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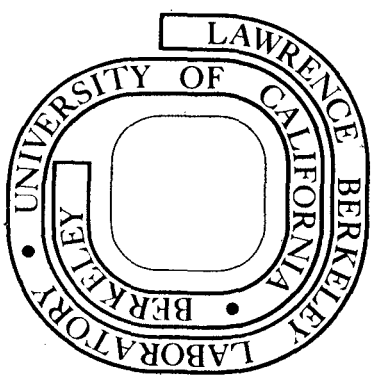

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HYDROGEN-MULTIVALENT ACCEPTOR COMPLEXES IN HIGH-PURITY GERMANIUM*

Eugene E. Haller, G. Scott Hubbard and William L. Hansen**

ABSTRACT

Using copper (a fast diffusing, multivalent acceptor impurity in Ge) we have shown that hydrogen can form complexes with multivalent acceptors. Hydrogen is incorporated in the Ge single crystal during its growth from a melt in a H_2 atmosphere. By analogy with the interaction between lithium and multivalent acceptors we find two acceptor like complexes: Cu-H and Cu-H_2. Using Photothermal Ionization Spectroscopy and Hall effect we assign the following energy levels: Cu-H: E_V + 17.5 meV and E_V + 170 ± 20 meV and Cu-H_2: E_V + 17.0 meV. According to our model the Cu-H_3 complex is neutral. Consequences for the performance of large volume radiation detectors are discussed.

INTRODUCTION

All high-purity germanium single crystals which are used in the fabrication of radiation detectors are pulled from a melt in a hydrogen atmosphere. Attempts to grow crystals in a different atmosphere (e.g. N_2, Ar, He) or in vacuum have failed insofar as these crystals contain too many trapping centers, which lead to an incomplete charge collection in detectors. Because no electrically active role was ever attributed to hydrogen the explanation for its successful use was based on the easily achieved purity (Pd-diffusion) and its reducing nature (oxygen-suppression).

Considering that all group IIIA elements of the periodic system form shallow acceptors and all of the group VA elements except nitrogen form shallow donors in Ge and from the fact that these levels are nearly identical one would expect to find similarities also between the elements hydrogen and lithium. Both elements occupy interstitial sites in Ge, which makes them fast diffusers. In contrast to hydrogen, lithium produces a shallow donor level. The small size of the hydrogen atom is, in general, used as an explanation for the absence of a donor level in the forbidden band.[1] From diffusion and permeability experiments at temperatures close to the melting point of germanium (1208K) it is known that the hydrogen is dissolved in atomic form in the latice. The solubility at the melting point is about 2 x 10^{14} cm^{-3}.[2] Extrapolating the high temperature data down to room temperature one finds a solubility of < 10^6 cm^{-3}. During the cooling of fast growing (12 cm/hr), big diameter crystals (3-5 cm), a large fraction of the hydrogen which is dissolved in the crystal near the melting point will be trapped. This results in a large supersaturation at room temperature. Recent attempts to obtain Electron Spin Resonance signals of the hydrogen atoms in Ge failed, despite sufficient sensitivity.[3] We conclude that hydrogen at room temperature and under supersaturated conditions is most probably present in molecular form at interstitial positions or in larger H-Ge conglomerates. Under this condition no donor level would form.

Whereas hydrogen does not produce an energy level in the forbidden band of Ge, recent experiments show that it can form an acceptor complex with divacancies in dislocation free Ge.[4] In this work we will present experimental proof that hydrogen is also involved in the formation of complexes with acceptor type impurities. In this respect we find a strong analogy between hydrogen and lithium. The lithium-double acceptor complexes are well studied.[5] For each Li-atom added to the acceptor one energy level disappears and the remaining levels moves closer to the valence band. This has been demonstrated for Zn[6], Hg, Mn and Ni.[5] The data reported for copper are inconclusive. This is unfortunate because copper is an ideal multivalent acceptor for complex formation studies. It can be introduced into Ge via interstitial diffusion from the surface and its concentration can be easily controlled by the choice of the diffusion temperature.[7] The electronic level structure of copper is well established. Each substitutional copper atom forms three acceptor levels: E_V + 44, E_V + 330 and E_C - 260 meV.[8] We have used copper to demonstrate that hydrogen does form acceptor type complexes with a reduced number of levels and reduced energies.

EXPERIMENTAL AND RESULTS

A large number of high-purity Ge crystals grown in hydrogen or nitrogen were available for our studies. Cu was introduced into 3 mm thick slices at 673K in an argon atmosphere from an electroplated layer on the surface. The slices were kept at 673K long enough to guarantee a homogeneous distribution of copper throughout the sample. Prolonged heating was avoided since it reduces the hydrogen concentration in the samples. After diffusion the crystal slices were sectioned into 8 x 8 mm^2 samples. The samples were lapped and etched, four In-contacts were soldered to the corners and using the van der Pauw geometry, Hall effect measurements were done between 300K and approximately 5K. A typical result obtained with a hydrogen grown, dislocated (~ 10^3 cm^{-2}) crystal #342-1.7 (Cu) which was lightly n-type (~ 10^{10} cm^{-3}) before the copper diffusion is shown in Fig. 1. It becomes immediately clear that besides the known copper level at E_V + 44 meV several other levels were introduced during the copper diffusion which were not present before. At the low temperature end unknown levels near E_V + 17 meV are deionizing. Photothermal Ionization Spectroscopy revealed two hydrogenic acceptors (A_1, A_2) at E_V + 17.0 and E_V + 17.5 meV (Fig. 2). The hydrogenic structure of the spectrum means that the levels are neutral and became singly ionized when they accept an electron. The E_V + 44 meV level belonging to the substitutional copper is followed by an E_V + 80 meV acceptor. This acceptor was assigned recently to the divacancy-hydrogen complex.[4] At higher temperatures a level A_3 at E_V + 175 ± 15 meV ionizes. At even higher temperatures the sample becomes intrinsic. The copper concentration is too small to allow one to detect the E_V + 330 meV level in the steep intrinsic slope. The three acceptor levels A_1, A_2 and A_3 cannot be detected when the sample is heated to 673K without copper introduction or when a nitrogen grown crystal is used. The levels disappear when

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the samples are heated to more than 773K for longer than about one hour. From these experimental facts we conclude that A_1, A_2 and A_3 must be assigned to a complex which includes both copper and hydrogen.

The copper-hydrogen complex model can be cross checked with the study of the copper-lithium complex. As mentioned above the previously reported results about such a complex are inconclusive. We have therefore repeated the investigation of this complex formation. Using the Ge samples which were already saturated with copper we introduced Li from an evaporated layer on a lapped surface at 573K for 10 min. After this initial diffusion step the excess Li-Ge compound was removed by etching, then the samples were annealed at 673K under an argon atmosphere. Hall effect measurements at regular intervals of several hours indicated when the sample had returned to p-type. The Hall effect results for sample (#342-1.7 Cu, Li) already shown in Fig. 1, but now doped with lithium, are shown in Fig. 3. The prolonged heating has driven out most of the hydrogen as can be seen from the disappearance of the A_1, A_2 and A_3 levels.

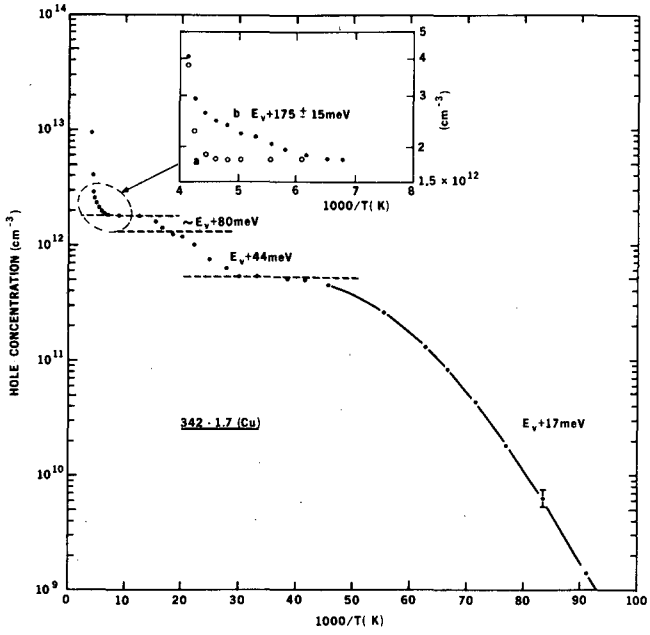

Fig. 1. Hall effect plot of the hole concentration versus 1000/T (K) of a hydrogen grown high-purity Ge sample #342-1.7 (Cu) doped with copper by diffusion at 673K. The various acceptor levels are discussed in the text. The expanded region shows the on set of extrinsic conduction of a sample with no deep acceptors (curve a) and of sample #342-1.7 (Cu) with an acceptor level at E_V + 175 ± 15 meV (curve b).

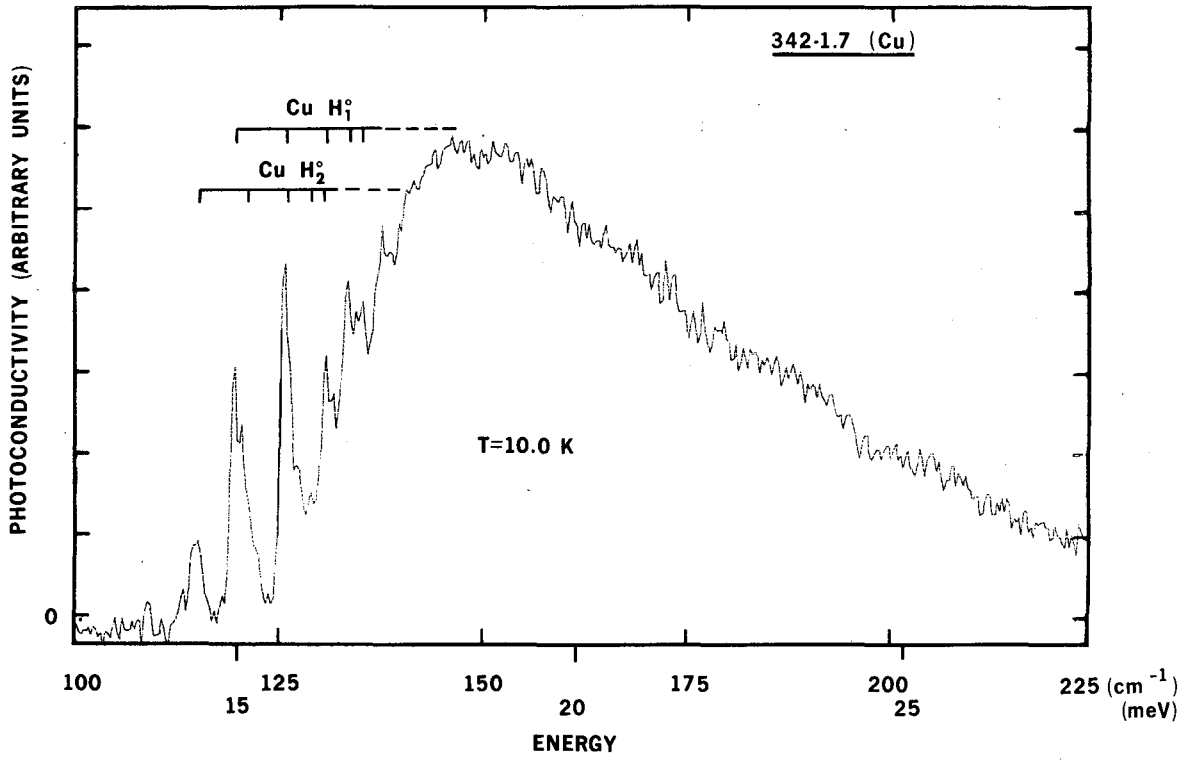

Fig. 2. Photoconductivity spectrum of sample #342-1.7 (Cu) from E = 12 to 28 meV. The two hydrogenic series of lines belong to acceptors with ground states at E = 17.0 and E = 17.5 meV.

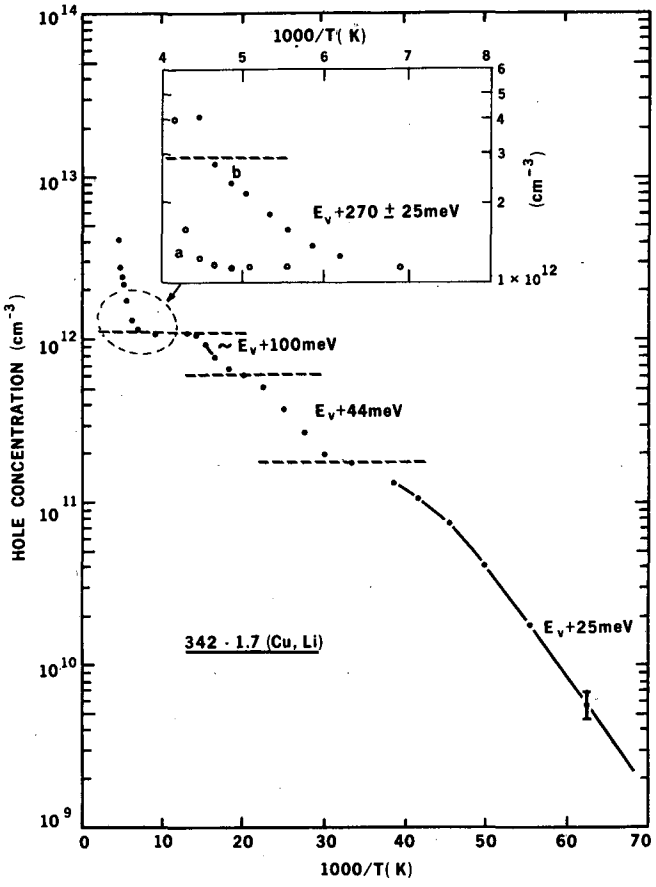

Fig. 3. Hall effect plot of the hole concentration versus 1000/T (K) of a hydrogen grown, high-purity Ge sample #342-1.7 (Cu, Li) shown in Fig. 1 but with lithium added. The various acceptor levels are discussed in the text. The blown up region shows a level E_V + 270 ± 20 meV (curve b). For comparison the freeze out of a sample with no deep acceptors is shown (curve a).

A series of new levels has been introduced. The shallowest level is located near E_V + 25 meV. The E_V + 44 meV level of copper is still visible. The divacancy-hydrogen level has disappeared but very close by at E_V + 100 meV the V_2 Li complex appears. At higher temperatures an unknown level B_3 appears at E_V + 275 ± 25 meV. Using spectroscopy, which has much higher sensitivity and energy resolution than Hall effect for shallow levels, we observe (in Fig. 4) traces of the levels A_1 and A_2 at E_V + 17.0 and E_V + 17.5 meV. Two new levels B_1 at E_V + 20.5 meV and B_2 at E_V + 25.0 meV with perfect hydrogenic structure show up. Similar to the case of the levels A_1, A_2 and A_3 we were able to produce B_1, B_2 and B_3 whenever both copper and lithium were present in a hydrogen grown crystal in similar concentrations. Difficulties occurred when we tried to create these levels in nitrogen grown germanium. Interference with oxygen might be a reason for this.

Summarizing our experimental results we come to the following model. The triple acceptor Cu can accept either free electrons, electrons from hydrogen atoms or lithium atoms to complete its strongly electron deficient site. In case of the acceptance of a free electron, further electrons have to be accepted against the Coulomb repulsion. A totally different situation occurs if either a hydrogen or lithium atom is forming a complex with copper. No Coulomb barrier is created against further addition of electrons. This makes the energy levels of the complex move closer to the valence band edge. We propose that the levels A_2 and A_3 are the neutral and singly ionized state of the double acceptor CuH. A_1 is the neutral state of the single acceptor CuH_2. The CuH_3 complex is believed to be neutral. Totally analogously we assign B_2 and B_3 to the neutral and singly ionized state of the double acceptor CuLi and B_1 to the single acceptor $CuLi_2$ or CuLiH. Again the $CuLi_3$ is expected to be a neutral complex. Figure 5 summarizes the proposed model.

DISCUSSION AND CONCLUSION

Our results have to be discussed in context with other impurities present in high-purity Ge like oxygen and silicon. Oxygen is present in varying concentrations depending strongly on the crucible material (quartz, graphite) and the growing atmosphere. Li-precipitation at room temperature from a high supersaturation is used to determine the oxygen concentration.[9] Li-O-donors are formed which give a direct measure. The precipitation rate is also an indicator for the oxygen concentration. The method is limited by the free lithium solubility and the intrinsic electron and hole concentration at room temperature to about 3.5 x 10^{13} cm^{-3}. Typical Ge-crystals grown in a hydrogen atmosphere out of quartz crucibles exhibit oxygen concentrations of around 5-7 x $10^{13}cm^{-3}$ where an accurate determination becomes questionable. Crystals grown out of graphite crucibles must have even lower oxygen concentrations ($<< 10^{13}$ cm^{-3}). This can be seen from their extremely small rate of precipitation. In nitrogen grown crystals one obtains clear results around 10^{14} cm^{-3}. The accurate knowledge of the oxygen concentration is important because this element can strongly compete in any type of complex formation. Analogous to the well known Li-O-[9] and Al-O-complex[10] formation it is very possible that hydrogen as well as copper form complexes with oxygen. We have at the present time no information about such complexes but we conclude from our experiments that they would be neutral. A further indication that such complexes form comes from the observation that the Cu-Li-complexes can only be formed in hydrogen grown crystals with low oxygen concentration. Attempts to reproduce these complexes in nitrogen grown crystals have failed. We cannot exclude, however, the possibility that the Cu-Li-complex also incorporates hydrogen in some form.

Silicon is present in quartz crucible grown crystals at concentrations as high as 10^{17} cm^{-3}. So far we were not able to detect any influence of silicon.

At present our data are not sufficient for a quantitative description of the complex formation processes. They allow us nevertheless to draw important conclusions. The fact that hydrogen, so far assumed to be electrically inactive in Ge, forms complexes with the multivalent acceptor Cu might explain why only hydrogen grown crystals have detector grade quality. Our results show that up to 10^{12} cm^{-3} deep acceptors can be partially or completely compensated. This means that the hydrogen concentration in as grown crystals is > 10^{12} cm^{-3} , a number which is much larger than the one extrapolated from high-temperature data.[2]

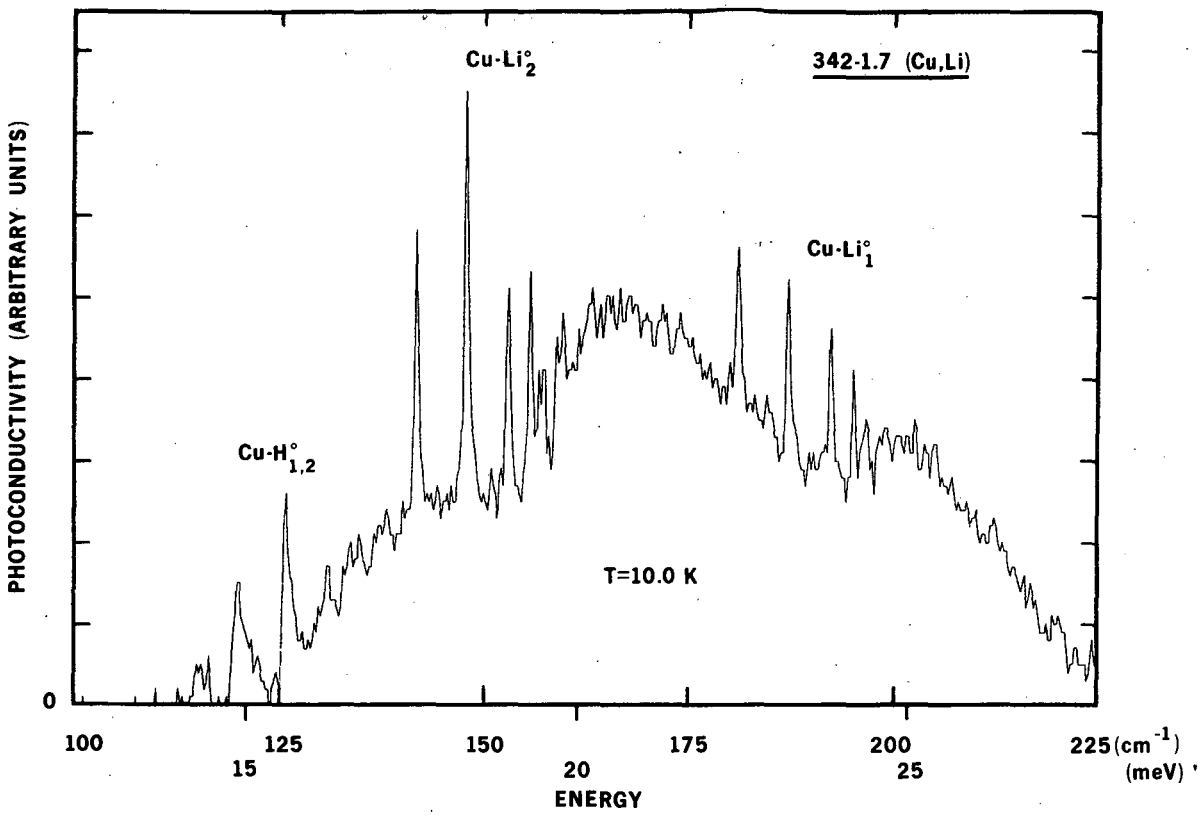

Fig. 4. Photoconductivity spectrum of sample #342-1.7 (Cu, Li). Besides the Cu-H-acceptors, two new hydrogenic series show up with ground state energies at E_V + 20.5 meV and E_V + 25.0 meV. The levels are assigned to Cu-Li-complexes.

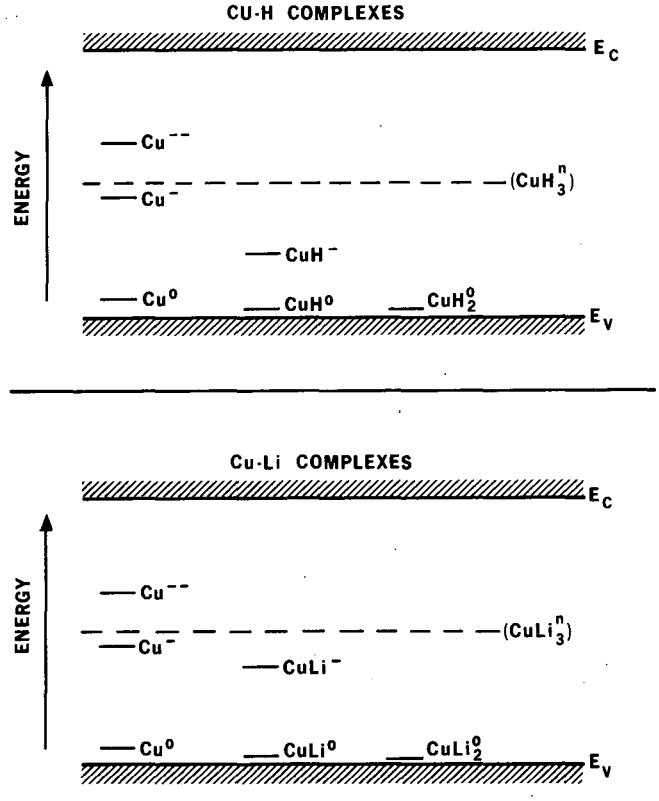

Fig. 5. Position of the acceptor levels of copper and its complexes with hydrogen and lithium in germanium.

We plan to investigate hydrogen complex formation with other deep acceptors. The influence of hydrogen on the radiation damage behavior of high-purity Ge detectors is expected to be important. The well known n-type 'coring' can now be explained with a radial dependence of the hydrogen concentration if we assume that hydrogen is compensating some of the dominent Al-acceptors. Near the seed end of the crystal the temperature falls more slowly and more hydrogen diffuses out of the crystal than near the tail end.

The next step in the hydrogen-multivalent acceptor complex studies would have to be more quantitative and should yield information about the binding energies of the various complexes.

An interesting question concerns the role of hydrogen in silicon. How far can the results obtained in Ge be extended to this technically much more important semiconductor?

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