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Energy levels in electron irradiated n-type germanium (*)

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Résumé. — Les niveaux profonds introduits par irradiation à température ambiante avec des électrons de 1 MeV dans des photodiodes au germanium p^+n ont été étudiés à l'aide de transitoires de capacité. Deux pièges à électron et un piège à trou sont observés après irradiation. Un second piège à trou apparaît après guérison du premier piège à trou (à 300 °C). Les niveaux d'énergie associés à ces pièges, leurs sections de capture et leur comportement pendant la guérison ont été déterminés.

Abstract. — Deep levels introduced by room temperature 1 MeV electron irradiation in p^+n photodiodes have been studied using deep level transient spectroscopy. Two electron traps and one hole trap have been observed after irradiation. A second hole trap is observed upon the annealing of the first hole trap. The energy levels associated with these traps, their cross-sections and their annealing behaviour have been determined.

1. Introduction. — Contrary to the case of silicon, defects in germanium have not yet been identified. At most there are good indications that when defects are produced by electron irradiation at low temperature in n-type material the vacancy-interstitial pairs recombine at 65 K [1] and that the 35 K annealing stage is connected with defects involving donor doping impurities [2]. The reason so little is known about defects in germanium is that spectroscopic technique either do not work (electron paramagnetic resonance) or have not been used extensively (IR absorption studies suggest that the vacancy becomes mobile at 90 K and forms the A centre [3]).

Most studies performed have used conductivity and Hall effect measurements which only provide the *total* defect concentration and, through isochronal annealing, the temperature at which the defects disappear. Various annealing stages have been observed depending upon the type and concentration of the doping impurities and upon the conditions of irradiation and many energy levels have been estimated mostly from *global* lifetime studies [4].

Recently the deep level transient spectroscopy (DLTS) technique [5] has been used to study deep

levels in silicon and other semiconductors. It offers an easy powerful technique to obtain energy levels, concentrations, and capture cross-sections for electron and/or hole traps. In electron irradiated silicon the technique confirms the energy level determination of many defects already identified by other techniques [6-10].

It seems therefore interesting to apply the DLTS technique to germanium since it will provide for the first time a spectroscopic study of defects in this material. In a first attempt, described in this paper, we study the defects introduced by electron irradiation at room temperature.

2. Experimental. — Two different types of p^+n germanium commercial photodiodes (OAP1 2 and PHG1) with doping concentrations of $3 \times 10^{13} \text{ cm}^{-3}$ and $3 \times 10^{14} \text{ cm}^{-3}$ respectively, were irradiated with various doses of 1 MeV electrons. The flux of irradiation is low ($\sim 0.5 \text{ A.cm}^{-2}$) in order to keep the temperature of the diode below 50 °C under irradiation. The carrier concentration were calculated from the capacitance-voltage data.

Energy levels and trap concentrations were measured using DLTS. The transient capacitance signal, recorded with a Boonton model 72 A capacitance bridge, is analysed with the help of two boxcars. Because of the geometry of the commercial diodes it was difficult to get a good thermal contact between

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the thermocouple and the germanium crystal and, consequently, the uncertainty in the measurements of the energy levels is larger than is usual (about 10 %). The aim of this paper being to study the introduction and annealing of the energy levels we only estimated the order of magnitude of the capture cross-sections by extrapolating the energy level data. Annealing of the diodes was performed in an argon atmosphere and the temperature was measured within $\pm 2^\circ\text{C}$.

3. Results. — Figure 1 shows a typical DLTS spectrum for an irradiated diode having a doping concentration of $3 \times 10^{13} \text{ cm}^{-3}$. Two electron traps, labelled E_1 and E_2 , and a hole trap, labelled H_1 , were

Fig. 1. — DLTS spectra of OPA1 2 diodes irradiated with 10^{15} cm^{-2} , 1 MeV electrons. The conditions of observation are the following : reverse bias : 2 V ; gate settings : 15 and 45 ms. The full line corresponds to the observation of majority carrier traps (2 V pulse) and the dashed line to injection conditions (pulse 5 V) for the observation of minority carrier traps.

Fig. 2. — DLTS spectrum of a OPA1 2 diode irradiated with $5 \times 10^{15} \text{ cm}^{-2}$, 1 MeV electrons and annealed at 300°C . The conditions of observation (injection) are those of figure 1.

observed. Annealing experiments show that E_2 disappears between 100°C and 200°C while H_1 anneals at 300°C and at the same time a new hole trap H_2 appears (see Fig. 2).

Table I gives the energy levels and capture cross-sections for E_1 , E_2 and H_1 traps (data taken from

Table I. — Energy levels and cross-sections of the traps observed in 1 MeV electron irradiated n-type germanium.

Trap	Energy level (eV)	Capture cross-section (cm^{-2})
E_1	$E_c - 0.2$	2×10^{-21}
E_2	$E_c - 0.40$	9×10^{-17}
H_1	$E_v + 0.25$	6×10^{-17}

figure 3) ; the concentration of H_2 traps was too small to allow a correct determination of its level. The energy levels are given by the slopes of the plots $\ln(\tau_m^{-1} T^{-2})$ versus T^{-1} describing the temperature behaviour of the time constant τ_m of the emission rates of the traps ; the cross-sections are estimated from the extrapolation of τ_m at $T^{-1} = 0$.

Fig. 3. — Variation of $\tau_m^{-1} T^{-2}$ versus $1000/T$ for the levels observed (the quantity τ_m is related to the gate settings t_1 and t_2 through $\tau_m = (t_2 - t_1)/\ln(t_2/t_1)$). PGH1 diode irradiated with $5 \times 10^{14} \text{ cm}^{-2}$, 1 MeV electrons : + ; OAP1 diode irradiated with $5 \times 10^{14} \text{ cm}^{-2}$, 1 MeV electrons : Δ ; OAP1 diode irradiated with $5 \times 10^{15} \text{ cm}^{-2}$, 1 MeV electrons : $\bullet$, $\circ$; OAP1 diode irradiated with 10^{15} cm^{-2} , 1 MeV electrons : $\blacktriangle$.

The DLTS spectra for a diode having a doping concentration of $3 \times 10^{14} \text{ cm}^{-3}$ is shown in figure 4.

This spectrum is similar to the spectra of figure 1 with the exception that there is, in case of injection, an additional broad background in the low temperature end. As shown in figure 4 this background increases with the injection current.

The annealing behaviour of all these traps is given in figure 5.

Fig. 4. — DLTS spectra of PHG1 diodes irradiated with 5×10^{14} , 1 MeV electrons. The conditions of observation are those of figure 1 except for the pulse amplitude : full line 2 V (observation of majority carrier traps); dashed and dotted lines 5 V and 3 V respectively (observation of minority carrier traps).

The relative peak heights are different in the two types of diodes irradiated with the same dose. Table II gives the introduction rates for the different traps. For each trap the ratio of the introduction rates between the two types of diodes is approximately identical, of the order of 10^{-4} for OAP1 2 diodes and of 10^{-3} for PHG1 diodes : the defect introduction rate increases by a factor of 10 when the doping concentration increases from

3×10^{13} to $3 \times 10^{14} \text{ cm}^{-3}$.

This is consistent with the observations of Calcott and MacKay [11] who found that in pure ($\sim 10^{13} \text{ cm}^{-3}$) n-type material irradiated at 4 K, the annealing fraction at 65 K is nearly 100 % (i.e. all the vacancy-interstitial pairs recombine) while for 10^{14} - 10^{15} cm^{-3} doped material the annealing fraction is lower ($\sim 90 \%$). This is a strong indication that the defects which are formed during the 65 K annealing, i.e. the defects we observe here, are complexes involving vacancies (or interstitials) and the donor impurities.

Table II. — Concentration and defect introduction rate for the different traps observed in 1 MeV electron irradiated n-type germanium.

Diode	Irradiation dose (cm^{-2})	Concentration (cm^{-3})			Introduction rate (cm^{-1})		
		E_1	E_2	H_1	E_1	E_2	H_1
OAP1 2 ($3 \times 10^{13} \text{ cm}^{-3}$)	5×10^{15}	—	1.0×10^{12}	1.5×10^{12}	—	2.0×10^{-4}	3.0×10^{-4}
PHG1 ($3 \times 10^{14} \text{ cm}^{-3}$)	5×10^{14}	8×10^{11}	1.1×10^{12}	3.9×10^{11}	1.6×10^{-3}	2.2×10^{-3}	7.8×10^{-4}

Fig. 5. — Unannealed fraction during isochronal annealing for the different traps in a PHG1 diode (O, +) irradiated with $5 \times 10^{14} \text{ cm}^{-2}$, 1 MeV electrons and in a OAP1 2 diode (●, ▲) irradiated with $5 \times 10^{15} \text{ cm}^{-2}$, 1 MeV electrons.

The E_1 level, which anneals at 100 °C, could be the level observed by Mashovets and Emtzev [12] and also by Abdurachmanova *et al.* [13] which they attribute to a complex with a dopant impurity (group 5) because the annealing temperature of this level changes monotonically with the nature of the group 5 impurity.

4. Conclusion. — In this paper we described preliminary results concerning the introduction of defects by electron irradiation at room temperature in n-type germanium, obtained by the DLTS technique. We observed two electron traps at $E_c - 0.2 \text{ eV}$, $E_c - 0.40 \text{ eV}$ and two hole traps, one of which is $E_v + 0.25 \text{ eV}$. We provided the order of magnitude of the cross-sections for these traps and described their annealing behaviour.

In order to identify the defects associated with these traps we are now investigating the introduction rates of the traps as a function of the nature and concentration of the doping impurity and as a function of the energy of irradiation. Low temperature electron irradiation will also be performed in order to study the possible annealing of defects in the range 65-300 K.

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