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Monovacancy–As complexes in proton-irradiated Ge studied by positron lifetime spectroscopy

M. Elsayed,[a,b,*] N. Yu. Arutyunov,[a,c] R. Krause-Rehberg,[a] V.V. Emtsev,[d] G.A. Oganesyan[d] and V.V. Kozlovski[e]

[a] *Department of Physics, Martin Luther University Halle, 06099 Halle, Germany*
[b] *Department of Physics, Faculty of Science, Minia University, 61519 Minia, Egypt*
[c] *Institute of Ionic-Plasma and Laser Technologies (Institute of Electronics), 700187 Tashkent, Uzbekistan*
[d] *Ioffe Physico-Technical Institute, St Petersburg 194021, Russia*
[e] *St Petersburg State Polytechnical University, St Petersburg 195251, Russia*

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Abstract—We applied positron annihilation lifetime spectroscopy to study the proton-irradiation-induced defects in germanium and its annealing behavior. The *n*-doped Ge ([As] = 9×10^{17} cm^{-3}) samples were irradiated at room temperature with a proton energy of 15 MeV at a dose of 10^{15} cm^{-2}. We distinguished a complex containing a vacancy and arsenic atoms. In addition, we observed shallow positron traps, which are ascribed to the impurities in a Ge lattice crystal. Isochronal annealing experiments were carried out in the temperature interval 300–820 K. Temperature-dependent positron lifetime measurements were performed after each annealing step. During isochronal annealing of the proton-irradiated Ge, a vacancy–As complex was found to dissociate to its constituents and the single monovacancies eventually anneal out. Two annealing stages were observed: the first, at ~450 K, was attributed to the dissociation of complexes and the second annealing stage, at 650 K, was assigned to annealing of vacancies. Shallow positron traps anneal in the temperature range 540–660 K.

Keywords: Germanium; Positron annihilation; Point defect; Proton irradiation; Vacancy–impurity complexes

1. Introduction

As silicon has dominated the semiconductor industry for the past several decades, it is one of the most widely studied materials. Germanium has attracted significant attention in the past few years due to the high mobility of electrons and holes in this material. The properties of Ge are much less well understood than those of Si, fundamentally thanks to the dominance of Si technology. Among the important properties that still need investigating are the formation mechanisms of point defects introduced by proton irradiation and their thermal evolutions. It is well known that point defects such as vacancies and vacancy–impurity complexes play an important role in determining the electrical and optical properties of semiconductors by introducing energy levels within the bandgap, acting as generation or recombination centers. In semiconductor materials, point defects can be introduced during crystal growth, diffusion, device fabrication and irradiation. However, they can be introduced in higher concentrations by means of irradiation, e.g. by protons. Intriguingly, irradiation can also be used to generate specific point defects in specific amounts to distinguish the properties. The study of the formation of point defects under these non-equilibrium conditions provides information on the physical properties of the semiconductor. Among all the different point defect types in semiconductors is the group-V-impurity–vacancy complex in Ge (or *E*-center). It involves a vacancy and a group-V donor atom (As, P or Sb). *E*-centers robustly impact not only the electrical properties but also the migration of impurities (dopants) [1,2]. The annealing behavior, structure and energy levels of the defects created by irradiation in Ge [3,4] were studied by using electrical measurements and spectroscopic techniques. Results of these studies were found to be related to the annealing mechanism of close Frenkel pairs [5,6] and interstitial atoms [7,8]. Besides, complex defects (e.g. vacancy–impurity pairs) may arise from the possible ionization-induced motion of interstitials [9]. Vacancy-like defects, as well as complexes involving doping and interstitial atoms, were studied in electron-irradiated Ge (dose, $\Phi < 10^{17}$ cm^{-2}) [3]. X-ray diffraction investigations of electron-irradiated Ge ($\Phi \sim 10^{19}$ cm^2) showed the formation of stable Frenkel pairs [10] and were found to

* Corresponding author at: Department of Physics, Martin Luther University Halle, 06099 Halle, Germany; e-mail: melabdalla@yahoo.co.uk

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anneal out at 70 K [3]. A second annealing stage in the temperature range 150–200 K was explained by the mobility of the neutral vacancy in this temperature range. The other defect complexes annealed above 400 K and are associated with the mobility of the divacancy. A complete recovery is observed at 600 K [10]. A deep level transient spectroscopy (DLTS) study of electron-irradiated Ge showed that impurities play a key role in the production of irradiation-induced defects [11]. An annealing stage at ~400 K was observed and assigned to divacancy–oxygen complexes. Fukuoka et al. have studied the defects formed by room temperature (RT) irradiation by γ-rays, electrons (1.5 MeV) and neutrons in As-, Sb- and O-doped Ge [12]. An annealing stage at 533 K was assigned to the annealing of vacancy clusters [12]. Three annealing stages were found in 4.4 MeV electron-irradiated Ge at 90 K [13]: the first stage at 150 K was ascribed to the annealing of the vacancy interstitial, the second in the temperature range 180–420 K to the vacancy complex annihilation and the production of stable complexes, and the third above 420 K to full recovery of all these defects. Vacancy–oxygen complexes were detected during annealing of 3 MeV electron-irradiated Ge [14,15], and were found to vanish completely at 550 K owing to dissociation and evaporation of the complex. Vacancies in germanium are found to be the main diffusion-mediating point defect in self-diffusion [16–20] and impurity diffusion [19,21]. A formation energy of ~2 eV for the negatively charged vacancy was determined [16].

In this paper we study the point defects induced in As-doped Ge by RT 15 MeV proton irradiation. We apply positron annihilation spectroscopy (PAS) in the mode of lifetime, which is a sensitive probe for both open volume defects (e.g. vacancies) and non-open volume defects (e.g. negative ions) [22]. Positrons trapped at vacancy-like defects are associated with subsequent changes in their specific annihilation parameters, such as lifetime [23]. The positron lifetime provides the size of open volume defect. When the positron wave function is weakly localized, the defects are named shallow positron traps; they are considered as negatively charged non-open volume defects such as negative ions [24]. Positrons are effectively trapped to these defects only at low temperatures due to the weak binding energy (<100 meV), and thus they are thermally detrapped at higher temperatures. The positron annihilation parameters in these defects are very close to those in defect-free bulk material.

A few positron studies of vacancy-like defects in irradiated Ge have been reported. A neutral divacancy was identified by PAS and found to be stable at RT [25]. A negative charge state for the divacancy was also reported [25]; these results are confirmed by DLTS study [26]. PAS investigations on germanium irradiated with electrons at low temperatures have been performed [14,15,27]. A defect positron lifetime τ_2 of 292 ps [14] and 290 ps [15] was observed. Polity and Rudolf [27] reported τ_2 of 281 ps, measured at 90 K, and assigned this value to a Ge monovacancy defect. An annealing stage at 200 K is detected, which is assigned to annealing of Frenkel pairs. A defect-related positron lifetime τ_2 of 292 ps was observed during the annealing in the temperature interval 77–675 K [15]. PAS study of weakly *n*-type Ge:Sb irradiated with protons at low temperature (35 K) showed a defect lifetime component of 272 ps at 35 K, which is assigned as a monovacancy [28]. In this study, two annealing stages were observed upon annealing in the temperature interval 35–300 K; the first at 100 K is ascribed to the annealing of the Frenkel pair and the second at 200 K to the annealing of the monovacancy. A defect positron lifetime of 315 ps is detected above 200 K, which is identified as a divacancy. This was assigned to the mobility of neutral monovacancies. Recently, our positron annihilation study of vacancy-like defects in proton-irradiated Ge:P showed the formation of relaxed monovacancy–*P* complexes [29].

In this work, we explore the production and thermal annealing of the point defects generated in Ge:As by RT irradiation with 15 MeV protons using positron annihilation lifetime spectroscopy. We present a direct observation of the monovacancy–As complexes in Ge and its thermal evolution. The samples were isochronally annealed in the temperature interval 300–840 K and PAS lifetime measurements in the temperature interval 35–300 K subsequent to each annealing step were carried out. The vacancy–As complexes and negative-ion type defects act as compensating centers and are introduced at a concentration $[V\text{–}As] = 10^{17}\ \mathrm{cm}^{-3}$ and $C_{st}\ 10^{15}\ \mathrm{cm}^{-3}$, respectively. The negative-ion type defects anneal out in the temperature range 540–660 K.

2. Experimental details

The investigated samples were cut from As-doped FZ-Ge bulk single crystal, in which the dopant concentration was $n = 9 \times 10^{17}\ \mathrm{cm}^{-3}$. The material was oxygen- and carbon-lean. The positron lifetime experiments were performed in as-grown single crystal Ge:As. The samples were irradiated with 15 MeV protons at RT to a dose of $10^{15}\ \mathrm{cm}^{-2}$. The samples had not been investigated until the level of induced radiation became acceptable and reached the value less than the maximum permissible dose for the working place. A thin surface layer of the samples is chemically etched after the irradiation in order to clean the near-surface region from possible non-radioactive contaminations.

The thickness of the samples was ~0.5 mm, which allowed us to neglect any considerable stoppage effects. In fact, the protons went through the samples very effectively because the stopping range of 15 MeV protons in the Ge material is ~ 0.85 mm. This numeral value is significantly higher than the mean penetration depth of positrons (~0.05 mm) emitted by a ^{22}Na radioactive source. Hence, virtually all positrons are annihilated in the layer affected by proton irradiation and where the radiation defects were produced quite homogeneously. The samples were mounted in the conventional sandwich setup, with a ^{22}Na e^+-source wrapped in a 2 μm aluminum foil. A conventional fast–fast coincidence system with a time resolution of 220 ps [30–33] and a 20 μCi ^{22}Na positron source was used for positron lifetime spectroscopy measurements. The samples were isochronally annealed for 20 min in the temperature range up to 820 K under vacuum conditions ~10^{-3} mbar, while they were cooled down slowly after each annealing step. Between the annealing steps, temperature-dependent positron lifetime measurements in the temperature interval 35–300 K were done. Typically 4×10^6 annihilation events were accumulated in each positron lifetime spectrum. Source contribution of 14.6% with three components was determined by measuring a defect-free reference sample; two lifetime components of 162 ps (9.6%) and 380 ps (4.8%) correspond to the annihilation of positrons in Al foil and NaCl,