are weakly soluble or have high heats of solution show strongly retrograde solubility near the melting point. By analogy, hydrogen permeation measurements in silicon²² suggest that the hydrogen solubility also is not retrograde in silicon.

The surprising effect of Cu in lowering the dissociation energy of bound hydrogen suggests comparisons with some types of catalysis as seen in liquid and gas phase chemical reactions. An obvious close analog is the hydrogenation of low melting fats to produce room temperature solids which is done on a very large scale. In this reaction, an unsaturated fat or oil is heated with hydrogen under pressure but the hydrogenation will not go spontaneously at temperatures below the decomposition temperature of the oil. However, if a powdered metal (nickel or platinum) is added, the reaction proceeds rapidly at reasonable temperatures. The metal appears to play the role of a catalyst which is able to lower the dissociation energy of the hydrogen so that the reaction can proceed at lower temperatures. It is tempting to speculate that we have found an example of chemical catalysis in the solid state and that this kind of effect may have more general application in analyzing other defect reactions in semiconductors.

Using the technique of annealing tritium doped detectors with active impurity gettering, it may be possible to measure the hydrogen dissociation directly without the apparent catalytic interference of impurities simply by using higher purity getters. This result would be of considerable theoretical interest in that we would have a quantitative measure for the influence of the germanium lattice on the H-H bond.

Note Added in Proof

A recent publication on palladium-doped germanium²³ provides evidence that the unknown impurity responsible for hydrogen dissociation in the Au-gettered samples is palladium. Golubev and Latyshev²³ made low temperature Hall effect measurements on Pd-doped p-type Ge and found an acceptor at $E_v+0.03\text{eV}$ while our measurements showed acceptors at $E_v+0.032\text{eV}$ and $E_v+0.017\text{eV}$. The diffusion constant of Pd is high enough ($1 \times 10^{-7} \text{cm}^2 \text{s}^{-1}$ at 800°C)²³ to have diffused into our samples at our annealing temperature of 600°C . From this we conclude that Pd is most probably the impurity responsible for the dissociation of hydrogen molecules or complexes in the Au-gettered Ge samples.

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