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DLTS Measurements on Hydrogen Implanted Germanium

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Deep levels introduced by 50 KeV hydrogen ions or 1.5 MeV electrons in undoped germanium have been studied using deep level transient spectroscopy. Five hole traps have been observed after implantation. The energy levels associated with these traps, their cross sections and their annealing behaviours have been determined. The two trap levels at $E_v+0.38$ eV and at $E_v+0.42$ eV annealed at the same temperature, and they are attributable to the defect levels associated with divacancy-hydrogen complex.

§1. Introduction

The deep level transient spectroscopy (DLTS) technique, which was originated by Lang,[1,2] has been used to study deep levels in silicon and other semiconductors. It offers an easy powerful technique to obtain defect levels, concentrations of the levels and capture cross sections for electron and hole traps. Kimerling[3] and Mooney *et al.*[4] have used for the first time the DLTS to study the defects in germanium produced by electron irradiation. Bourgoin *et al.*[5] observed many vacancy-related defects, associated with oxygen and with the doping impurity. The DLTS technique has been also applied to the study of the recombination-enhanced defect reaction in germanium.[6] Using the correlator technique, many peaks due to acceptor levels observed in high-purity germanium diodes by Haller *et al.*[7] The levels due to substitutional copper, to copper-hydrogen complexes and to divacancy-hydrogen defects have been positively identified.

The primary purpose of the present work is to study an interaction of hydrogen atoms with point defects in germanium. Effects of hydrogen in germanium are studied in an undoped crystal implanted with hydrogen ions by the DLTS technique.

§2. Experimental Procedure

In this study we used the undoped p-type germanium crystal of which carrier concentration was about $1.3\times10^{12}cm^{-3}$ before irradiation. For the DLTS measurements Schottky diodes were fabricated by evaporating a thin layer of aluminum on the undoped crystals. The samples were implanted at room temperature with 50 KeV hydrogen ions up to fluence of $1.5\times10^{14}cm^{-2}$. For the sake of contrast, some schottky diodes were irradiated with 1.5 MeV electrons of $5.0\times10^{15}\text{cm}^{-2}$ from a Dynamitron accelerator. Behaviour of the traps introduced by irradiation were observed using DLTS. The transient capacitance which was recorded with a capancitance meter was analyzed with the help of a lock-in amplifier. In this method the temperature scanning was made over a range from 100 K to 300 K. Isochronal annealing was carried out in the temperature range 300–500 K.

§3. Experimental Results

Figure 1 shows typical DLTS spectra for the sample irradiated with 1.5 MeV electrons of $5.0\times10^{15}\text{cm}^{-2}$ under various reverse-bias voltages and lock-in center frequency of 25 Hz. Two hole traps labelled H_1 and H_2 were observed. The energy level positions of the traps can be determined by plots of the thermal emission rates of traps as a function of temperature. The results showed that the levels are located at $E_v+0.42$ eV (H_1) and $E_v+0.25$ eV (H_2) for hole traps. In this figure, the change in the peaks of the spectra is expressed by changing the pulse heights of majority carrier. It can be deduced that H_1 and H_2 levels are distributed uniformly in the sample.

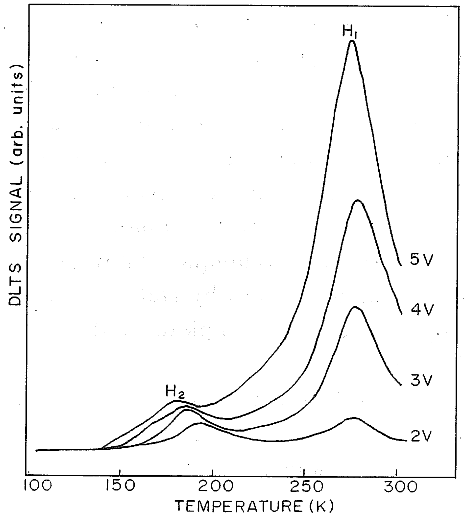

Fig. 1. DLTS spectra after 1.5 MeV electron irradiation under various reverse bias voltages.

Results of 20 minutes isochronal annealing of the traps H_1 and H_2 are shown in Fig. 2. From this figure, it is evident that $E_v+0.42$ eV (H_1) level annihilated by annealing at about 450 K, whereas the density of traps at $E_v+0.25$ eV (H_2) increased in the temperature range 350–420 K and some of them remained at 450 K.

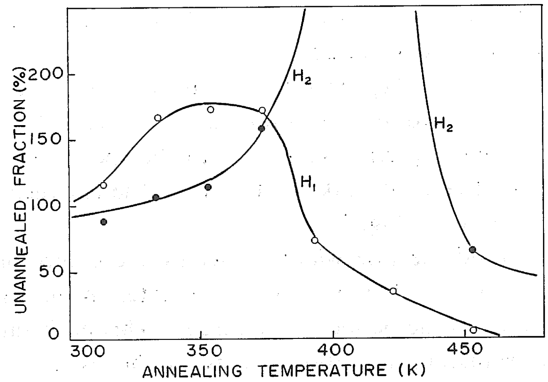

Fig. 2. Isochronal annealing curves of the two traps observed after irradiation with 1.5 MeV electrons.

Figure 3 shows the DLTS spectra on the sample implanted with 1.5×10^{14} hydrogen ions/cm^2 under a reverse bias of 5 V and lock-in center frequency of 25 Hz. It is found that five hole traps are introduced in hydrogen implanted germanium. The

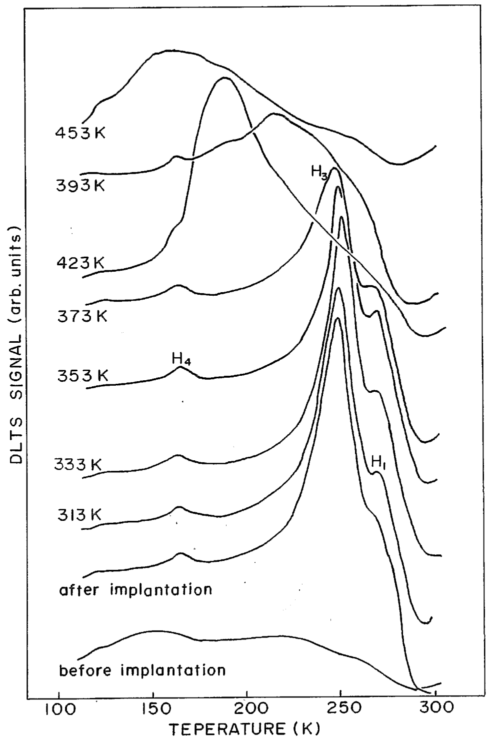

Fig. 3. DLTS spectra after implantation with 50 KeV hydrogen ions and after various isochronal anneals.

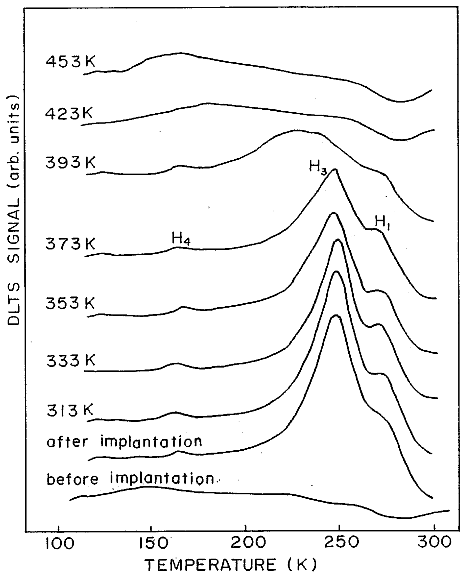

Fig. 4. DLTS spectra after implantation with 50 KeV H_2^+ and after various isochronal anneals.

levels causing the new peaks were located at $E_v+0.38$ eV (H_3), $E_v+0.17$ eV (H_4) and $E_v+0.12$ eV (H_5) for the three hole traps.

The results on a 1.5×10^{14} H_2^+ ions/cm^2 implanted sample are showin Figs. 4 and 5. Figure 4 illustrates a record for this sample under a reverse bias of 5 V and lock-in frequency of 25 Hz. These spectra are similar to the spectra of Fig. 3 with the exception that there is no dominant peak of H_2 trap. The enlarged figure of the lower temperature region is shown in Fig. 5.

In the lock-in method the rate widow is set by the choice of lock-in operating period. Data such as those in Fig. 6 result. It is noted in this figure that the peaks shift to lower temperature as the period is increased. This peak shift allows the determination of the corresponding activation energy in the usual way from Arrhenius plots, as indicated in Figs. 7 and 8. The energy levels are given by the slopes of the plots $\ln(\tau T^2)$ vs T^{-1} describing the temperature behaviour of the time constant τ of the emission rates of the traps. The cross sections are estimated from the extrapolation of τ at $T^{-1}=0$. As a result it was revealed that the levels are located at $E_v+0.17$ eV (H_4) and $E_v+0.12$ eV (H_5) for the two hole traps. The hole capture cross sections of traps H_4 and H_5 were 5.1×10^{-15}cm^2 and 4.7×10^{-15}cm^2 respectively. The energy

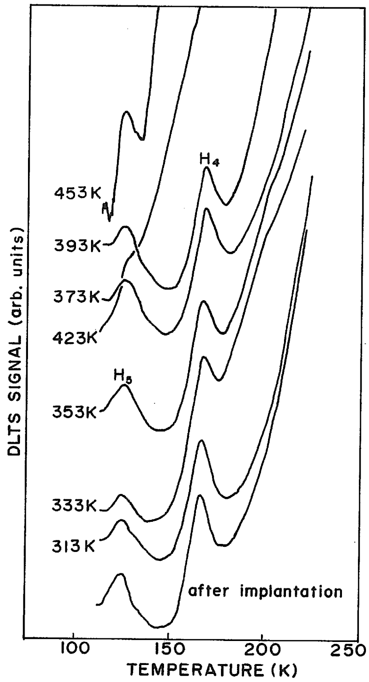

Fig. 5. DLTS spectra in lower temperature region, after implantation with 50 KeV H_2^+ and after various isochronal anneals.

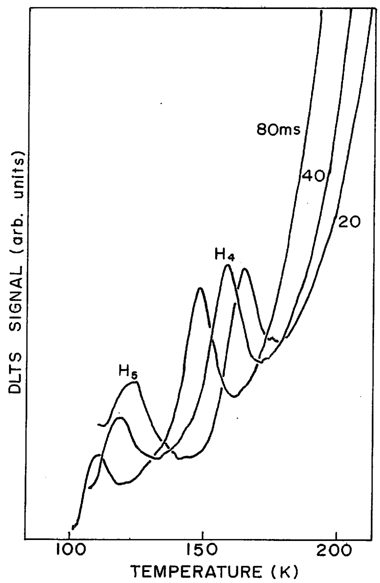

Fig. 6. DLTS spectra as a function of temperature and lock-in center period.

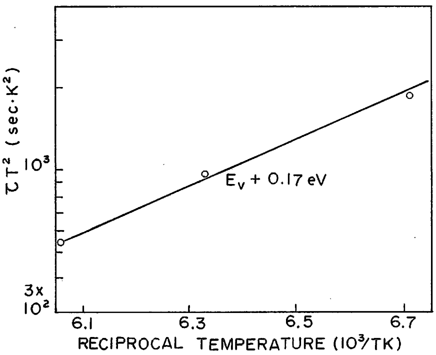

Fig. 7. Variation of τT^2 vs $10^3/T$ for the hole trap H_4.

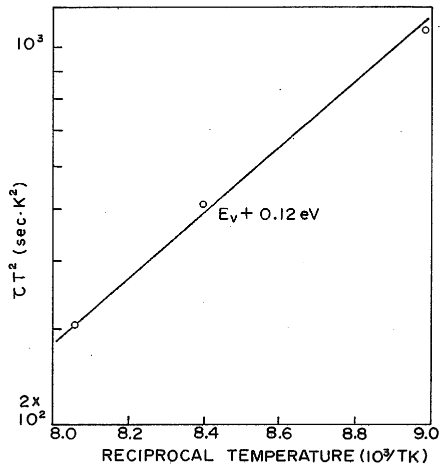

Fig. 8. Variation of τT^2 vs $10^3/T$ for the hole trap H_5.

Table 1. Energy levels and capture cross sections of all traps observed in undoped germanium.

	H_1	H_2	H_3	H_4	H_5
E_T (eV)	0.42	0.25	0.38	0.17	0.12
σ_P (cm^2)	2.3×10^{-16}	5.7×10^{-13}	4.7×10^{-17}	5.1×10^{-15}	4.7×10^{-15}

level positions and the cross sections of hole trapping of all traps are given in Table 1.

The isochronal annealing curves for the traps H_1, H_3, H_4 and H_5 in the H_2^+ implanted sample are shown in Fig. 9. The trap H_3 annealed together with trap H_1 in

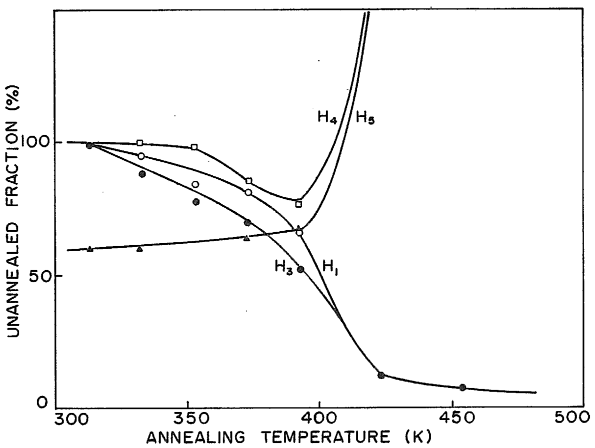

Fig. 9. Isochronal annealing curves of the traps observed after implantation with 50 KeV H_2^+.

the temperature range from 330 K to 450 K. Traps H_1 and H_3 are probably associated with the same defect. The densities of traps H_4 and H_5 increased at the temperature above 390 K and did not recover up to 500 K.

§ 4. Discussion

Various papers based on DLTS data have been published, discussing the energy levels of radiation induced defects in germanium, their annealing behaviours and their models.[4-11] However our knowledge of point defects in germanium remains far behaind that of defects in silicon. One of the reasons is that spectroscopic techniques, which have been so powerful in identifying most of the simple defects in silicon, don't work so well in germanium. The way to identify the defects associated with trap is to correlate annealing stages, energy levels and their dependence on the nature of the impurities contained in the sample.

In this study, undoped samples were used to prevent the participation of impurity atoms in the defect formation process. We previously observed rearrangement of a divacancy-like defect which is not related to impurities.[12] Its annealing behaviour seemed to correlate with the 24 μm infrared absorption band in silicon.[13] From the study of the variation of the introduction rate of traps with the energy of irradiation, Poulin and Bourgoin[11] observed two traps associated with divacancy. These two traps annealed at the same temperature (150°C). The divacancy in germanium also observed by the stress-induced dichroic photoconductivity, and this defect annealed in the stage centered at 120°C.[14]

We find the two hole traps at $E_v+0.42$ eV (H_1) and $E_v+0.25$ eV (H_2) in undoped germanium crystals irradiated with 1.5 MeV electrons. The H_1 trap shows the same annealing behaviour as the levels ascribed to the divacancy by bourgoin *et al.*[5] Comparison of the annealing behaviour of the H_1 trap observed with other results presented in the above literatures leads to reasonable candiate for the unknown defect in our samples. It is suggested that the defect associated with $E_v+0.42$ eV (H_1) level is a divacancy.

A number of hydrogen related centers in germanium have been studied by Haller *et al.*[7,15-18] In dislocation-free hydrogen-atomosphere grown germanium, they found a single acceptor at E_v+80 meV which was attributed to a divacancy-hydrogen complex. They found other hydrogen related shallow acceptors $A_{1,2}$. From some experimental results it has been suggested that $A_{1,2}$ belong to one center of a hydrogen atom trapped at and tunneling around a substitutional silicon impurity. Closely related to the hydrogen complex in germanium, the first experimental measurement of the structure of hydrogen related center in silicon was carried out by Picraux *et al.*[19,20] Using implantation, alpha-back scattering, channeling and nuclear reactions, they did an extensive study on the distribution and position of hydrogen in the silicon lattice. They concluded that atomic hydrogen site is in an antibonding direction, 1.6 Å away from a silicon atom. Their channeling measurements did not indicate silicon-hydrogen bonding in vacancy defects. Kleinhenz *et al.*[21] found by extended Hückel calculations that the dangling bonds of a vacancy or of a divacancy could be saturated with hydrogen. A model of hydrogen associated with defect aggregates explains the experimental data and the calculations.

In the present study, the dominant trap at $E_v+0.38$ eV (H_3) was present in the hydrogen implanted sample and appeared always together with the trap H_1 at $E_v+0.42$ eV due to the divacancy. The trap H_1 should be modified into the two traps H_1 and H_3 by hydrogen implantation. In comparison of the behaviour of these traps with other results in the literature, we attribute the traps to a divacancy-hydrogen complex.

Our results have to be discussed in context with other impurities present in high-purity germanium like oxygen. Oxygen is present in varying concentrations depending strongly on the crucible material and the growing atmosphere. The knowledge of the oxygen concentration is important, because this element can strongly compete in any type of complex formation. Our germanium crystals are grown in nitrogen atmosphere containing a few percent of hydrogen out of carbon coating quartz crucibles. The oxygen concentration is expected to be around $10^{14}cm^{-3}$ in our samples. The $E_v+0.25$ eV (H_2) trap has the same annealing behaviour as the 715 and 808 cm^{-1} IR bands due to an oxygen complex attributed by Whan.[22] Its annealing temperature is the temperature at which Bourgoin *et al.*[5] observed the annealing of DLTS spectra associated with an oxygen defect. In this view trap H_2 should be ascribed to a defect containing oxygen.

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