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Positron probing of point V-group impurity-vacancy complexes in γ-irradiated germanium

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Abstract

For the first time the positron probing of the vacancy—V-group-atom impurity complexes, which were created by γ-irradiating ^{60}Co ($T_{irr.} \approx 280$ K) in the oxygen-lean n-Ge$\langle$V$\rangle$ (V = As, Sb, or Bi), has been conducted systematically both before and after n-p-conversion of material. The one-dimensional angular correlation of the annihilation radiation (ACAR) has been registered for crystallographic directions [1 1 1], [1 1 0], and [1 0 0]. The concentration of defects in the same samples was determined from the temperature dependencies of the carrier density and mobility obtained over the range of 4.2–300 K.

It was found that (i) the trapping cross section of positrons by the radiation complexes is over the range of $(0.7–4.3) \times 10^{-15}$ cm^2, and (ii) the size of V-group-atom situated in nearest environment of the positron plays crucial role in generating elementally specific emission of the annihilation γ-quanta. The positron-sensitive vacancy—V-group-atom impurity complexes, or E centres, are formed under γ-irradiation at room temperature in oxygen-lean n-Ge$\langle$V$\rangle$ (V = As, Sb, or Bi); this process is accompanied by removing free electrons and at higher doses of irradiation the n-p-conversion occurs. Deeply converted material of p-type contains acceptor centres whose energy levels depending on V-group-atom size are over the range of $E_v + (0.1–0.16)$ eV. The positron annihilation data are interpreted in terms of successive trapping of vacancies by the E centres to be formed, in particular, before n-p-conversion of γ-irradiated material.

Keywords: Germanium; Positron; Annihilation radiation; Angular correlation; Point radiation defects

1. Introduction

The problem of identification of point radiation defects in germanium is basically a very complicated one owing to well-known difficulties of an unambiguous interpretation of the broadened EPR-spectra related to a considerable amount of paramagnetic nuclei of ^{71}Ge isotope in the investigated samples (see [1] and references therein). Under these conditions a phenomenon of the positron localization on defects of crystal lattice makes it possible to apply this particle as a unique probe of the microstructure of the positron-sensitive centres inasmuch as the annihilation radiation provides elementally specific data coming from the nearest surroundings of positron [2]. One obtains it by recording the ACAR spectra for different

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crystallographic directions chosen for an investigation [3]. For a variety of reasons this structural information is inaccessible for obtaining by studying the Doppler broadening of the annihilation radiation or by measuring the positron lifetime (in particular, due to the detection of the isotropic flow of the 2γ-annihilation radiation underlying these two methods [4]). Earlier there has been established that the point defects formed in germanium both under γ- and neutron irradiation are capable of trapping positrons [5]. In this work, for the first time the ACAR spectroscopy has been systematically applied for studying the microstructure of point defects both in n- and p-type material of γ-irradiated germanium doped with V-group-atom impurities (Ge$\langle$V$\rangle$, V = As, Sb, or Bi).

2. Experimental

The single crystals of oxygen-lean germanium ($[O_i] \leqslant 5\times10^{16}\,cm^{-3}$) with lower carbon concentration $[C_i] \leqslant 10^{16}\,cm^{-3}$ have been investigated. The concentration of V-group-impurity atoms was $\sim 7\times10^{14}\,cm^{-3}$–$10^{16}\,cm^{-3}$. The density of dislocations did not exceed $\sim 3\times10^{3}\,cm^{-2}$. These single crystals were cut into samples oriented along the [1 1 1], [1 1 0], and [1 0 0] crystallographic axes. The samples were irradiated with the γ-quanta ^{60}Co at 280 K; the power of dose was $\sim 5\times10^{12}\,cm^{-2}\,s^{-1}$. The concentrations of defects (N_d) in the same samples were determined from the temperature dependences of the carrier density and mobility obtained in the range 4.2–300 K (the method of the analysis of these dependences one may find in [1]).

The long-slit scheme has been used for measuring of the ACAR spectra at room temperature with the resolution $\Delta \approx 0.9\times10^{-3}$ radian (see Fig. 1). The magnitude of angle of registration of the annihilation γ-quanta (θ) to be emitted out of the sample is known to be approximately proportional to the component of the momentum of electron, $p_Z \approx \theta m_0 c = p$, which is directed in parallel to the investigated crystallographic axis (m_0 is the electron mass, c is the velocity of light in vacuum). By this way the anisotropy of the ACAR spectra has been investigated for the radiation defects (see below). The isotope ^{22}Na (~20 mCi) has been applied as the positron source. The statistical error of measurements of the ACAR spectra was over the range of $\geqslant$0.3%–$\leqslant$0.7%.

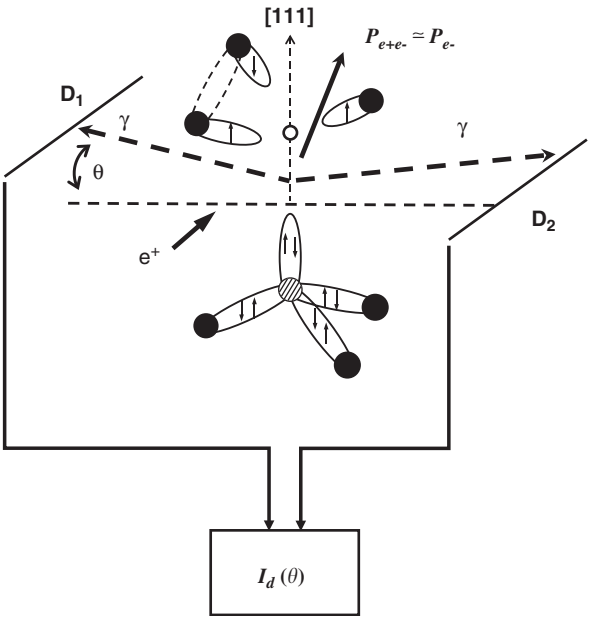

Fig. 1. The principle way of experiments: the positron (e^+) to be emitted from the radioactive source into the sample is trapped by the complex of V-group-impurity atom with vacancy, then two γ-quanta with total momentum $P_{e^+e^-}$ are generated, and their angular correlation is registered by the long-slit detectors, D_1 and D_2. Open and shaded circles designate the vacancy and V-group-impurity atom in the E-centre, respectively. The arrows indicate the occupation of orbitals; the closing of the dangling bonds is possible near the vacant site (dashed line).

3. The analysis of results of ACAR measurements

The relation between the positron trapping rate k and the concentration of defects N_d was used for estimating the positron trapping cross section σ_+ [4]:

$$\frac{P_d}{1-P_d}\,\tau_0 = k = \sigma_+ v_+ N_d, \tag{1}$$

where τ_0 is the positron average lifetime in the non-irradiated material ($\tau_0 \cong 217$–225 ps for the defect-"free" germanium, see, e.g. [4,9]); P_d and $(1-P_d)$ are the probabilities of observable events of the positron annihilation, namely, in the region of a defect and out of it; $v_+ \leqslant 10^7$ cm/s is the velocity of the thermalized positron at room temperature. The assumption about the two-component ACAR for irradiated material (I_Σ) is used:

$$I_\Sigma = I_d P_d + I_0 P_0, \quad P_d + P_0 = 1, \tag{2}$$

$$\frac{P_d}{1-P_d} = \frac{|I_\Sigma - I_0|}{|I_d - I_\Sigma|}, \tag{3}$$

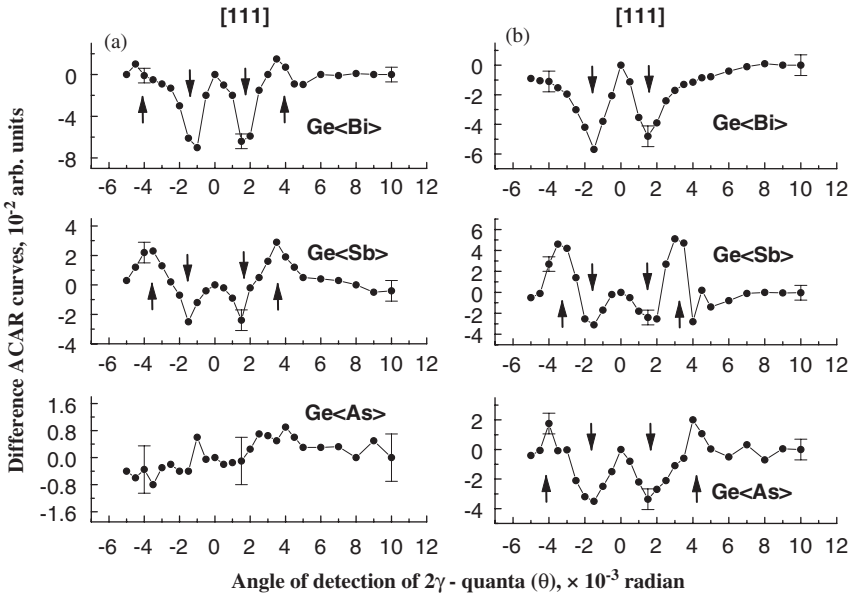

Fig. 2. The difference ACAR curves recorded for the crystallographic direction [1 1 1] of the γ-irradiated (^{60}Co/Tirr. = 280 K) and initial oxygen-lean n-Ge$\langle$V$\rangle$ (V = As, Sb, or Bi): (a) and (b) are the data obtained before and after n-p-conversion, respectively (n-I_dP_d and p-I_dP_d curves, see Eq. (5)). The arrows indicate the features resulted from the presence of different V-group atoms in the microstructure of the radiation complexes.

where I_d and I_0 are the ACAR spectra for the region of defects and in the defect-"free" bulk of the crystal, respectively. The value of P_d has been estimated by experimental data

$$P_d \cong \int_0^{15} I_\Sigma(p)\,dp - \int_0^{15} I_0(p)\,dp \Big/ \int_0^{15} I_\Sigma(p)\,dp, \tag{4}$$

assuming that the efficiency of emission of γ-quanta from the region of defects is substantially weaker in comparison with the resulting one, i.e. $I_d \ll I_\Sigma$ and $P_d \ll 1$. The $I_d(\theta)$ component reflecting anisotropy of the electron momentum distribution in the investigated defect has been obtained by the ACAR curves recorded for different directions in the crystals of γ-irradiated germanium (see Fig. 2):

$$I_d \cong [I_\Sigma - I_0(1 - P_d)]P_d^{-1}. \tag{5}$$

It was found that the configuration of defect affects substantially the mean values of $\langle I_dP_d\rangle$ (see Fig. 3). The P_d values obtained by ACAR for [1 1 1] crystallographic directions have been used for estimations of σ_+ (see Eq. (1) and Fig. 4).

4. Results and discussion

4.1. Initial materials Ge:V(V = As, Sb, or Bi)

Typical anisotropic ACAR curves for initial material the reader may find in [3,5–8]. Any influence of shallow centres of the V-group impurities on the parameters of the ACAR spectra was not found within the accuracy of experiments. The direction of bonds in the crystal lattice is a crucial factor affecting anisotropic properties of two-quantum annihilation radiation [6,9–11]).[1]

4.2. Irradiated materials Ge:V(V = As, Sb, or Bi), before n-p-conversion

Here the anisotropy of ACAR depends on the size of atom of the donor impurity thus suggesting the influence of V-group atoms on the electron–positron momentum distribution (see Fig. 2a). In particular, this dependency manifests itself in rising

[1] A role of the atomic environment in generating elementally specific ACAR related to the annihilation of positrons in the vacancy complexes in some diamond-like semiconductors and nitrides is considered in [2].

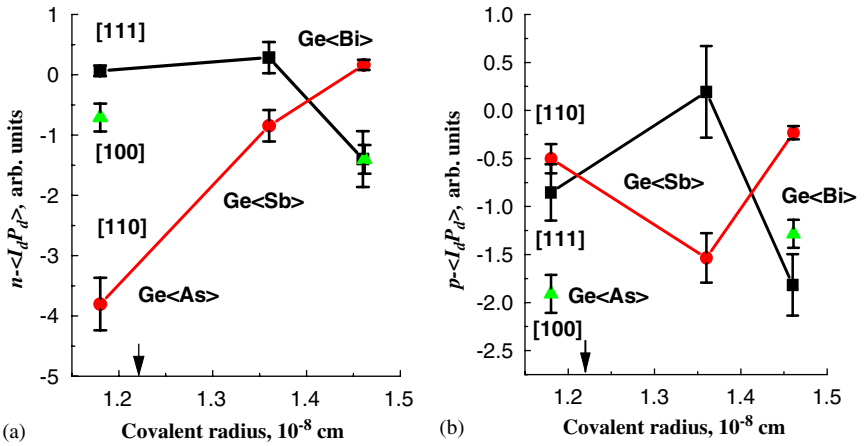

Fig. 3. Mean value of the difference function $\langle I_d P_d \rangle$ (see Eq. (5)) characterizing the electron momentum distribution in the radiation complexes vs. the covalent radius of V-group-impurity atom in γ-irradiated germanium before (a) and after (b) n-p-conversion: ■—crystallographic direction [1 1 1], ▲—[1 0 0], and ●—[1 1 0]. The arrows show the value of covalent radius of germanium (the lengths of radii are cited by [15]).

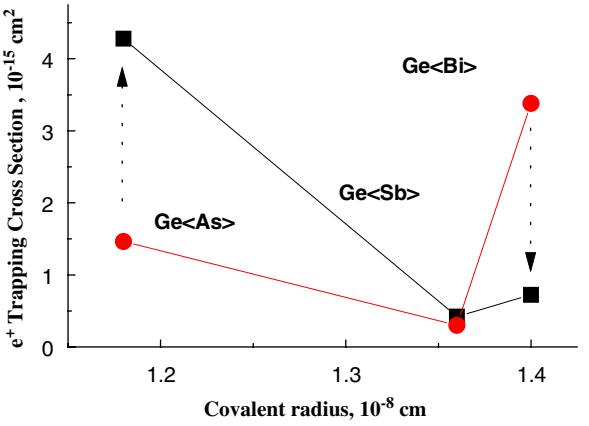

Fig. 4. The trapping cross section of positrons by the radiation complexes (σ_+) in γ-irradiated germanium vs. the covalent radii of the V-group-impurity atom: ●—the configuration "mono-vacancy + V-group-impurity atom" in n-Ge$\langle$V$\rangle$ (V = As, Sb, or Bi); ■—"multi-vacancy + V-group-impurity-atom" in p-Ge$\langle$V$\rangle$ (V = As, Sb, or Bi). The arrows show the changes of σ_+ magnitudes in passing from one configuration of the centre to another.

of the mean value n-$\langle I_d P_d \rangle$ in passing from As to Bi for the crystallographic direction [1 1 0] whereas there is observed an opposite tendency for [1 1 1] direction (see Fig. 3a). The positron trapping cross section (σ_+) is slightly increased depending on the rise of the covalent radius of V-group-atom (see Fig. 4). Probably, the order of magnitude of $\sigma_+ \cong 10^{-15}\,\mathrm{cm}^2$ indicates the distortions of the crystal lattice conducive to the positron trapping by the complexes of V-group-atom with vacancies.[2] Interestingly, that much larger value $\sigma_{ph} \cong (0.875–1.8) \times 10^{-13}\,\mathrm{cm}^2$ has been obtained by DLTS for so-called apparent capture cross section of holes by V-group-atom vacancy complexes of a such type [14].

The changes of the anisotropy of ACAR spectra are maximal for the impurity atom whose covalent radius is different most considerably from the one of germanium, i.e. for the As-contained positron traps (r_0(Ge) ≅ 1.22 Å and r_0(As) ≅ 1.18 Å, the values of the covalent radii are cited by [15]). For the larger differences of $\{r_0(\mathrm{Ge}) - r_0(\mathrm{V} = \mathrm{As, Sb, Bi})\}$ there are more considerable changes registered in the emission of the annihilation γ-quanta from the radiation impurity complexes when [1 1 0] crystallographic direction is under study and, on the contrary, the opposite picture is observed for [1 1 1] axis (see Fig. 3a). Also, the difference between r_0(Ge) and r_0(V = As, Sb, Bi) affects the positron trapping cross section showing a tendency to its rise vs. the increase of size of V-group atom (see Fig. 4, dots). The formation of these positron traps is accompanied by the lost of donor activity of V-group-impurity atoms in γ-irradiated Ge:V(V = As, Sb, or

[2]Yet larger cross section (10^{-12}–$10^{-13}\,\mathrm{cm}^2$) of the positron trapping is predicted for the vacancy-type centres in silicon [12]; the values 10^{-15}–$10^{-16}\,\mathrm{cm}^2$ have been obtained for the impurity centres of atoms of the transition metals in GaP [13]. Theoretical predictions concerning the trapping cross section of positrons by the vacancy complexes in germanium are absent.

Bi); the donor–acceptor pair "vacancy + V-group-atom" is electrically neutral (or inactive) in the material of n-type[3] [1]. Interestingly, that thermal stability of complexes of V-group-impurity atoms with vacancies is getting larger with an increase in the size of donor atoms [1,14].

4.3. Irradiated material Ge:V(V = As, Sb, and Bi), after n-p-conversion

The ACAR anisotropy related to the point radiation defects is different from the one observed for the material investigated before its n-p-conversion suggesting that the configuration of the defects has been changed in passing from n-type material to the one of p-type (see Fig. 3a and b).

A decrease of the mean value of p-$\langle I_d P_d \rangle$ manifests itself quite distinctly for [1 1 1] and [1 0 0] crystallographic directions (by ~68% and ~56%, respectively), whereas there is observed its uprise by ~98% for [1 1 0] crystallographic direction.[4] After n-p-conversion the positron trapping cross section is slightly diminished for p-Ge:Bi, and, on the contrary, for p-Ge:As one may see its increase (see. Fig. 4, squares). The results of analysis of the temperature dependencies of the concentration and mobility of carriers in the materials under study indicate a considerable amount of the defects having acceptor levels in the forbidden gap [1,8]: $E_v + 0.1$ eV (Ge:As), $E_v + 0.12$ eV (Ge:Sb) and $E_v + 0.16$ eV (Ge:Bi). The configuration including V-group-impurity atom and four vacancies is most suitable for a consistent interpretation of the kinetics of accumulation of these complexes; this implies that the centre "V-group-donor + vacancy" is capable of trapping more vacancies [1].[5]

The formation of the defects under discussion is known to be accompanied by fast free electron removal and, according to the evidence obtained by DLTS measurements, there are registered a pronounced changes in the values of enthalpy and entropy of the ionization of vacancy-group-V-atom impurity complexes in γ-irradiated germanium; there have been argued that such defects may have three charge states, namely, neutral, single negative, and double negative ones [14]. In the light of these data it is only quite natural that the order of magnitude of the estimated positron-trapping cross sections ($\cong 10^{-15}\,cm^{-2}$, see Fig. 4) corresponds to the attractive centres.

5. Conclusion

It has been established for the first time that the impurity complexes of V-group atoms with vacancies are the centres of localization of positrons in γ-irradiated germanium of n- and p-type ($T_{irr.} \cong 300$ K). A crucial role in forming both spacial and angular distributions of the annihilation γ-quanta plays the chemical nature of atoms in the nearest environment of the positron trapped by defects. The positron-sensitive centres "V-group-atom-impurity + vacancy" dominate in the material of n-type. Such defects are capable of incorporating vacancies under further γ-irradiation and they continue to be an effective positron traps in the material of p-type.

The present results of the positron probing of microstructure of complexes of V-group- impurity atoms with vacancies support the data on the kinetics of accumulation of the radiation defects in γ-irradiated germanium,—in the material, for which classic ways of obtaining structural information about the point defects such as EPR- and IR-spectroscopy, have proved to be ineffective.

[3] The attempts to observe the intrinsic interstitial atoms have been undertaken by using different methods but reliable evidences have not been obtained, perhaps, owing to a high mobility of the interstitial atoms [1].

[4] The mean value $\left(\sum_{i=3} p_i - \langle I_d P_d \rangle\right)/3$ estimated for three investigated materials Ge:V(V = As, Sb, Bi) was assumed to be equal to 100%.

[5] It is implicitly assumed that some other non-dominant positron traps such as, e.g., vacancy–oxygen complexes whose concentration is equal to a several percents from the dominating one do not produce a detectable contribution into the resulting flow of the emission of the annihilation radiation.

References

[1] Emtsev VV, Mashovets TV. Impurities and point defects in semiconductors, in Russian, Izdatel'stvo Radio i Sviaz', Moscow, 1981. p. 248.
[2] Arutyunov NYu. Atomic environment of positron in diamond-like semiconductors and related materials: ACAR data. In: Das MP, editor. Condensed matter—new research. New York: Nova Science Publishers; 2006 in press.
[3] Arutyunov NYu, Baltenkov AS, Gilerson VB, Trashchakov VYu. Sov Phys Semicond 1986;20:1099.
[4] Brandt W. Appl Phys 1975;5:1.
[5] Arifov PU, Arutyunov NYu, Emtsev VV. Sov Phys Semicond 1981;15:898.
[6] Berko S, Mader J. Appl Phys 1975;5:287.
[7] Shulman M, Beardsley G, Berko S. Appl Phys 1975;5:367.

[8] Arutyunov NYu, Emtsev VV. Positron trapping by vacancy–impurity complexes in gamma-irradiated germanium. Semiconductors, 2006;40: in press.
[9] Puska MJ, Nieminen RM. Rev Mod Phys 1994;66:841.
[10] Arutyunov NYu, Emtsev VV. Solid State Phenomena 2005; 108–109:615.
[11] Arifov PU, Arutyunov NYu, Emtsev VV. Sov Phys Semicond 1979;13:914.
[12] Van Vechten JA. Phys Rev B 1986;33:2674.
[13] Abagyan SA, Arifov PU, Arutyunov NYu, Ivanov GA, Ilyasov AZ, Kuznetsov YuN, et al. Sov Phys Semicond 1979;13:1810.
[14] Markevich VP, Hawkins ID, Peaker AR, Emtsev KV, Emtsev VV, Litvinov VV, et al. Phys Rev B 2004;70:235213.
[15] Suchet J. Chemical physics of semiconductors, 2nd ed. London: Van Nostrand Ltd., 1965, Russian trans. In: Goryunova NA, editor. Metallurgia, Moscow; 1969. p. 135.