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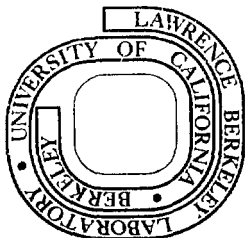
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HYDROGEN IN GERMANIUM

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HYDROGEN IN GERMANIUM*

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Abstract

Hydrogen is shown to form molecular acceptors and donors in pure germanium. Piezospectroscopy reveals that the hydrogen-related shallow donor D has non-tetrahedral symmetry. One hydrogen atom is incorporated in D as shown with an isotope shift in the donor ground state. Oxygen is also involved in the formation of D.

The hole emission rates of two copper-hydrogen acceptor complexes were determined with Deep Level Transient Spectroscopy. They are

$$e_1^{\text{Cu-H}} = 1.5 \times 10^8 T^2 \exp(-.195 \text{ eV}/kT) K^{-2} \text{ s}^{-1}$$

and

$$e_3^{\text{Cu-H}} = 5.0 \times 10^8 T^2 \exp(-.068/kT) K^{-2} \text{ s}^{-1} .$$

1. Introduction

Diffusion and solubility of hydrogen in silicon and germanium have been studied extensively (van Wieringen and Warmholtz 1956, Frank and Thomas 1960). Recent work has shown that hydrogen plays an active role in the saturation of dangling bonds in α -Si (Zanzucchi, et al 1977), in the formation of Si-H bonds in implanted layers (Suein 1975), in the formation of levels in the band gap of pure germanium (Haller 1978a) and in the divacancy-hydrogen complex in germanium (Haller, et al 1977a). Whereas effects of hydrogen in silicon are studied in a heavily disturbed semiconductor, ultra-pure germanium crystals grown in a hydrogen atmosphere provide the opportunity to study hydrogen-related centers in a nearly perfect lattice. This makes possible the application of very powerful diagnostic techniques, such as Photoelectric Spectroscopy (Kogan and Lifshits 1977), Hall Effect and Deep Level Transient Spectroscopy (Lang 1974).

2. Hydrogen-Related Shallow Centers

2.1 General

Hall (1975) discovered an acceptor and a donor in small, rapidly quenched samples of pure germanium. Using Photoelectric Spectroscopy, it has been shown that the quenching actually produces two shallow acceptors A_1 and A_2 as well as the shallow donor D (Haller 1978a and Skolnick, et al 1974). Measurements on crystals grown in a deuterium atmosphere revealed an isotope shift of A_2 and D, thereby proving that hydrogen atoms were associated with A_2 and D (Haller 1978b). We report here the the results of photoelectric studies on stressed germanium samples to resolve the nature of

the donor D. The dependence of the formation of D on the residual oxygen concentration has also been investigated as part of this study.

2.2 Experimental

A Fourier Transform Far Infrared Spectrometer exhibiting an energy resolution of 8 μeV is used in this work. IR-radiation is guided through 1/2" brass pipe onto the sample contained in a helium cryostat. A spring and lever mechanism is used to apply uniaxial stress to $6 \times 10^9 \text{ dyn cm}^{-2}$ parallel to the long axis of the rod-shaped Ge-samples ($6 \times 1 \times 1 \text{ mm}^3$). The temperature of the sample can be controlled between 1.2 and 12.0 K.

Samples are cut, with their long axis parallel to the desired crystallographic orientation, from ultra-pure Ge single crystals. Lapping and etching ($\text{HNO}_3:\text{HF} = 3:1$) are followed by rinsing in methanol. Two pure tin contacts 3 mm apart are alloyed under an argon atmosphere to one long face. The contact formation process also serves the purpose of producing the donor D. Depending on the desired concentration of the donor D, samples are quenched from temperatures between 600 and 650 K in an ice-water mixture. Bonding of fine wire connections, reetching and heating to $\sim 350 \text{ K}$ for 1 hour to reach the maximum concentration of D completes the sample preparation.

2.3 Uniaxial Stress Results

Figure 1 shows IR spectra corresponding to bound excited states of the donor D and of phosphorous at three different values of stress along the [111] direction. Both spectra have "hydrogenic" character (Faulkner 1969). The phosphorous spectrum follows the predicted pattern for a substitutional donor (Fritzsche 1962). The D-spectrum exhibits several unexpected features:

- 1) The lines are exceptionally sharp at any stress.

- 2) They do not change their position up to a stress $\sim 2 \times 10^8$ dyn cm⁻² where they show a slight splitting.
- 3) At a stress $\geq 2 \times 10^8$ dyn cm⁻² a new set of "hydrogenic" sharp lines appears while the intensity of the "low stress" lines drops rapidly. The "high stress" ground state lies 2.7 meV closer to the valence band edge than the "low-stress" ground state.

The D-spectrum has also been investigated with stress in the [110] and [100] directions. The stress value at which the "low-stress" spectrum vanishes and the "high-stress" spectrum appears is about four times higher for stress in the [110] and [100] directions than for stress in the [111] direction.

Spectra recorded at various temperatures up to 9 K show that the "high-stress" spectrum only appears under stress. The "low-stress" spectrum reappears at high stress when the temperature is raised and the line intensity ratio of the two spectra approaches 1.

These results cannot be interpreted in terms of a substitutional donor with tetrahedral symmetry (Fritzsche 1962). More generally, it appears that no one ground state configuration of a donor in Ge could be consistent with these results. Therefore, we propose that the donor has a structure which reorients itself at high stresses leading to a new, different ground state closer to the valence band edge. Phonons of sufficient energy can reverse the reorientation.

2.4 Isotope Shift and Oxygen Dependence

Stress experiments can give information about the structure of a point defect but not about its chemical composition. To further elucidate the nature of the donor D, we have used the fact that an isotope

shift occurs in the ground state of the donor D to determine the number of hydrogen atoms involved in the donor D. With the assumption that each of the possible hydrogen atoms in D contributes to an isotope shift when replaced by a deuterium atom, an unambiguous determination of the number of hydrogen atoms involved in D becomes possible. Table 1 illustrates the situation for one, two and three hydrogen atoms. Figure 2 shows the IR spectra of D for crystals grown in pure hydrogen, pure deuterium and in a mixture of hydrogen and deuterium. No elaborate peak analysis is necessary to see that the middle spectrum contains only two peaks for each excited state. Therefore, only one hydrogen atom can contribute to the isotope shift and this is also most probably the total number of hydrogen atoms in the center.

Ultra-pure Ge crystals are in general grown in an H₂-atmosphere from a melt in a quartz crucible. Such crystals exhibit oxygen concentrations between 7 and 10x10¹³ cm⁻³. Crystals grown from a melt in a graphite crucible contain much lower oxygen concentrations (< 10¹² cm⁻³). Efforts to produce A₂ and D in these crystals have completely failed. This clearly indicates that one or more oxygen atoms must be incorporated in A₂ and D.

3. Copper-Hydrogen Complexes

Copper produces a well-known triple acceptor in Ge in the substitutional position. It can be introduced easily into germanium in its interstitial form at quite low temperatures. These properties make it well suited for complex-formation studies.

Crystals grown in hydrogen, vacuum and nitrogen atmospheres have been investigated. Full area slices, 3 mm thick, have been cut, lapped

and polish etched. After plating with copper, the samples are heated in an inert atmosphere at 620 K for 24 hours. The Cu-Ge compound on the surface is lapped off and a lithium diffused contact (n^+) is produced on one face. Boron implantation forms the p^+ -contact on the other face. We then investigate these diode structures with Deep Level Transient (DLT) Spectroscopy (Lang 1974) using the correlator technique (Miller 1975). Preliminary results demonstrate clearly that hydrogen plays an active role in the formation of several new, deep acceptor levels. Figure 3 shows DLT spectra of these diodes. The well-known $E_V + 330$ meV level of doubly ionized copper produces a peak at about 145 K (using a correlation time constant $\tau = 3$ ms). Five time constants between 1 ms and 100 ms have been used to determine the emission rate $e_4^{Cu^{--}} = 6 \times 10^9 T^2 \exp(-.34 \text{ eV/kT}) \text{ K}^{-2} \text{ s}^{-1}$ of this level. The DLT spectrum of the vacuum grown crystal does not show any further peaks down to $T = 30$ K. The spectrum of the nitrogen grown crystal shows an additional small peak with $e_2 = 4.8 \times 10^8 T^2 \exp(-.092 \text{ eV/kT}) \text{ K}^{-2} \text{ s}^{-1}$. This peak is observed in all crystals containing oxygen at concentrations $> 5 \times 10^{13} \text{ cm}^{-3}$. Two additional large peaks are present in the hydrogen grown crystal with $e_1^{Cu-H} = 1.5 \times 10^8 T^2 \exp(-.195 \text{ eV/kT}) \text{ K}^{-2} \text{ s}^{-1}$ and $e_2^{Cu-H} = 5.0 \times 10^8 T^2 \exp(-.068 \text{ eV/kT}) \text{ K}^{-2} \text{ s}^{-1}$. They appear always and only together with the copper peak. We attribute these peaks to copper-hydrogen complexes. Their relative intensities depend slightly on heat treatment and the copper concentration. In a few cases we have extended DLTS down to temperatures low enough to observe the peak due to the singly ionized copper level at $E_V + 44$ meV. This level has been observed in all samples containing copper.

The DLTS studies confirm the results obtained from the Hall Effect

measurements on copper doped, hydrogen grown germanium crystals (Haller, et al, 1977b, Haller and Hubbard 1978). The two techniques complement each other, permitting detailed quantitative studies of other deep levels in the future.

4. Discussion and Conclusions

Our present experiments and results are of a preliminary nature. A comprehensive model of hydrogen in germanium still has to be developed. Our results are conclusive insofar as they demonstrate, unambiguously, that hydrogen is involved directly in the formation of shallow and deep levels in the band gap of germanium.

The role hydrogen plays can be compared to that of lithium. An electron is donated to an electron deficient site in the lattice. This, in the case of germanium, is an especially interesting property because most line and point defects and impurities create electron deficient sites (i.e., acceptor levels) in the lattice. The important difference between lithium and hydrogen is obviously that the former is by itself a shallow donor while the latter is believed to be a "very deep" donor inside the valance band (Wang and Kittel 1973).

The hydrogen-related energy levels have some noteworthy properties. The donor D is the first shallow center in Ge with a ground state which does not exhibit the tetrahedral symmetry of substitutional centers. A second donor, the lithium-oxygen complex, has also been found to exhibit non-tetrahedral symmetry (Haller and Falicov 1978). The ground state is not fully understood, but we know that it is sensitive to a change of the mass of the hydrogen atom. It is the first shallow donor in Ge observed to exhibit an isotope shift in its ground state (Haller 1978b). The independence on uniaxial stress of the ground state and the bound

excited states at all but very high stresses results in extremely sharp lines in the photoelectric spectrum. This will allow separation of stress-related from other line-broadening mechanisms in the case of normal substitutional donors. It may be possible to estimate much more accurately, random residual stress in nearly perfect crystals.

A last point has to be made concerning the possible interaction of radiation damage and hydrogen. The introduction of sensitive measurement techniques, such as photoelectric and deep-level transient spectroscopy to studies of low level radiation damage in pure germanium could lead to the discovery of several hydrogen-related centers. This might have practical importance in the understanding of the degradation of large volume germanium gamma-ray and particle detectors and in understanding the observed differences in damage sensitivity in detectors made from different crystals.

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Figure Captions

Figure 1. Photoelectric spectra of the donors phosphorous and D in pure germanium at three values of uniaxial stress along [111]; T = 4.5 K.

Figure 2. Photoelectric spectra of the donors phosphorous and D in crystals grown in pure hydrogen (top), in a deuterium-hydrogen mixture (~1:1, middle) and in pure deuterium (bottom). The letter behind the crystal identification number indicates the typness of the sample; T = 6.5 K.

Figure 3. Deep Level Transient spectra of three diodes containing copper made from germanium single crystals grown in vacuum a.), in a nitrogen b.) and a hydrogen atmosphere c.). Peaks 1 and 3 are due to copper-hydrogen complex acceptors. Peak 4 is due to the doubly ionized copper acceptor level. Peak 2 appears in all crystals containing oxygen $>5 \times 10^{13} \text{ cm}^{-3}$.

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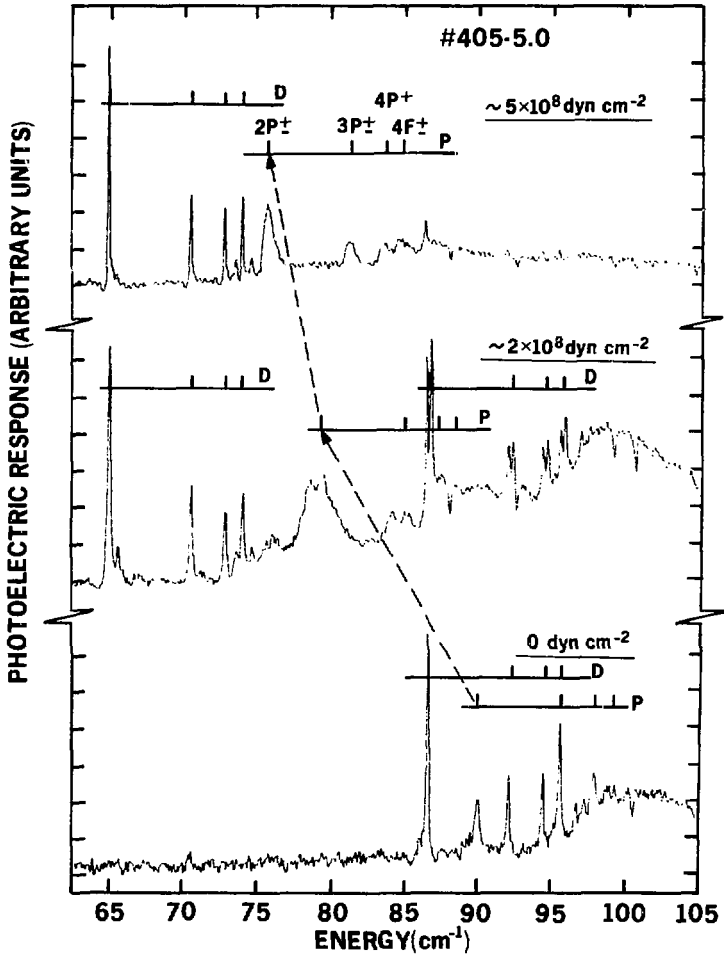
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NUMBER OF HYDROGEN ATOMS IN DONOR D	POSSIBLE COMBINATIONS OF HYDROGEN/DEUTERIUM	CONCENTRATION RATIOS (H:D = 1:1)	SPECTRUM (2P± LINES)
1	H	1	$< 51\mu\text{eV} >$
	D	1	
2	H ₂	1	
	HD	2	
	DH		
	D ₂	1	
3	H ₃	1	
	H ₂ D	3	
	HDH		
	DH ₂		
	D ₂ H	3	
	DHD		
	HD ₂		
D ₃	1		

Table 1

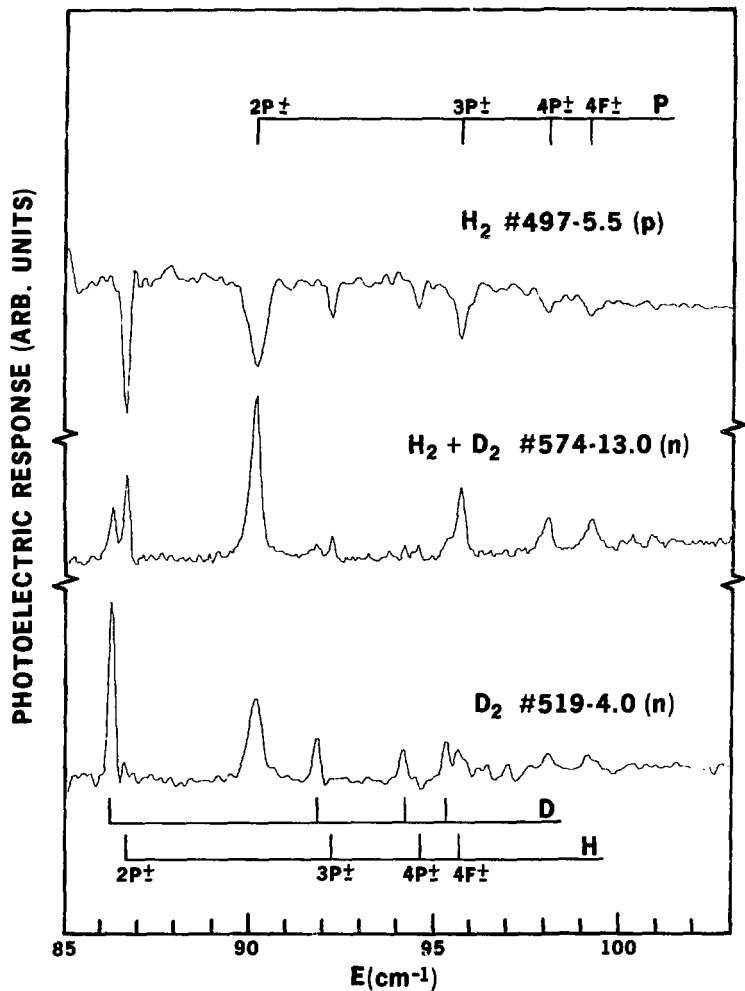
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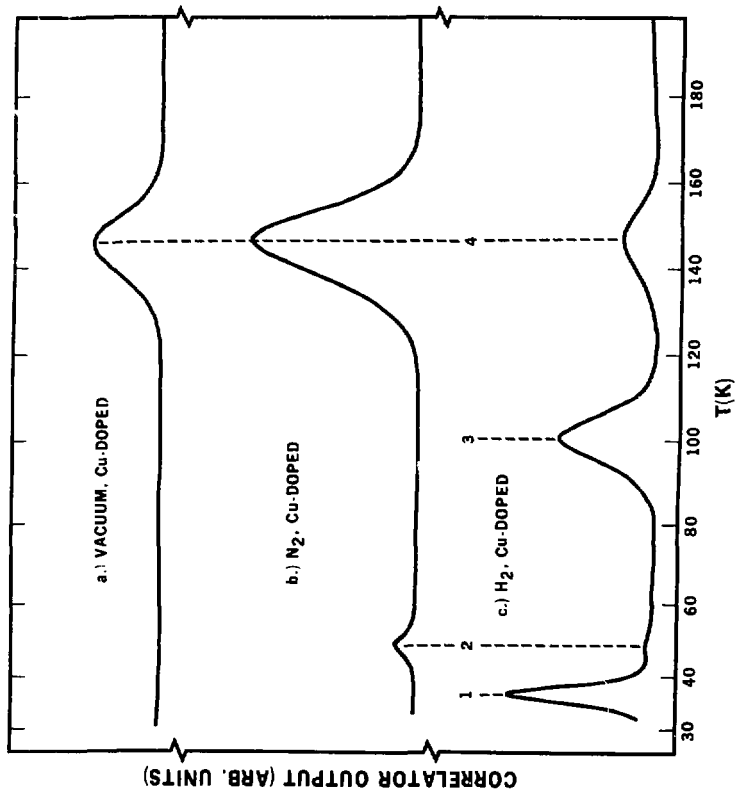
XBL 7710-6740 A

Figure 1



XBL 788-10100

Figure 2



XBL 788-10029

Figure 3

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