Presented to the First Seminar on Photoelectric Spectroscopy of Semiconductors, Moscow, USSR, May 23 to 25, 1977

LBL-6432

CONF-770563--1

IMPURITY COMPLEX FORMATION IN ULTRA- PURE GERMANIUM

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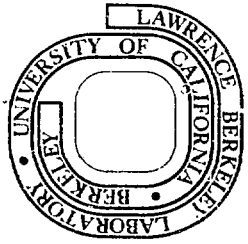
May 1977

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48



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ABSTRACT

Several unknown, hydrogenic acceptors and donors were recently discovered in ultra-pure germanium by photoelectric spectroscopy. These centers are not created by elemental impurities. Comparative analysis of a large number of crystals grown under various conditions lead to the conclusion that copper, a fast diffusing multivalent acceptor, together with lithium and/or hydrogen, is responsible for several of the unknown centers. This is the first time that hydrogen has been recognized as playing the role of a donor pairing with an acceptor. Hall effect measurements complementing the photoelectric spectroscopy results lead to a tentative assignment of the following energy levels:

(Cu, Li) complexes: E_V + 20.5 meV*, E_V + 25.0 meV*, E_V + 275 meV

(Cu, H) complexes: E_V + 17.0 meV*, E_V + 17.5 meV*, E_V + 175 meV

*hydrogenic acceptor

Experiments which may help determine the structure of the complexes are proposed.

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INTRODUCTION

Photoelectric spectroscopy has greatly facilitated the analysis and understanding of the behavior of shallow centers in ultra-pure germanium (Bykova et al, 1975, Haller and Hansen, 1974). The sensitivity and energy resolution of this technique have made possible the detection and identification of all elemental shallow acceptors and donors down to concentrations of $< 10^7$ cm^{-3} (Haller et al, 1975). Besides the well understood elemental centers, a large number of unknown, hydrogenic series of lines, belonging to unknown acceptors and donors, have been discovered (Haller, 1977 this volume). At the present time, very little is known about the precise nature of these centers. Some correlations can be found between various unknown centers and electrically inactive impurities, such as hydrogen. We have tried to turn the purely analytical approach into a more synthetic one by intentionally creating complexes between impurities.

This approach has been extensively used in the past for the study of pairing of impurities (e.g. Morin and Reiss, 1956). It is convenient to introduce one of the impurities during crystal growth and the other via diffusion from the surface. Since pairing is a purely Coulombic effect, complexes are usually formed between acceptors and donors. For these reasons, the pairing of lithium with multivalent acceptors has been widely studied. The most recent work was done by Lo Vechio (1972), who used Hall effect and IR absorption techniques. The poor energy resolution and sensitivity made the use of large impurity concentrations necessary, and a high percentage of pairing was required to produce measurable changes. We have used a similar concept, but with photoelectric spectroscopy as the analytical tool. For this preliminary work, we concentrated on the most convenient candidates, copper and lithium. Both are fast diffusing impurities and have high solubilities at temperatures in the range of a few hundred degrees centigrade. Copper is important because it is an effective trapping center. Such centers reduce the charge collection efficiency in large volume Ge radiation detectors and are, therefore, strongly detrimental to detector performance.

EXPERIMENTAL AND RESULTS

The formation of complexes was studied in high-purity Ge crystals grown in hydrogen and nitrogen atmospheres. All crystals used were p-type with $N_A-N_D < 10^{11}$ cm^{-3}. Copper was introduced into 2 mm thick, full area slices by diffusion under a protective atmosphere (Argon) from an electroplated surface layer. Diffusion temperatures between 400 - 500°C and times sufficiently long to assure homogeneity were chosen. After the diffusion, square samples (7 x 7 mm^2) were cut, lapped and polish etched, then In or InGa-eutectic contacts were applied. The samples were then investigated, using low-temperature Van der Pauw Hall-effect method and photoelectric spectroscopy. Nitrogen-grown crystals exhibited only the well known E_V + 44 meV and E_V + 330 meV energy levels of substitutional copper in the plot of free hole concentration versus 1/T. No unknown shallow levels were discovered with spectroscopy. Hydrogen-grown crystals however, exhibited a wealth of new acceptors. Hall-effect measurements revealed a level (or levels) around E_V + 175 meV. Figure 1 shows a spectrum of such a sample. Two closely spaced hydrogenic series due to acceptors at E_V = 17.0 meV and E_V + 17.5 meV appear. When a thin sample is heated at temperatures over 500°C for prolonged time (> 100 hours) all the new acceptors disappear. These results strongly suggest that the hydrogen dissolved in the crystal at concentrations of about 10^{13} - 10^{14} cm^{-3} is actively involved in the formation of these acceptors. When lithium is added to Ge samples containing copper, more energy levels appear. Figure 2 shows spectra of the sample used in Figure 1, but after a limited amount of lithium was diffused into it. Two hydrogenic series, belonging to acceptors at E_V + 20.5 meV and E_V + 25.0 meV, are present. The (Cu, H) levels are still visible. If the hydrogen is diffused out of the sample before lithium is added, the lower acceptor at E_V + 20.5 meV is not observed when the sample is measured. Since this is only a preliminary set of results, we will not attempt to assign the observed energy levels to specific complexes. The recent development of techniques which are sensitive and have reasonable resolution for deep levels, such as Deep

Level Transient Spectroscopy (DLTS), (Lang, 1974, Miller et al, 1975 1977), may complement photoelectric spectroscopy in the analysis of multivalent complexes.

DISCUSSION

Until recently, hydrogen was assumed to be a neutral, inert impurity in germanium. Its diffusion coefficient and solubility have been studied at high temperatures by Frank and Thomas (1960). Near the melting point of Ge the solubility is a few x 10^{14} cm^{-3}. During crystal growth a large fraction of the hydrogen gets trapped in the crystal. Studies of dislocation free Ge have revealed an acceptor at E_V + 80 meV which was assigned to the divacancy-hydrogen complex (Haller et al, 1977). By analogy, it is not surprising that hydrogen forms complexes with multivalent impurities which produce sites in the crystal which are strongly disturbed and electron deficient. These local disturbances can be lessened by attaching hydrogen atoms which share their electron. In this simple qualitative model, hydrogen is seen as a donor, partially or fully compensating multivalent acceptors. The reduction of the number of energy levels of a specific multivalent acceptor and the reduced ground state energies of the remaining levels are a direct consequence of the model. A more subtle point is the larger reduction of ground state energies in hydrogen related complexes than in Li-related ones. Theory predicts precisely such a behavior. (Baldereschi, 1976). A better understanding of impurity complexes will require more studies on other multivalent acceptors, such as Zn, Be, Hg, Ni, Ag, etc. Most of these elements have been shown to pair with lithium.

Details of the microscopic structure of complexes (i.e. molecules), may be recorded by experiments with uniaxial stress or magnetic fields. It is possible that the symmetry and energies of the ground states of complexes could be affected by the microscopic structure. Since excited states are strongly delocalized, they can reveal very little about the structure of the complexes.

ACKNOWLEDGMENTS

Prof. P. L. Richards and his group at the University of California, have contributed substantially to this work by allowing us continual use of their IR-Fourier Transform Spectrometer Systems. Special thanks also go to F. S. Goulding and W. L. Hansen, Lawrence Berkeley Laboratory (UC-Berkeley) who have initiated and continuously stimulated the high-purity Ge program.

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FIGURE CAPTIONS

Fig. 1 Photoelectric spectrum of the hydrogen-grown Ge-sample 342 - 1.7 (Cu). Sample size: 7 x 7 x 1.5 mm^3. The hydrogenic series belong to acceptors at E_V + 17.0 meV and E_V + 17.5 meV which are due to complexes between Cu and H.

Fig. 2 Photoelectric spectrum of the same sample as in Fig. 1, but with a limited amount of lithium added. The hydrogenic $(Cu, Li)_1$ series is created by an acceptor at E_V + 20.5 meV and is believed to be due to a complex involving Cu, H and Li. The hydrogenic $(Cu,Li)_2$ series is due to an acceptor at E_V + 25.0 meV and only involves Cu and Li.

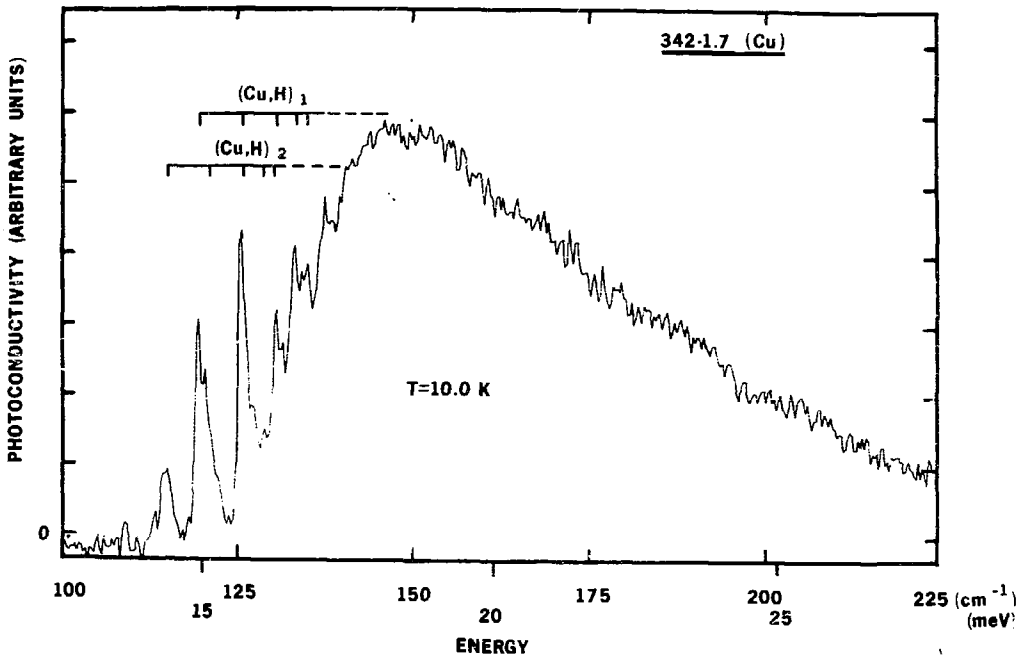

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FIG. 1

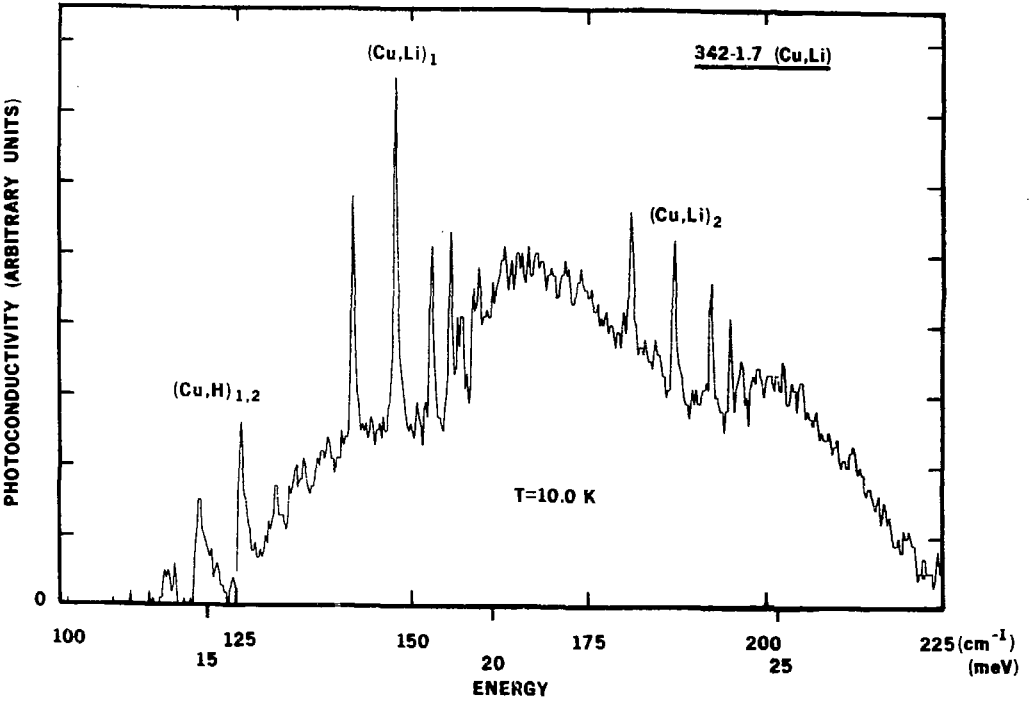

FIG. 2

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