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Hydrogen Passivation of Oxygen-Related Defects in Germanium

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Thermal donors in undoped germanium were produced by heat treatment at 350°C for 200 h, and the level position for the thermal donors was tentatively estimated to be 0.36 eV from the conduction band. When the sample was subsequently implanted with 25 keV hydrogen, concentration of the level associated with the thermal donors was drastically reduced and the position of DLTS peak corresponding to the level shifted to lower temperature. The restoration of the neutralized thermal donor electrical activity began after a 15 min annealing at 200°C and essentially completed after annealing at 280°C.

§1. Introduction

Interaction of hydrogen with the thermal donors in silicon has been studied using DLTS, FTIR and SPR.[1–3] It has been found that a large degree of thermal donor passivation can be achieved by hydrogen plasma exposure at 120°C and there is a selective passivation of the thermal donor clusters. Annealing at 200°C almost completely reactivates the low concentration of the thermal donors present in these samples.

The present study focuses on the effects of hydrogen on the defects containing the thermal donors in germanium, and selectively hydrogen passivation of these defects is demonstrated.

§2. Experimental

An undoped n-type germanium crystal were grown in nitrogen atmosphere containing 7% hydrogen from a quartz crucible coated with pyrolytic graphite. Carrier concentration of the sample was about $4.0\times10^{12}\mathrm{cm}^{-3}$ before any treatment. For introducing the thermal donors, the samples were chemically cleaned and heat-treated at 350°C for 200 h in Ar atmosphere. Hydrogen was incorporated into the germanium crystals by implantation with 25 keV hydrogen ions up to fluence of $5.3\times10^{15}\mathrm{cm}^{-2}$ at 78 K. Isochronal annealing was carried out in the temperature range between 20°C and 600°C.

Behavior of the traps introduced by heat treatment in the samples were observed

using DLTS technique. For the DLTS measurements Schottky diodes were fabricated by evaporating a thin layer of gold on the materials.

§3. Results

The thermal donor defects were generated with a 200 h furnace anneal at 350°C in flowing Ar gas. A broad peak at 170 K is observed in Fig. 1 and the level causing the peak was located at 0.36 eV from the conduction band for electron trap. When the sample was subsequently implanted with 25 keV hydrogen ions of $4.6\times10^{15}\text{cm}^{-2}$, the peak height for the 0.36 eV level became small and the position of the peak shifted to the lower temperature, as shown in Fig. 2. Hydrogen implantation reduced the concentration of the thermal donor defects by a factor of 4.3. The energy level position of the trap shifted by hydrogen implantation is located at $E_c-0.33$ eV for the electron trap. The electrical properties of $E_c-0.33$ eV level are summarized in Table 1, by comparison with the pre-implantation level at $E_c-0.36$ eV.

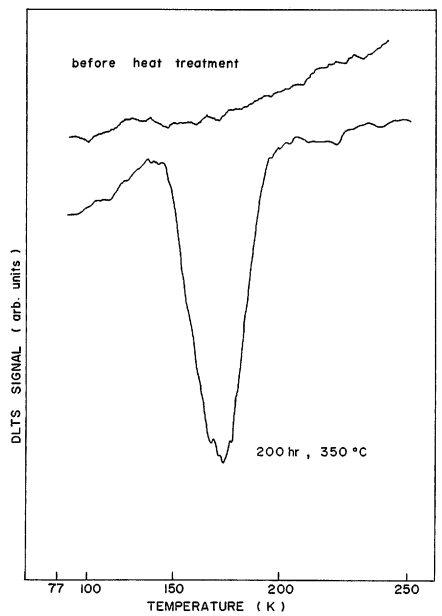

Fig. 1. DLTS spectra before and after 350°C heat treatments.

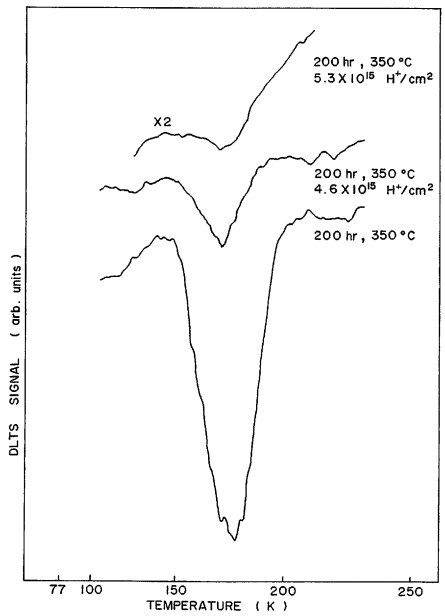

Fig. 2. DLTS spectra after 25 keV hydrogen implantation following 350°C heat treatment.

The question of the thermal stability of the passivation effect is obvious importance. A comparison of the annealing behavior of the hydrogen neutralized $E_c-0.33$ eV level with the annealing curve of the thermal donor ($E_c-0.36$ eV) is shown in Fig. 3. It can

Table 1. Energy level positions E_t, capture cross sections σ_n and concentrations N_t of the traps observed.

	E_t(eV)	σ_n(cm^2)	N_t(cm^{-3})
200 h, 350°C	$E_c-0.36$	2.0×10^{-12}	4.3×10^{12}
200 h, 350°C and 25 keV H^+	$E_c-0.33$	6.4×10^{-14}	1.0×10^{12}

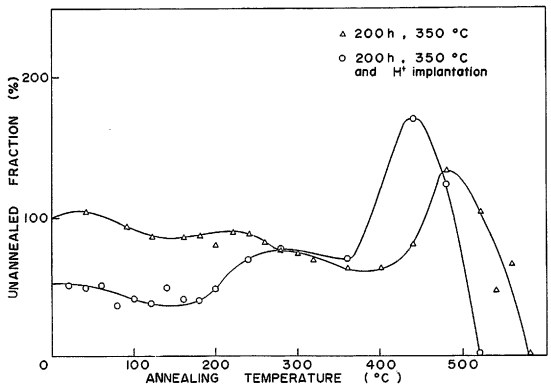

Fig. 3. Isochronal annealing curves of the trap observed after 350°C heat treatment and after 25 keV hydrogen implantation following the heat treatment.

be seen that the restoration of the thermal donor electrical activity begins after a 15 min anneal at 200°C, and essentially completes after a 15 min anneal at 280°C. Continued annealing at a higher temperature leads to an increase in thermal donor concentration in the temperature region between 360°C and 440°C, and decrease of the thermal donors themselves occurs at temperature above 440°C.

§4. Discussion

The spectroscopic illustration of the thermal donor electrical activity in germanium is provided by DLTS measurement, as shown in Fig. 1. The starting materials are the undoped n-type germanium crystals which are grown in nitrogen atmosphere containing 7% hydrogen from a quartz crucible coated with pyrolytic graphite. The oxygen concentration is expected to be around 10^{14}cm^{-3} in our samples. For the DLTS measurement, the condition of the heat treatment at 350°C for 200 h was adjusted to produce a low thermal donor concentration (4.3×10^{12}cm^{-3}) comparable to the carrier concentration of the undoped germanium crystals (4.0×10^{12}cm^{-3}). This enabled standard capacitance transient analysis. Formation of the state corresponding to the E_c-

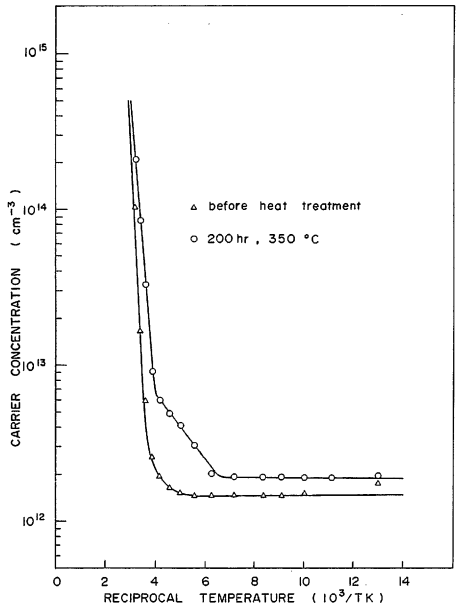

Fig. 4. Temperature dependences of carrier concentration before and after 350°C heat treatment.

0.36 eV level obtained by DLTS was also confirmed by Hall measurement, as shown in Fig. 4. The broad DLTS peak centered at 170 K appears as the superposition of some unresolved emission signals which correspond to the electrical character of the thermal donor clusters.

The effects of hydrogen implantation on the thermal donor electrical activity are shown in the DLTS spectra in Fig. 2. It can be seen that oxygen related donor electrical activity is significantly reduced. However, effect of hydrogen implantation is not simply to decrease the concentration of E_c-0.36 eV level. After 25 keV hydrogen implantation of 4.6×10^{15}cm^{-2}, the DLTS signal is reduced by a factor of 4.3, and shifted to lower temperature. The level position corresponding to the shifted peak was tentatively estimated to be 0.33 eV from the conduction band. As shown in Table 1, the capture cross section of the level is also significantly reduced by two orders magnitude (from 2.0×10^{-12}cm^2 to 6.4×10^{-14} cm^2), which means the neutralization of the trap activity. These observation can be explanined by a change of the nature of the trap according to a selective passivation of thermal donor clusters.

We have also investigated the thermal stability of passivated thermal donors (see Fig. 3). Essentialy complete restoration of the thermal donor electrical activity occurred after a 15 min annealing at 280°C, and decrease of the 350°C thermal donors themselves occurred at temperatures above 440°C. It is suggested that there is dissociation of hydrogen from the thermal donor complexes at the temperature range between 200°C and 280°C, and that at even higher temperatures there is removal of a relatively stable hydrogen from germanium crystal, previously we ovserved the loss of hydrogen

from germanium crystal above 500°C.[4)]

In conclusion, we have observed a selective hydrogen passivation of the 350°C thermal donor clusters in undoped germanium crystals. The passivated donors are reactivated by annealing above 200°C and essentially complete restoration of electrical activity occurs after annealing at 280°C.

Acknowledgments

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