YU ISSN 0015—3206
FZKAAA 14 (3) 155 (1982)

STUDY OF LATTICE DEFECTS IN QUENCHED AND IRRADIATED GaAs SINGLE-CRYSTALS

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Received 20 April 1982

UDC 538.91

Original scientific paper

Thermal defects as well as neutron and Co^{60} gamma rays induced defects have been studied in *n*-type and *p*-type GaAs. Three annealing stages have been revealed. Stage I (260—320°C), which is present only in the irradiated specimens, is assigned to the motion of intrinsic defects. Stage II (around 400°C) is discussed as impurity-defect complexes disintegration. The defects making complexes with impurites which are mobile even at room temperature, probably vacancies of Ga, are negatively charged in *n*-type GaAs. In *p*-type GaAs their charge state is dependent on the Fermi level position being negative at room temperature and positive above 500°C. Stage III (450—530°C) present in quenched and irradiated *n*-type and *p*-type GaAs is explained as the annealing of clusters of defects. The defects induced by quenching, neutrons and Co^{60} gamma rays, which are stable up to 200°C, are similar to each other.

1. Introduction

Most of the published data concerning the problem of lattice defects in GaAs were reviewed by several authors[1,2,3]. It was established that in GaAs processing, particularly with the material of low conductivity, the remarkable changes in conductivity occur, either *n*-type or *p*-type, as a consequence of thermal treatment even when the contamination is avoided[4,5,6]. An important feature in this case is that the acceptors involved are shallow, similar to the effective-mass impurities[7]. Also, two kinds of donor, deep one and one shallow, seem to be involved[8,9]. All these features of thermally treated GaAs can not be simply interpreted on the basis of creation and migration of Ga and As vacancies as it was proposed, for example, by Chaing and Pearson[5].

Micrea and Bois[3] suggested the most plausible general mechanism in which the disintegration of electrically inactive (donor + defect) or (acceptor + defect) complexes is followed by the diffusion of defects toward the surface and donor and/or acceptor thus liberated expresses their electrical activity.

The radiation eflects in GaAs have been studied extensively too[1,3]. For example, in electron irradiated GaAs, by transient emission spectroscopy, five electron traps and one hole trap were resolved. Lang et al.[10] have found that all these states are associated with Ga displacements. This implies either that the defects related to As not have localized states, or that they anneal below room temperature. However, in some earlier experiments[11,12] it was concluded that As sublattice defects do not anneal until 260°C.

Pons et al.[13] indicated that different kinds of GaAs single-crystals behave differently under electron irradiation at room temperature. It is not quite clear whether these differences are impurity or native defects dependent.

So many uncertainties in explaining the nature of lattice defects in GaAs that are induced in every way have been taken as a good stimulation in defining the aim of this work, the main subject of which is the study of thermally induced defects and their relationship with defects induced by reactor neutrons and Co^{60} gamma rays. In this purpose the quenching, irradiation of quenched and unquenched GaAs by reactor neutrons and Co^{60} gamma rays have been used.

2. *Experiment*

Single-crystals of undoped *n*-type GaAs (free carrier concentration 1.1×10^{16} cm^{-3}) and Cd-doped *p*-type GaAs (free carrier concentration 2.2×10^{16} cm^{-3}) have been used in this work. The specimens of rectangular shape ($18 \times 2 \times 1$ mm^3) have been prepared by mechanical polishing and etching by the chemical solution of $H_2O : 30\% \, H_2O_2 : H_2SO_4 = 1 : 1 : 3$.

The quenching procedure consisted of specimens heating in high vacuum (1×10^{-4} Pa) by resistance heating, and cooling down to liquid nitrogen temperature with an initial cooling rate about 1000 deg/s. The range of quenching temperatures was from 450°C up to 637°C which is the decomposition temperature of GaAs below which the compositions of vapour and solid phases are congruent.

In the irradiation experiments the quenched and unquenched specimens of GaAs have been irradiated in nuclear reactor with certain neutron fluence at approximately 50°C, as well as by the known fluence of Co^{60} gamma rays at room temperature.

The electrical conductivity and the Hall coefficient have been measured before and after quenching and irradiation, and after each cycle of isochronal and isothermal annealing. For the convenience in using the pressure point contacts, the reference measuring temperature was 200°C. All the annealing stages, if exist below this temperature, were not considered in this work.

3. *Results and discussion*

The difference in the carrier concentrations in the specimens before and after quenching, which was taken to be proportional to the concentration of thermally induced defects, as a function of quenching temperature, is shown in Fig. 1. From the slope of these curves the formation energies of defects have been determined.

In the *n*-type GaAs (undoped) the concentration of electrons has been decreased with the quenching temperature increasing. It means that the quenched-in defects are acceptor-like, or more probably they are neutral (donor + defect) complexes formed during crystal heating.

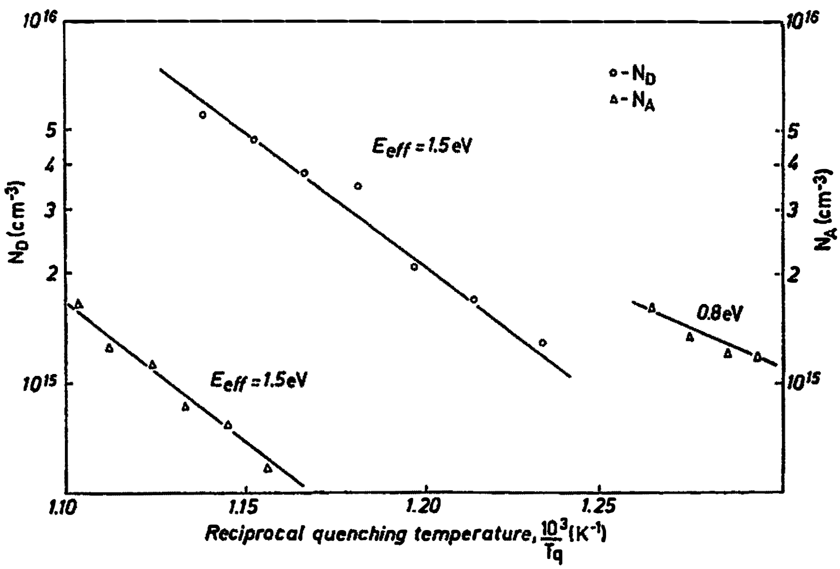

Fig. 1. Concentration of thermal defects, N_A and N_D, versus reciprocal quenching temperature: Δ- *n*-type GaAs, *o*- *p*-type GaAs.

In the *p*-type GaAs (Cd-doped), in the temperature region up to 500°C, an increasing of hole concentration occurs. It seems that a certain acceptor is activated during the heating, with the activation energy estimated as $E = 0.8$ eV. This energy being not far from the activation energy of Cd diffusion in GaAs, which is concentration dependent[28], the acceptors activated by the heating up to 500°C can be assumed as Cd-atoms liberated from certain precipitates, or from complexes with native defects formed during crystal growth. Further quenching of the *p*-type GaAs from 500°C up to 637°C resulted in decreasing of hole concentration with the quenching temperature increasing. The reduction of hole concentration may be considered as donor-like, or (acceptor + defect) complexes formation.

The effective formation energies of the above effects in both *n*-type and *p*-type GaAs, $E_F^{eef} = 1.5$ eV, suggests that almost the same defects are generated during the heating, being negative in the *n*-type and positive in the *p*-type GaAs.

The results of isochronal annealing of quenched (curve 1), unquenched and quenched reactor neutrons irradiated (curve 2), and the Co^{60} gamma rays irradiated (curve 3) n-type GaAs are shown in Fig. 2. The isochronal data of quenched and the Co^{60} gamma rays irradiated Cd-doped p-type GaAs are shown in Fig. 3.

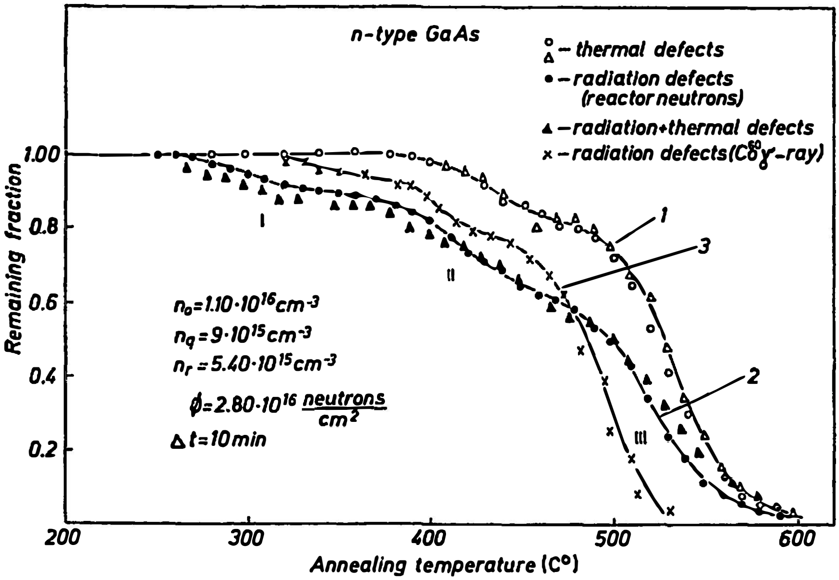

Fig. 2. The isochronal annealing of radiation and thermal defects in n-type GaAs: 1-thermal defects; 2-reactor neutrons induced defects in quenched-(Δ) and unquenched-(o) specimens; and 3- Co^{60} gamma rays induced defects.

The remaining fraction in Fig. 2 and 3 is defined as $(n_0 - n_t)/(n_0 - n_x)$, where n_0 is the concentration of free carriers in specimens before quenching or irradiation, n_t-free carrier concentration after the annealing at certain temperature during the determined time interval ($\Delta t = 10$ minutes), and n_x designates either the free carrier concentration after quenching-n_q, or after irradiation-n_r, or after quenching and irradiation-n_{qr}, respectively.

The annealing of thermal defects occurs via two stages at temperatures of 390°C and 490° C in the n-type GaAs and at 380°C and 450°C in the p-type GaAs. The gamma rays induced defects anneal via three stages in the n-type GaAs at 320°C, 380°C and 450°C. In the p-type GaAs the gamma rays induced defects disappear via two stages at 320°C and 450°C. The reactor neutrons induced defects anneal via three stages at 260°C, 390°C and 490°C, which are almost the same with those in the quenched and the reactor neutron irradiated n-type GaAs.

Comparing the data from figures 2 and 3 one can see that thermal defects and radiation defects induced by neutrons and gamma rays anneal via three stages. The stage I, between 260—320°C, which is present in the Co^{60} gamma rays irradiated p-type and n-type GaAs, in the quenched and unquenched reactor neutrons irradiated n-type GaAs, does not exist in specimens which have been quenched only. In reactor neutrons irradiated specimens this stage is more pronounced and

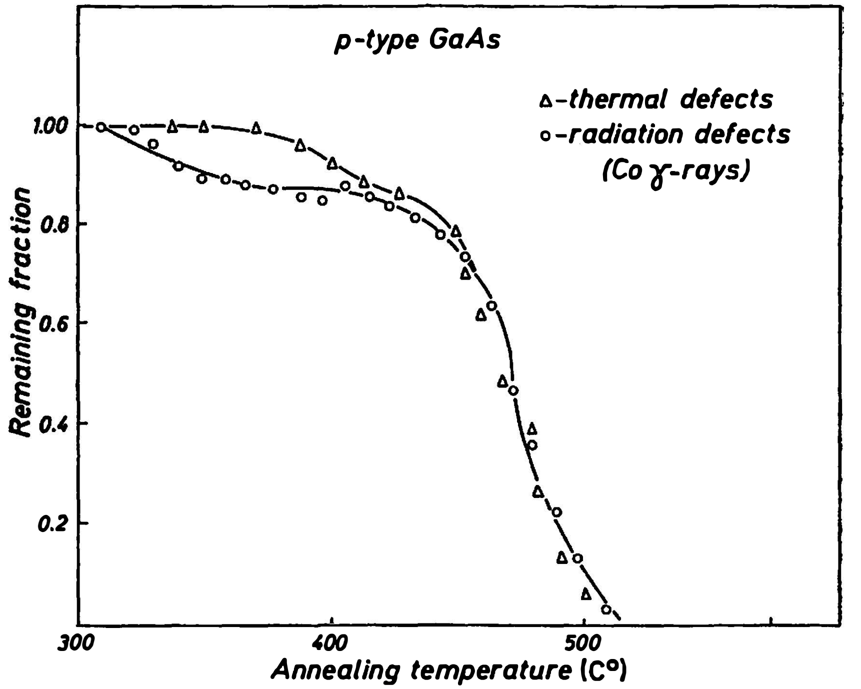

Fig. 3. The isochronal annealing of thermal and radiation defetcs in p-type GaAs: 1-thermal defects; 2-Co^{60} gamma rays induced defects at room temperature.

extended towards the lower temperatures. Stage I with the activation energy of 0.8 eV is well described by the first order kinetic and it lies close to the earlier reported stage at 240°C. This stage has been related wi h donor-vacancy complexes[14] but none of these impurity-defect complexes have been reported in *DLTS* spectra, perhaps because they are so shallow. Lang[2] has noticed that the impurity effects are not very noticeable in the properties of irradiated GaAs at room temperature, but do become important above 230°C. The stage I we observed is presumably due to the motion of isolated intrinsic defects and in some respect it is similar to hose found by Aukermann and Graft[15] and Brailovskii et al.[16] in electron irradiated GaAs. The fact that this stage I does not exist in the quenched n-type and p-type GaAs supports the idea about isolated intrinsic defects motion in this stage.

The stage II around 400°C has been discovered in iradiated GaAs by other authors. Brailovskii and Brundnyi[17] and Brailovskii et al.[16,18] proposed that the stage 400°C is due to the clustering of individual point defects formed during the annealing of stage 230° C. According to these authors, 400°C stage becomes more pronounced after a high fluence (10^{17} cm^{-2}, 1 MeV), or a high energy (3 × 10^{15} cm^{-2}, 45 MeV) electron irradiation. A similar high fluence effect for 1 MeV electron irradiation was seen by Kalma and Berger[20] and Kalma[19]. The stage 400°C is dominant for fast neutron irradiation of n-type GaAs as it was established by Aukermann et al.[21].

We established that the annealing stage II around 400°C, with activation energy of 1.0 eV, obeys the kinetic of the first order. It appears in the quenched *n*-type and *p*-type GaAs, in both quenched and unquenched reactor neutrons irradiated *n*-type GaAs, in room temperature Co^{60} gamma rays irradiated *n*-type GaAs, but not in the gamma irradiated *p*-type GaAs. This stage is more pronounced in the quenched and unquenched *n*-type GaAs irradiated by neutrons in the gamma irradiated *n*-type GaAs (Fig. 2). The absence of this stage in the gamma irradiated *p*-type GaAs may help in explaining the origin of the stage II. Presuming that individual intrinsic defects disappear at lower temperatures (stage I) by clustering[16,17,18], and that the 400°C stage is due to cluster disintegration, than the question is why these clusters do not exist in the gamma irradiated *p*-type GaAs in which stage I is evidently present. There is also a question how it is possible that in the quenched *p*-type GaAs the stage II is present even when the stage I is absent.

We have assumed that at irradiation temperatures (room temperature for gamma irradiation and about 50°C in the reactor neutron irradiation) two kinds of isolated intrinsic defects are formed. A mobile defect can make self-clusters, and interacting with impurities, the impurity-defect complexes. In *n*-type GaAs the positive donor-D^+ can associate via coulombic interaction with those mobile defects which are in opposite charge state. Supposing that Ga vacancies are such defect, during the quenching and the irradiation as well, the following reaction may occur: $D^+ + V_{Ga}^- = (D^+ V_{Ga}^-)^\circ$. Thus the concentration of electrons will be reduced proportionally to the concentration of these neutral complexes. In the *p*-type GaAs it seems that these mobile defects are in the same charge state as Cd acceptors, so the coulombic repulsion dominates. Because of that, in the *p*-type GaAs irradiated by Co^{60} gamma rays the stage II does not exist. On the contrary, this stage is present in the quenched *p*-type GaAs because the condition for complex formation is fulfilled. Namely, at higher temperatures the position of Fermi level is reduced so that the mobile defect changes from negative or even neutral charge state into positive state being now able to associate with negative Cd^- acceptor. This complex, $(Cd^- V_{Ga}^+)$, and the complex $(D^+ V_{Ga}^-)$ may disintegrate via the discussed annealing stage II around 400°C.

The impurity-defect complex formation at room temperature is in agreement with the results of Thompson et al.[27] who have found that the impurity dependent defects at room temperature irradiated GaAs are induced with relatively small rate of induction which was estimated to be 10^{-2} cm^{-1}.

The stage III around 500°C, which is present in all the above discussed cases, belongs probably to the clusters of defects. The activation energy for this stage, which is determined to be $E_a = 1.5$ eV, indicates the strong binding of defects in the clusters. Several high temperature annealing stages have been observed in GaAs, as refered in literature. Hutchinson and Dobson[22] observed long-range interstitial motion at 450°C. Cho[23] found that amorphous films of GaAs crystallize within less than one hour at 500°C. In large-fluence implants Hunsperger and Wolf[25], Borders[24] and Grob et al.[26] discovered a new stage appearing in the vicinity of 600—700°C. The last two stages are similar to the annealing of heavily disordered (nearly amorphous) ion implanted regions, which support the idea of defect clusters breaking-up in the stage III.

There were many attempts to associate the high temperature annealing stages with self-interstitials in GaAs, which might be included in a mechanism o defect dissapearing as stage I (260—330°C) either as individual defect or together with vacancies as close Frenkel's pairs, but it is not clear how interstitials can disappear via stages II and III in GaAs if the above discussion is correct.

4. Conclusion

According to the above experimental results concerning the lattice defects study in *n*-type and *p*-type GaAs, the following conclusions can be drown. By quenching of GaAs from temperatures below its decomposition temperature (637°C), nearly equal concentration of defects are induced in both *n*-type and *p*-type GaAs (10^{14}—10^{15} cm^{-3}). The same value of the effective formation energy, $E_F^{eef} = 1.5$ eV, as well as the annealing data generaly support the idea that almost the same defects are created in both materials. They make (donor + defect) in *n*-type GaAs and (acceptor + defect) complexes in *p*-type GaAs disappearing around 400°C, and also they cluster in defects the annealing of which occurs around 450—530°C.

In neutron and gamma rays irradiated *n*-type GaAs three annealing stages are revealed (stages I, II and III), and in gamma irradiated *p*-type GaAs two stages are observed (stages I and III). Stage I which appears in all irradiated specimens is explained by the motion of isolated intrinsic defects. Other two stages are equivalent with those observed in quenched specimens indicating that neutron and gamma rays induced defects, disappearing in stages II and III, are similar to thermal defects (impurity-defect complexes, stage II and clusters of defects, stage III). The formation of the stage II defects in the *n*-type GaAs during the irradiation with neutrons at about 50°C and by Co^{60} gamma rays at room temperature, shows that some of the radiation created defects, probably vacancies of Ga, are mobile even at room temperature.

In the *p*-type GaAs during gamma irradiation at room temperature the formation of complexes (acceptor-defect) does not occur (absent stage II) probably because ionized acceptors and mobile defects are in the same charge state. At higher temperatures these defects associate with negative acceptors (the stage II is present in quenched *p*-type GaAs) because of changing the charge state from negative into positive. According to this fact one can conclude that room temperature mobile defects created by radiation in *p*-type GaAs have charge state dependent on the Fermi level position.

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PROUČAVANJE STRUKTURNIH DEFEKATA U ZAKALJENIM I OZRAČENIM MONOKRISTALIMA GaAs

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Originalni naučni rad

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Proučavani su termički defekti, kao i defekti koji su indukovani neutronima i gama zračenjem Co^{60} u *n*- i *p*-GaAs. Otkrivena su tri stanja odgrevanja. Stanje I (260—320°C) koje je prisutno samo u ozračenim uzorcima, pripisano je odgrevanju sopstvenih defekata. Stanje II (oko 400°C) objašnjeno je kao dezintegracija kompleksa primesa-defekat. Defekti koji s primesama formiraju komplekse, a koji su pokretni na sobnoj temperaturi, su negativno naelektrisani u *n*-GaAs. U *p*-GaAs njihovo stanje naelektrisanja zavisno je od položaja Fermijevog nivoa tako da su na sobnoj temperaturi negativni a na višim temperaturama pozitivni. Stanje III (450—530°C) objašnjeno je kao odgrevanje klastera defekata. Defekti koji su indukovani kaljenjem, neutronima i gama zračenjem, a koji su stabilni do 200°C, su slični međusobom.