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THE EQUILIBRIUM CONCENTRATION OF THERMAL ACCEPTORS IN p-TYPE GERMANIUM

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Abstract: The temperature and time dependence of thermal acceptors concentration in quenched, galium doped ($6 \cdot 10^{13}$ cm^{-3}), p-type germanium was studied. It is confirmed that the time for thermal acceptor equilibrium concentration reestablishment is considerably shorter than previously reported. The observed thermal acceptor formation energy, $E_A^F = 1.18$ eV, which is smaller than the formation energy of single vacancy ($E_{1V}^F = 1.64 - 2.54$ eV), and the descendant part of the curve $\ln N_A = f(1/T)$ from 870 K to near the melting point of germanium, shows that the process of thermal defects introduction is very complex. The process of single vacancies generation is followed by other processes, such as the formation of divacancies and the associations of vacancies and divacancies including the effects of dislocations which are not negligible.

1. Introduction

There are two aspects of lattice defects study in semiconductor materials:

— since the migration energies of point defects (vacancies and interstitials) in silicon and germanium are too small, it is necessary to perform the measurements at lower temperatures in order to get some information about the single defects;

— at higher temperatures the defects must be regarded as the associations of point defects themselves (divacancies, three-vacancies, ..., clusters) as well as the associations of vacancies and divacancies with the impurities and some other lattice imperfections.

The defects in germanium and silicon have been treated by many authors, but a great number of fundamental problems still exists. Considering the thermal defects as the most interesting problems are the following:

— the sort of thermal defects, introduced by quenching, is not yet completely known;

— the physical meaning of the effective formation energy of thermal acceptors also is not clear. The calculated values of the formation energy of vacancies in germanium, for example, from 1.6 to 2.54 eV[1, 2, 3] can be correlated in some way with vacancies as the thermal acceptors. Moreover, the approximative theoretical values and largely dissipated experimental results, often dependent on the experimental procedure, indicate that any interpretation of phenomena of defects formation will be, more or less, speculative until the nature of defects is definitely solved;

— the time and temperature dependence of equilibrium concentration of thermal defects is insufficiently studied also. In this instance, as the most interesting are the results of Ishino et al.[4] which showed that in antimony doped germanium the equilibrium concentration of thermal acceptors is achieved for 120 min, while in arsenic doped germanium only for 20 min. However, according to the latest results these times are expected to be considerably shorter;

— further problem are models describing the mechanisms of kinetics of thermal defect annealing, based on the single vacancy migration energy of about 1 eV, which are not correct. This statement is stimulated by the fact that in the temperature range from 77 to 300 K several annealing stages of thermal defects exist and some of them can be explained as the migration of single vacancies[5, 6].

The low migration energy of single vacancies in germanium (0.2 eV)[6, 7, 8] and silicon (0.33 eV)[9], among others, emphasized the problem of determination of the equilibrium concentration of thermal defects. The importance of this problem can be comprehended from the single relation between the activation energy of self-diffusion-Q^{Sd}, with the formation energy of vacancy-E^{F}_{IV}, and the migration energy of vacancy-E^{M}_{IV}, so that $Q^{Sd} = E^{F}_{IV} + E^{M}_{IV}$.

Taking the previously known values and the new ones for these quantities the following equations are valid:

$$(Q^{Sd})\ 3\ \text{eV} = 2\ \text{eV}\ (E^{F}_{IV}) + 1\ \text{eV}\ (E^{M}_{IV})\ ,$$

$$(Q^{Sd})\ 3\ \text{eV} = 2\ \text{eV}\ (E^{F}_{IV}) + 0.2\ \text{eV}\ (E^{M}_{IV}) + E_{x}.$$

Assuming that the activation energy of self-diffusion[6, 7] and the formation energy of single vacancies[1, 2, 3] are correct, the excess energy E_x is in question. To solve this problem and to find more precise correlation function between the coefficients of self-diffusion and of vacancies diffusion and their concentrations, $D^{Sd} = D_{IV} f_{IV} c_{IV}$, special attention should be drawn to the equilibrium concentration of thermal defects.

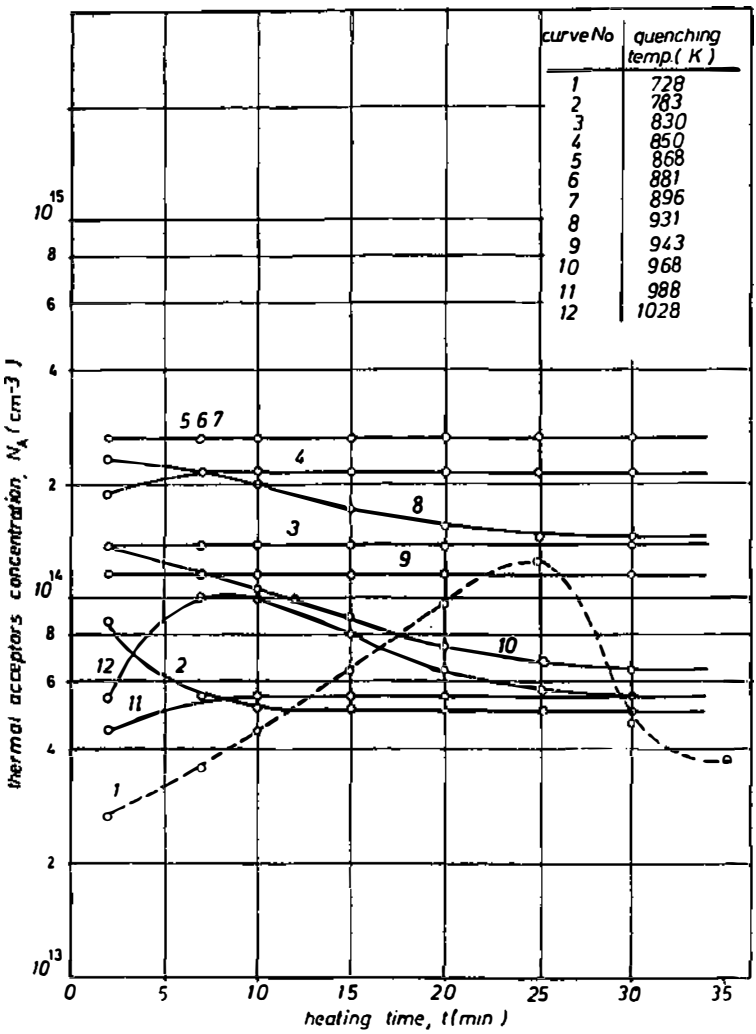

Fig. 1. The concentration of thermal acceptors vs. heating time for various quenching temperatures.

The study of thermal defects equilibrium concentration through their electrical activity is the main subject of this paper.

2. *Experimental method and result*

The thermal acceptor concentration has been measured by original technique and experimental procedure[5, 11]. Samples were cooled from the quenching temperature down to the liquid nitrogen temperature with an initial cooling rate of 10^3 °C/s. The electrical conductivity and Hall coefficient were

measured permanently in the range of 77—1200 K. The horizontally grown galium doped germanium monocrystal was used. The concentration of galium was $6 \cdot 10^{13}\,cm^{-3}$. After the quenching, from the relative variation of hole concentration in respect to its value before quenching, the concentration of

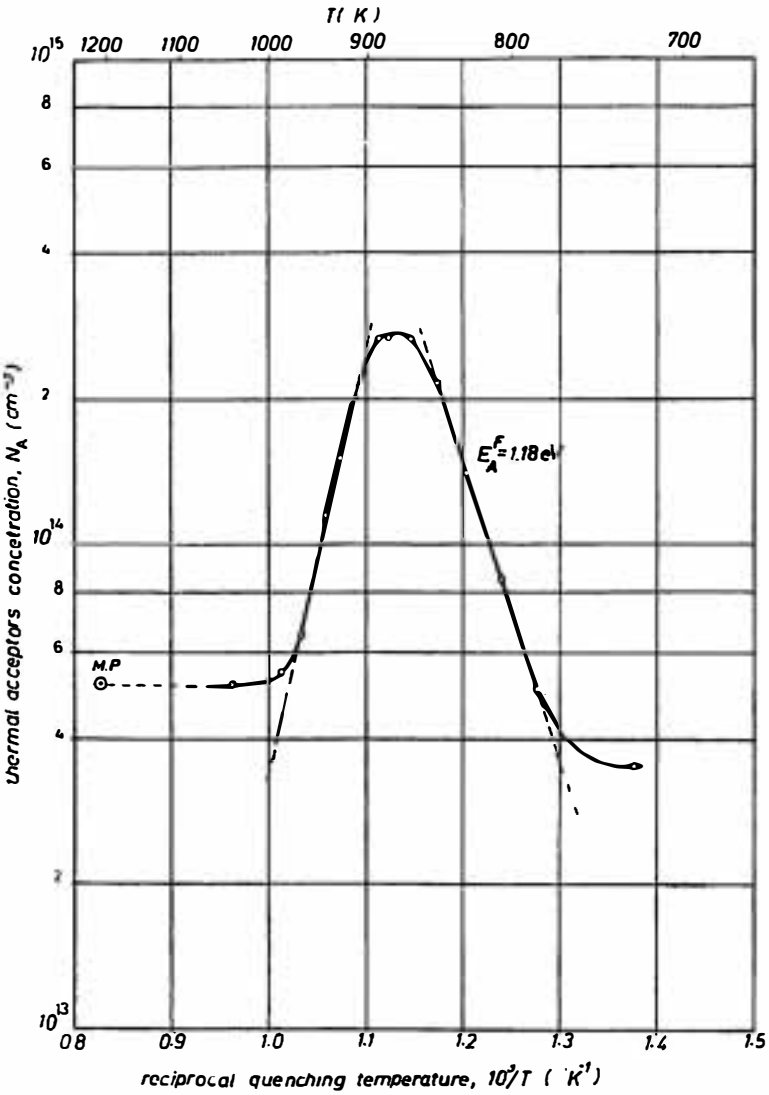

Fig. 2. The equilibrium concentration of thermal acceptors vs. quenching temperature.

thermal acceptors was determined. This concentration, at a given temperature, is measured as a function of heating time until the equilibrium value is reestablished. The complex results given in Fig. 1 show that the time to reach the saturation concentration of thermal acceptors is shorter than

reported by Ishino et al.[4]. The saturated values, in the case of vacancies, have to follow the well-known Arrhenius relation $N_V = N_0 \exp(-E^F_{IV}/kT)$ so the slope of the linear curve $\ln N_V = f(1/T)$ defines the formation energy of vacancies E^F. However, here obtained results shown in Fig. 2 are quite contradictory. From the slope of the linear part of this curve to 870 K the formation energy of thermal acceptors $E^F_A = 1.18$ eV is obtained while from the slope of the descendent part of the same curve, in the interval from 870 K up to the near melting point of germanium the energy $E^Y_X = 1.78$ eV.

Assuming that divacancies or associations vacancy impurity and divacancy-impurity are acceptors, the energy of 1.18 eV can be considered as an effective formation energy E^F_{IVeff}, which consists of binding energy of association E_{IV} and the real formation energy of single vacancy, E^F, thus $E^F = E^F_{IV} - E_B$.

The decrease of effective thermal acceptor concentration in the temperature range from 870 K to the near melting point of germanium, with activation energy of 1.76 eV, can be interpreted in two ways. During the heating at some temperatures from the mentioned range the defects as donors are forming or the defects change its charge state. This will result in the decrease of the fraction of thermal acceptors of impurity acceptor concentration. On the other hand, it is possible that the effective acceptor trap centres are forming, let us say in the process of clustering through the introduced dislocations, whose concentration increases with increasing quenching temperature. The dislocations themselves can act as electrically active entities reducing the properties of studied samples[12, 13]. The above results together with the results of the proceeding study of isochronal and isothermal annealing will give the possibility for a more correct interpretation of phenomena of thermal defects introduction including the interpretation of positive slope of the curve $\ln N_A = f(1/T)$.

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RAVNOTEŽNA KONCENTRACIJA TERMALNIH AKCEPTORA U p-Ge

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Sadržaj

Proučavana je vremenska i temperaturna zavisnost koncentracije termalnih akceptora u kaljenom p-Ge koji je dopiran sa galijumom ($6 \cdot 10^{13}$ cm^{-3}). Utvrđeno je da je vreme za postizanje ravnoteže koncentracije termalnih akceptora znatno kraće od onoga koje su našli drugi autori.

Dobivena energija formiranja termalnih akceptora, $E_A^F = 1{,}18$ eV, koja je manja od energije formiranja elementarne vakancije ($E_{IV}^F = 1{,}64 - 2{,}54$ eV), i opadajući deo krive $\ln N_A = f(1/T)$ od 870 K do blizu tačke topljenja germanijuma, pokazali su da je proces uvođenja termalnih defekata jako složen.

Proces generacije prostih vakancija praćen je jednim ili sa više drugih procesa, kao što su formiranje divakancija i asocijacija divakancija i vakancija sa primesama uključujući i efekte dislokacija koji nisu zanemarljivi.

Tisak: Riječka tiskara — Rijeka