Nanoobject sizes of defects in porous systems and defective materials according ADAP method

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Abstracts. - It is shown, that positrons effectively probe free nanoobject volumes (basically vacancies, divacancies and pores) with the sizes ≤ 1 -100 nanometer both in metals and alloys, and in semiconductors and porous systems.

It is shown [1], that positrons effectively probe free nanoobject volumes (basically vacancies, divacancies and pores) with the sizes $\leq 1 - 100$ nanometer both in metals and alloys, and in semiconductors and porous systems. We receive on the basis of model of movement of a particle in a plane limited by round cylindrical absolutely impenetrable wall [2-4], more correct formulas for definition of radiuses R_c cylindrical (symbol) c and the specified formulas of radiuses spherical (symbol) sp of nanopores in the width a component of angular distribution of annihilation photons (ADAP) $\theta_{1/2}$ and energies E_{1c} and E_{sp} of the basic parapositronium state, annihilated in pores in porous silicon and aluminium dioxyde

$$R_c[\overset{0}{A}] = \frac{21,1}{\theta_{1/2}[mrad]}, R_c[\overset{0}{A}] = \left(\frac{30,58}{E_{1c}(eV)}\right)^{1/2}, \qquad (1)$$

$$R_{sp}[\overset{0}{A}] = \frac{16,6}{(\theta_{1/2})[mrad]}, R_{sp}[\overset{0}{A}] = \left(\frac{18,85}{E_{1sp}(eV)}\right)^{1/2}, \qquad (2)$$

where R and $\theta_{1/2}$ are expressed in Å and $mrad$ accordingly. Let's note, that in formulas (1), (2) and further in (5), (6) numbers 16,6, 18,85, etc. have dimensions [Å] while value $\theta_{1/2}$ in $[mrad]$ actually is size dimensionless.

For experimental value in porous silicon $\theta_{1/2} = 0,8$ мрад [1], have received average value of radius of cylindrical times $R \approx 26,4$ Å ≈ 3 nanometer. Their concentration in a porous layer has appeared equal ~ $5,6 \cdot 10^{13}$ cm^{-3}. Approach of spherical pores gives size $R_{sp} \approx 20,75$ Å ≈ 2 nanometer and $N_{sp} \sim 1,3 \cdot 10^{14}$ sm^{-3}.

Consideration of the kinetic scheme of anniyilation disintegrations and transformation of a positron and positronium states in a porous layer enables to receive communication between their speed of capture k_{tr} by pores and intensity components I_{g2} [1]

$$k_{tr} \cong I_{g2}\lambda_{cr}, \text{ s}^{-1} \qquad (3)$$

Here $\lambda_{cr} \approx \lambda_s = 0,8 \cdot 10^{10}$ s^{-1} - speed of annihilation disintegration of parapositronium (p - Ps), value $I_{g2} \approx 0,015$ (see table 1) in [1] and λ_{cr} in the formula (3), we receive average speed of p - Ps capture by pores $k_{tr} = 1,2 \cdot 10^8$ s^{-1}. The size of speed of capture k_{tr} can be in turn certain on the basis of known expression

$$k_{tr} = \sigma_{tr}\upsilon N_{tr}, \text{ s}^{-1} \qquad (4)$$

Here σ_{tr} - average value of section of capture by pores (defects) of positronium and a positron; υ - speed of thermal positronium or a positron; N_{tr} - average concentration of pores (defects) (in porous (defective) area of a crystal), sensitive to thermal volumetric positronium and a positron states. Thus, from the resulted

expressions it is possible to define sizes k_{tr}, N_{tr} and R_{tr} if such parameters are known, as well as $\lambda_1, \sigma_{tr}(i)$ $\mathcal{V}$. Average thermal speed of positronium and a positron at a room temperature $T = 293K$ was estimated under the formula $\upsilon = \left(8k_0 T / \pi m_+^*\right)^{1/2} \approx 7,52 \cdot 10^6$ of cm/s, for a positron $v \approx 1,05 \cdot 10^7$ of cm/s, where $k_0 -$ Bolzman constant, $m_+^* \approx 2m_0$ - effective mass of positronium, $m_+^* \approx m_0$ - effective mass of a positron, $m_0 = 9,1 \cdot 10^{-28}$ г - mass of a free positron. We assume, that section of capture of positrons and positronium by pores to equally average value of geometrical section of pore (defect) $\sigma_{tr} \approx \pi R_{tr}^2 = 1,256 \cdot 10^{-13}$ cm^2. Having certain by us above value $R_{tr} \approx 2 \cdot 10^{-7}$ of cm, k_{tr} and $\mathcal{V}$, have defined under the formula (3) average value of the centers of p - Ps capture in a porous layer of silicon $N_{tr} \approx 1,27 \cdot 10^{14}$ of cm^{-3}.

Experiments have shown [1], that the basic part of positrons is in porous silicon from positron states no positronium type in volume of pores annihilated. We shall consider, that such type positron states are the positrons localized in volume of pores in the same way, as well as positronium atoms. In this case formulas (1) and (2) will be transformed in

$$R_c^0[\overset{0}{A}] = \left(\frac{61,1}{E_{1sp}(eV)}\right)^{1/2}, R_c^0[\overset{0}{A}] = \frac{29,7}{\theta_{1/2}[mrad]},$$ (5)

$$R_{sp}^0[\overset{0}{A}] = \left(\frac{37,7}{E_{1sp}(eV)}\right)^{1/2}, R_{sp}^0[\overset{0}{A}] = \frac{23,4}{\theta_{1/2}[mrad]},$$ (6)

Investigated by a method by positron annihilation spectroscopy (PAS) samples of porous silicon in the sizes 10×20×10 mm^3 have been cut out from the whole plates of silicon p – type with orientations <111>. For researches two samples designated by us as 164 (1) (the initial monocrystal sample), PR 86, PR16, PR17 (the sample of porous silicon received by a method of electrochemical processing in solution HF:C$_2$H$_5$OH have been chosen, at force of current J=20 mA/cm^2). Parameters of investigated plates of silicon and the basic characteristics of ADAP spectra are resulted in tabl.1.

Table 1

Characteristics of ADAP spectra of investigated samples of porous silicon of p-type and parameters of cylindrical pores

№ образца	$I_g=S_g/S_{sum}$	$I_p=S_p/S_{sum}$	$k_{tr} \cdot 10^{-9}$, с$^{-1}$	R_{tr}, Å	$N_{tr} \cdot 10^{-15}$, см$^{-3}$
164(1)	0.335±0.031	0.665±0.035			
PR86	0.493±0.052	0.492±0.044	7.21	13	1.31
PR16	0.483 ± 0.045	0.517±0.041	6.76	13	1.23
PR17	0.511 ± 0.051	0.489±0.044	8.00	13	1.55

From tabl.1 the difference between intencities of gauss components I_g(oxidized), that is the oxidized plates of silicon, and I_g (not oxidized) (the initial not oxidized plate) in ADAP spectra, can be written down in the form of

$$\Delta I_g = I_g \text{ (oxidized) - } I_g \text{ (not oxidized) = } k_{tr}\tau_1$$ (7)

That is average value of speed of capture by pores makes size

$$k_{tr} = \Delta I_g / \tau_1,$$ (8)

Let's estimate value k_{tr}, under the formula (8), for value $\Delta I_g = 0,665 - 0,493 = 0,172$ [1]. With this value ΔI_g under the formula (8) $k_{tr} \cong I_{g2}\lambda_{cr} = 7,9 \cdot 10^8$ s^{-1} for value $\tau_1 = 2,19 \cdot 10^{-10}$ s it is received $k_{tr} \approx 7,9 \cdot 10^8$ s^{-1}. The size of pores and energies in a annihilation place on external valent electrons E can be found also, using only ADAP data. Thus, on energy in a annihilation place on external valent electrons E it is possible to find also radiuses of pores, using only ADAP data. For this purpose we shall result the expression connecting energy of annihilated electron-positron pair with $\theta_{1/2}$ ($FWHM$ (full width half-maximum)) [1]

$$E = 6,9 \cdot 10^{-2} (\theta_{1/2})_g^2 \qquad (9$$

Here E-energy in eV, and $(\theta_{1/2})_g$ - ($FWHM$ (full width half-maximum)) full width of ADAP curve in мрад. So for samples of silicon the measured size $(\theta_{1/2})_g$ has made 11,1 mrad and to it there corresponds average energy of annihilation electron-positron pairs, equal $E = 8,5$ eV and caused by average energy of electrons an external environment of atom of silicon on a wall of a pore which can be accepted equal energy of electron on an external environment of the isolated atom of silicon. Thus it is considered, that up to annihilation a positron and positronium are in pore thermal and the measured energy is defined, basically, energy of electron. Tabulared value of energy for $Si(3p^2 - {}^3P_0)$ an electronic external environment of silicon $E(Si) = 8,1517$ эВ [5]. As we see, the consent of these sizes energies E and $E(Si)$ quite satisfactory. Thus, positrons are basically on external valent electrons of silicon atoms of "wall" of a pore annihilated. It is possible to believe, that the difference of sizes $E - E(Si) = 0,35$ эВ is caused by the contribution of energy of bond of the positron which is being a pore in energy of annihilated electron-positron pairs. In this case for definition of the size of cylindrical pores it is rational to use expression (3)

$$R_c = \left(\frac{61,1}{E - E(Si)} \right)^{1/2}, \qquad (10)$$

Thus, at value $E = E - E(Si) = 0,35$ eV for the size of pores is equal 13,2 Å.

Further with value $R_{tr} \approx 13,2$ Å have defined average value of section of positron capture by defects $\sigma_{tr} \approx 5,5 \cdot 10^{-14}$ of cm^2. For estimations of average values of concentration of pores have accepted $k_{tr} \approx 7,9 \cdot 10^8$ s^{-1}, $\sigma_{tr} \approx 5,5 \cdot 10^{-14}$ cm^2 and $v \approx 10^7$ cm/s. Have received value of concentration of pores $N_{tr} = k_{tr} / v \cdot \sigma_{tr} \approx 1,4 \cdot 10^{15}$ cm^{-3}.

Knowing the general porosity (45 %) [1] and average volume of a pore, we can estimate concentration of pores from simple geometrical reasons and, having compared it with calculated N_{tr} to check up reliability of accepted assumptions. Certain by us under the formula (2) average size of pores $R_{tr} \approx 3$ nm there corresponds their average volume $V_{tr} = \pi R_{tr}^2 \cdot h \approx 2,8 \cdot 10^{-16}$ of cm^{-3}, here h - thickness of a layer of porous silicon. For a case of "dense packing» such pores their concentration proceeding from size of the general porosity 0,45 could be equal $N_{tr}^G \sim 0,45/(V_{tr} = 2,8 \cdot 10^{-16}) = 1,6 \cdot 10^{15}$ cm^{-3}. Divergences of size N_{tr}^G with us the certain concentration $N_{tr} = 1,4 \cdot 10^{15}$ of cm^{-3} it is not so great. Thus, the samples of porous silicon studied by ADAP method is represent microporous cylindrical nanoobjects with the sizes of the order 1 - 3 nanometers and concentration $\sim 10^{15}$ of cm^{-3}.

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