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Elemental specificity of ion cores and ionization entropy of vacancy-group-V-impurity atom pairs in Ge crystals: ACAR and DLTS data

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ABSTRACT

The positron probing of the donor-vacancy (DV) complexes created in the single crystals of n-Ge⟨D⟩ (D = P, As, Sb, or Bi) by γ -irradiation Co-60 ($T_{\mathrm{irr.}} \approx 315$ K) has been carried out by measuring the angular correlation of the annihilation radiation (ACAR). The maximum overlapping of the positron and electron wave functions in the subvalent shells of the ion cores has been determined for [111] crystallographic direction by normal approximation method. It has been found that this maximum is shifted from the nuclei of DV complexes in passing from the ion cores of atoms of a relatively small "size", P and As, to more volumetric ion cores, Sb and Bi, respectively. The shift itself is accompanied by the increase of the probability of the high-momentum annihilation process of the trapped positron during its lifetime. This increase correlates well with the augmentation of the entropy of ionization revealed by DLTS (Markevich et al. Phys. Rev. B70 (2004) 235213) for group-V-impurity atom pairs in germanium. Kolmogorov-Chapmen formalism has been used for studying the probability of the high-momentum annihilation of positron trapped by DV complexes. The results obtained suggest that the growth of the configurational entropy in passing from the ion cores of relatively small "size" to more volumetric ones is accompanied by the relaxation of the ion cores inward towards the free volume related to the vacancy in DV complex.

1. Introduction

The quest for the materials capable of functioning in ultra-fast devices over the range of frequencies of tens of GHz has renewed anew interest to germanium and, as a consequence, to the donor-vacancy complexes (DV) (D = P, As, Sb, Bi) of radiation origin in this material so long as they are known to affect the device yield and performance. The positron probing have a promising perspectives in studying these defects because chemical nature of group-V-impurity atom located in the nearest environment of the positron plays crucial role in generating elementally specific emission of the annihilation 2γ-quanta [1–4]. In this work we are going to demonstrate immanent interrelation between this phenomenon and the configurational entropy related to the entropy of ionization of the vacancy-group-V-impurity atom pair observed by means of capacitance transient techniques with the use of Au–Ge Schottky barriers [5].

2. Experimental

The single crystals of oxygen–lean germanium ($[O_i] \leqslant 5 \times 10^{15}\,\mathrm{cm}^{-3}$) with lower carbon concentration ($[C_i] \leqslant 10^{16}\,\mathrm{cm}^{-3}$) have been investigated (for more detail

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see also [1]). Samples for the positron studies were similar to the ones used for fabricating Schottky diodes for capacitance measurements performed in [5]. The concentration of group-V-impurity atoms was ranging from $\sim 7\times 10^{14}$ to $10^{16}\,\mathrm{cm}^{-3}$. Using the approach described in [6], we shall restrict ourselves to considering the ACAR data obtained for [111] crystallographic direction. The samples were irradiated with the γ-quanta ^{60}Co at 315 K. Doses of irradiation were in the range of $\sim(10^{18}–10^{19})$ cm^{-2}. The concentrations of defects (n_{d}) in the same materials have been controlled by the samples-satellites for which ones the values of concentrations were determined from the temperature dependences of the carrier density and mobility obtained over the temperature range of ~4.2 to 300 K (the examples of analysis of these dependences one may find in [7]).

A comprehensive study of the kinetics of accumulation of point radiation defects in these crystals of germanium has shown that the vacancy-group-V-impurity atom pairs are the dominant radiation-induced defects which in the material of *n*-type (before its *n*–*p*-conversion) are identified as *E* centers (for more detail see [5,7] and references therein); it is these defects that are the subject of our consideration so long as they are effective positron traps [1].

In asmuch as the momentum distribution of the core electrons retains its atomic character sufficiently for characterizing chemical nature of atoms around the positron we have concentrated attention on the elementally specific annihilation radiation which is emitted, mainly, from subvalent shells of the ion cores [6]. Characteristics of ACAR obtained for the ion cores of As, Sb, and Bi have been chosen as the reference quantities; the defect-"free" α-type As and high-quality ~99.99% pure Bi and Sb polycrystals have been used; the latter two materials were annealed (in vacuum) below the melting point during some hours. We applied the long-slit scheme of high resolution $\Delta\approx 0.9\times 10^{-3}$ radian ($1\,\mathrm{mrad}\approx 0.06^\circ$) for recording the ACAR spectra at room temperature.

The electron–positron ion radius (r_{m}) has been reconstructed by normal approximation method applied for the high-momentum component of ACAR spectra. On the basis of Kolmogorov-Chapmen formalism allowing one to calculate semi-empirically the probability of the annihilation of positrons with the core electrons (P_{c}) we have analyzed the data obtained by the positron probing of DV complexes and by DLTS applied for studying similar radiation defects: we have found the correlation between the probability of annihilation of positron with the electron in the subvalent shells and the entropy of ionization revealed by DLTS measurements, i.e., the correlation between the two quantities which are closely related to the configurational entropy of DV complexes in germanium (see below).

3. Saturation of positron trapping by vacancy-group-V-impurity atom pairs in *n*-Ge

The positron localization at DV (D = P, As, Sb, Bi) complexes is characterized by the trapping cross section ranging from $\sigma_{+}\sim 5\times 10^{-15}$ to $\sim 10^{-15}\,\mathrm{cm}^2$; these values depend on the chemical nature of the donor atom [1][1] and they have been estimated by solving the system of equations of the Chapman-Kolmogorov-type that connect the probability (P_{d}) of the positron annihilation in a certain defect with the magnitude of the positron trapping rate (k):

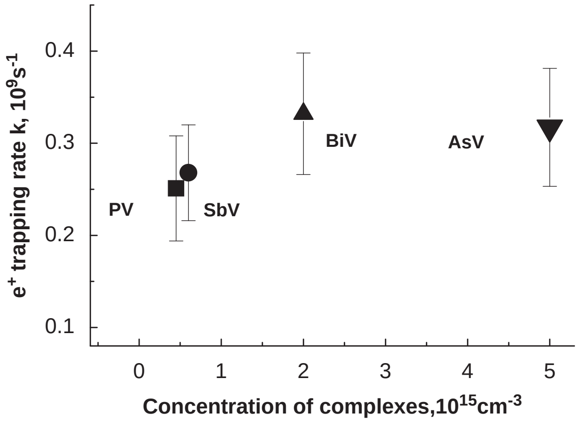

Fig. 1. The positron trapping rate (k) versus the concentration of DV (D = P, As, Sb, Bi) complexes in γ-irradiated *n*-Ge ($^{60}\mathrm{Co}/T_{\mathrm{irr.}} = 280\,\mathrm{K}$) before *n*–*p* conversion of materials.

$$\frac{P_{\mathrm{d}}}{(1-P_{\mathrm{d}})}\lambda_0 = k, \tag{1}$$

$$\sigma_{+} = k/v_{+}n_{\mathrm{d}}, \tag{2}$$

where λ_0 and v_{+} are the positron annihilation rate in the bulk and the velocity of the thermalized positron, respectively; the positron escape from the trap is neglected and in this case one may obtain Eq. (1) by best-known positron trapping model (for more detail see, e.g., [6,8–12]). As seen from Fig. 1, the positron trapping rates vary weakly with the changes of concentration of DV complexes (n_{d}). Such behavior of $k(n_{\mathrm{d}})$ dependency is characteristic of saturation and, accordingly, the emission of annihilation radiation from the region of defects dominates [1]; it will be emphasized that the vacancy-group-V-impurity atom complexes are prevailing type of defects in the investigated materials [7][2]. Thus, the saturation mentioned above allows one to consider the ACAR spectrum as a sum of the broad and narrow components:

$$I_{\mathrm{broad}}(p)P_{\mathrm{c}}^{\mathrm{d}} + I_{\mathrm{narrow}}(p)P_0^{\mathrm{d}} \approx I(p), \tag{3}$$

$$P_{\mathrm{c}}^{\mathrm{d}} + P_0^{\mathrm{d}} = 1, \tag{4}$$

[1] The positron trapping cross sections, perhaps, are understated not less than by the order of magnitude owing to inevitable undervaluing the probability of positron trapping under certain conditions (for more detail see, e.g., [1]).

[2] Perhaps, the values of $k(n_{\mathrm{d}})$ shown in Fig. 1 are much larger in view of the predicted positron trapping cross section by the vacancy in silicon which is equal to $10^{-12}–10^{-13}\,\mathrm{cm}^2$ [10]; the predictions of such kind for germanium are unknown to the authors.

where the former reflects the elemental specificity of the ion cores of atoms involved into the microstructure of the positron trapping center; substantial merit of the ACAR spectroscopy is that it enables us to record directly the spectrum $I_{\mathrm{broad}}(p)$ with high precision [3,4].[3]

4. Elemental specificity of ACAR related to ion cores in DV complex

The high-momentum electron-positron momentum distribution $\rho_{\mathrm{broad}}(\mathbf{p})$ which is detected by ACAR measurements is expressed by best-known formula:

$$I_{\mathrm{broad}}(p_z) \approx \int_{p_{\mathrm{F}}}^{\infty} \mathrm{d}p_y \int_{p_{\mathrm{F}}}^{\infty} \rho_{\mathrm{broad}}(\mathbf{p})\,\mathrm{d}p_x \cong \int_{p_{\mathrm{F}}}^{\infty} p\rho_{\mathrm{broad}}(p)\,\mathrm{d}p, \quad (5)$$

$$\overline{\theta_m} \cong \int_0^{\infty} \theta|\rho(p_z)|\,\mathrm{d}\theta = p_m/m_0c, \quad (6)$$

where $\rho_{\mathrm{broad}}(p)$ is approximately isotropic function, $p_{\mathrm{F}} = \hbar k_{\mathrm{F}} \approx \theta_{\mathrm{F}} m_0 c$ is the maximal value of momentum for the Fermi gas of the bonding electrons.[4] The average magnitude of momentum (p_m) may serve as a unified characteristic of the elemental specificity of the ion cores surrounding positron; θ is the angle of registration of the annihilation radiation, $p_z \approx \theta m_0 c \approx p$, where m_0 and c are the electron mass and the velocity of light in vacuum, respectively [1,6,9]. The $I_{\mathrm{broad}}(p)$ spectrum is the normal one (or close to it) if the Gaussian-like function gives a good fit to the experimental data [11][5]:

$$I_{\mathrm{broad}}(p)P_{\mathrm{c}}^{\mathrm{d}} \approx P_{\mathrm{c}}^{\mathrm{d}} I_{\mathrm{c}}^{\mathrm{d}}(q, r_m) \approx L(q, r_m)\exp(-q^2), \quad (7)$$

where $q = C(r_m)^{1/2}\theta$, $C(r_m) \approx$ constant, and $L(q,r_m)$ is slowly varying function in comparison with the exponential part. In this connection, one may consider linearized Eq. (7) where $X = q^2$ as a sum of the functions having different parameters A, B:

$$Y = \ln I_{\mathrm{broad}}(p_z > p_{\mathrm{F}}) = A - B \times X = \ln I(p_z), \quad (8)$$

$$B = B_1 + \cdots + B_n = C'(r_{m1} \ldots r_{mn}) = \langle r_{mn} \rangle = r_m, \quad C' \approx \text{constant}. \quad (9)$$

Eqs. (8) and (9) are justifiable for a wide variety of substances including the elements of group-IV and -V [4,6]. The distances $r_m(V_{\mathrm{group}})$ are close to the lengths of ion radii (r_i) of materials selected as the standards: $r_m(V_{\mathrm{group}})/r_i(V_{\mathrm{group}}) \approx 0.996$, ≈ 1.33, ≈ 1.11, for As^{5+}, Sb^{5+}, Bi^{5+}, respectively. As an observable example, the logarithmic functions $\ln I(p_z) = A - B \times p_z^2$ of the ACAR spectra recorded for the subvalent shells of ion cores in As and Bi and corresponding data of fitting are shown in Fig. 2 (on the left); for the ion cores in non-irradiated Ge similar graph is shown for comparison (here the ratio $r_m(\mathrm{Ge})/r_i(\mathrm{Ge}^{4+})$ is equal to ≈ 1.056). This regularity, namely, the approximate equality $r_m \cong r_i$ is of crucial importance for identifying DV complex by decomposing r_m on its constituents whose obvious convolution product is the sum:

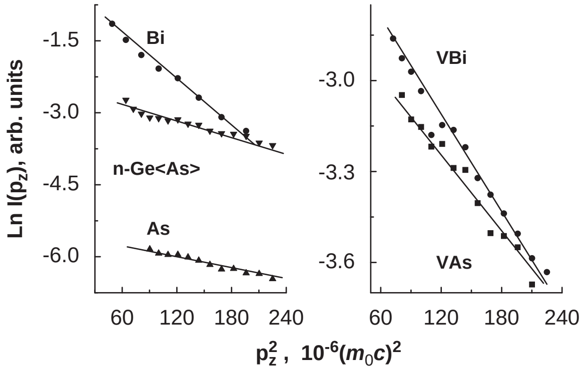

Fig. 2. Logarithmic functions $\ln I(p_z) = A - B \times p_z^2$ of the ACAR spectrum (dots) characterizing the increase of average electron–positron ion radius r_m (DV) in passing from AsV to BiV complexes in γ-irradiated n-Ge (right); data for standards (As, Bi and Ge) are shown for comparison (left). Lines are the fitted data; see Eq. (8). Typical standard deviation and correlation coefficient were within the ranges of ~0.029–0.033 and ~0.989–0.992, respectively.

$$r_{m\,(n=4)}^{\mathrm{convoluted}} = 0.25[r_m(\mathrm{D}^{5+}) + 3r_m(\mathrm{Ge}^{4+})], \quad (10)$$

where n is the number of r_m parameters: three for the ion cores of Ge atom and one for the ion core of group-V-impurity atom, respectively, (D = P, As, Sb, Bi).

The $r_{m\,(n=4)}^{\mathrm{convoluted}}$ function as the linear combination of r_m magnitudes in Eq. (10) implies the existence of the full-vacancy configuration of DV complex including positron in the vacancy. Numeral value of $r_{m\,(n=4)}^{\mathrm{convoluted}}$ is proportional to the distances r_m (DV) in DV complex (see Fig. 3)[6]; it is this observation that indicates the existence of the full-vacancy configuration of DV complexes in germanium predicted by the data of spin density functional modeling study [2].

5. HMC ACAR and DLTS: comparison of results for DV complexes in germanium

Let us demonstrate now that the number of events of high-momentum annihilation in DV complex is proportional to the volume to be occupied by the ion cores. This volume is closely related to the configurational entropy which, in its turn, affects the entropy of ionization of the E

[3] Spectroscopy of the Doppler broadening of annihilation radiation to be applied widely for studying defects in semiconductors possesses of the resolution lower by a factor of 4–6 in comparison with the ACAR technique [9].

[4] The annihilation 2γ-quanta with total wave vector $\vec{k}' = \vec{k} + \vec{K}$, where $\vec{K}$ is the reciprocal lattice vector, are always present in the emitted annihilation radiation. There has no been observed a marked $I(|k'|)$ component for ACAR in germanium (for more detail see [1,6,9] and references therein).

[5] Basically, the validity of assumption of normality of $I_{\mathrm{broad}}(p)$ spectra has also been checked by conventional methods of statistical testing of hypothesizes for a number of materials of microelectronics (see, e.g., [3,6]).

[6] For evaluation of $r_m^{\mathrm{convoluted}}$ magnitudes for PV complex by Eq. (10) as the $r_m(D^{5+})$ parameter there was used conventional value of the ion radius $r_i(P^{5+}) = 0.34 \times 10^{-8}$ cm [13].

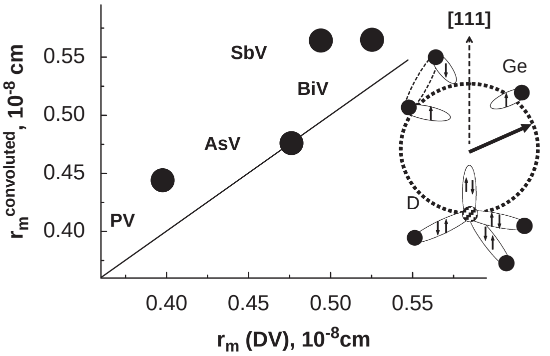

Fig. 3. Experimentally obtained magnitudes of electron–positron ion radii r_m (DV) in DV complexes versus calculated $r_m^{\text{convoluted}}$ lengths. The error is about doubled diameter of the dot, the line corresponds to the hypothetical equality $r_m^{\text{convoluted}} = r_m(DV)$, see Eq. (10). The inequality $r_m(DV) \leqslant r_m^{\text{convoluted}}$ which is clearly observed for all investigated DV complexes indicates the relaxation shift of the ion cores directed inward towards the vacancy. Full-vacancy configuration of DV complex is shown on the right (the scheme is cited by [7]): the shaded and black circles are D (D = P, As, Sb, Bi) and Ge ion cores, respectively (scales are not observed). The occupied states and the dangling bonds are shown by small arrows; the closing of the dangling bonds is possible near the vacant site (designated by thin dashed line). The circle (dashed line) having the radius equal to the r_m (DV) distance (bold arrow) symbolizes the position of maximum of the electron-positron overlapping in the region of the ion cores (see also Eqs. (8)–(10) and Fig. 2 for clarity).

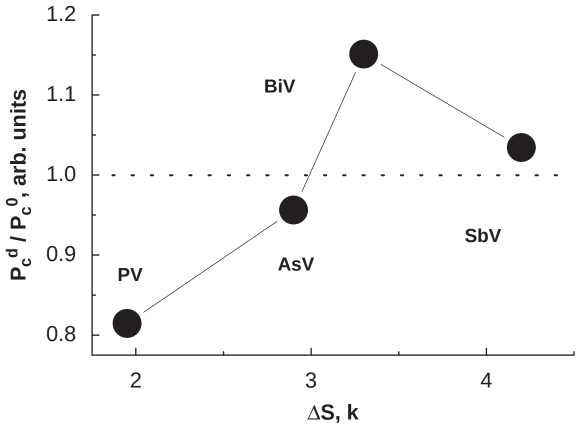

Fig. 4. The reduced probability of the emission of the high—momentum 2γ-gamma quanta from the ion cores of the DV complexes (P_c^d/P_c^0) in γ-irradiated n-Ge (^{60}Co/$T_{\text{irr.}} = 280$ K) versus the changes of the entropy of ionization (ΔS) which, according to the results of Laplace DLTS measurements [5], accompany the emission of an electron from the doubly negatively charged E-centers: numeral values below and above the dashed line correspond to comparatively compact (P, As) and more volumetric ion cores (Sb, Bi) in the composition of DV complexes, respectively; see also text in Section 5 and Eq. (11).

centers whose change depending on the "size" of D atom has been observed by DLTS [5].

The probability of the positron annihilation in the configurational volume occupied by the ion cores, $P_c^d(r_m)$, one may obtain by integrating Eq. (7):

$$P_c^d \approx \int_0^{3\theta_F} L(q, r_m)\exp(-q^2)\,dq. \tag{11}$$

Obviously, in the core region of DV complex this probability reflects a resulting overlapping of the positron and electron wave functions whereas in the non-irradiated material Ge^{4+} ion cores dominate in generating of the high-momentum annihilation. Having reduced the magnitudes of P_c^d to the ones obtained for the non-irradiated material, P_c^0, we may evaluate P_c^d/P_c^0 ratio which reflects the changes of contribution of the high-momentum events of annihilation in the core region of a given DV complex. As seen from Fig. 4, these changes correlate well with the augmentation of the entropy of ionization of DV complexes observed by DLTS measurements. For more compact ion cores P and As the ratio $P_c^d/P_c^0 < 1$ whereas for more volumetric ion cores of Sb and Bi the ratio P_c^d/P_c^0 exceeds unit thus indicating the emission of the high-momentum annihilation radiation not only from the subvalent shells of the ion cores of Ge atoms dominating in this process but, probably, also from the ion cores of group-V-impurity atoms. The correlation revealed between large changes of the entropy of ionization and probability of the positron annihilation in the core region suggests (i) the presence of the ion core of donor atom in the close proximity to the positron trapped by the vacancy and (ii) it is indicative of the full-vacancy configuration of investigated DV complexes.

6. Summary

Spectral characteristics of the angular correlation of 2γ-quanta to be emitted from the ion cores in the process of the positron annihilation bear the information about the chemical specificity of the elements inasmuch as the wave functions of the core electrons in the subvalent shells retain their atomic character sufficiently for using them as an indicator of individual atomic components near the annihilation site. The subvalent ion core shells in germanium and materials of group-V elements are capable of generating the angular distribution of 2γ-quanta close to the normal one sufficiently for determining a certain averaged distance (r_m) from the nuclei to the maximum overlapping of the wave functions of annihilating positron and core electron. We have obtained numeral values of these distances for the point radiation defects created in the single crystals of n-Ge$\langle$V$\rangle$ (V = P, As, Sb, or Bi) with γ-rays Co-60 ($T_{\text{irr.}} \approx 315$ K) and compared them with relevant standards whose r_m magnitudes are closed to the radii of ions in their valence state. The probability of the annihilation of positron with electrons of the sub-valent shells of the ion cores involved into the composition of the donor-vacancy pair has also been determined.

It has been established that the value of distance from the nuclei to the maximum overlapping of the wave functions of positron and electrons in the region of the subvalent shells follows the magnitude of the ion radius of group-V-impurity atom in DV complex. The position of the maximum mentioned above, however, is somewhat shifted towards the nuclei in comparison with the one obtained for non-irradiated materials. This shift suggests the relaxation of the atoms whose core electrons participate in the annihilation process. Analysis of results obtained suggests that the relaxation of both ion cores of group-V-impurity atoms and the ion cores of Ge is directed towards inward the volume related to the vacancy in the DV complex.

At the same time, more volumetric ion cores in the composition of DV complex give rise to comparatively higher probability of the high-momentum electron-positron annihilation. This increase of probability indicates the growth of the number of electron microstates involved into the process of the annihilation of positron in the core region of DV complex. The Laplace DLTS evidence supports this fact and demonstrates the augmentation of the entropy of ionization in passing from comparatively compact P and As atoms in the composition of DV complex to much more volumetric Sb and Bi ones, respectively.

Acknowledgments

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