The Influence of Forms and Sizes of Microheterogeneous Systems on the Band Bending in AgBr-AgI

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Abstract – Nonideal heterojunction of AgBr-AgI has been considered. The Poisson equations for heterojunction in planar, spherical and cylindrical geometries have been solved in linear approximation. The expressions for band bending of heterojunctions are derived. Calculations of band bending vs. the size, forms of the core and the surface charge on the interface have been carried out.

To increase of the efficiency of transforming the photon energy into the latent image centers it is necessary to segregate electrons and holes, that is, to reduce their recombination velocity. To solve this problem methods of synthesis of silver halide microcrystals (MC) of a heterojunction type, a "core-shell", on the basis of AgBr-AgI are developed [1–3]. Silver particles in these systems upon exposure are formed on the interface. Silver halides are known to be large band-gap, disordered according to Frenkel, ionic semiconductors. In the heterojunction area of AgBr the band bending is directed downwards and in the heterojunction area of AgI – the band bending is directed upwards [4]. The thickness of the shell of AgI is 0,12 μ*m*. The size of the core of AgBr is 0,25 – 0,4 μ*m* and comparable with the Debye length of defects. The size of the band bending on the heterojunction interface depends both on the core size and on the form of the heterostructure. Hence, changing the form and the sizes of the "core-shell" heterosystem it is possible to govern their photosensivity.

Let us solve the problem of the influence of the form and the size of the "core-shell" heterosystem on the band bending on the heterojunction by means of [5]. The qualitative scheme of the distribution of the potential in the heterojunction of AgBr-AgI is represented in Fig. 1, where ψ_C is the junction potential difference caused by different work functions of electrons from AgBr and AgI; $\delta\psi_1$ – the band bending in AgBr on the AgI interface; $\delta\psi_2$ – the band bending in AgI on the AgBr interface; ψ_1 – the distribution of the potential in AgBr; ψ_2 – the distribution of the potential in AgI; ψ_0 – the potential arising in the center of AgBr MC, because the volume charge in the center of the MC comparable with the Debye length is not equal to zero; h_1 – a characteristic size of the AgBr microcrystal. The ψ_C, $\delta\psi_1$, $\delta\psi_2$, ψ_1, ψ_2 potentials and the ψ_0 are normalized on k_BT/q, where k_B is the Boltzmann constant, q – an elementary charge.

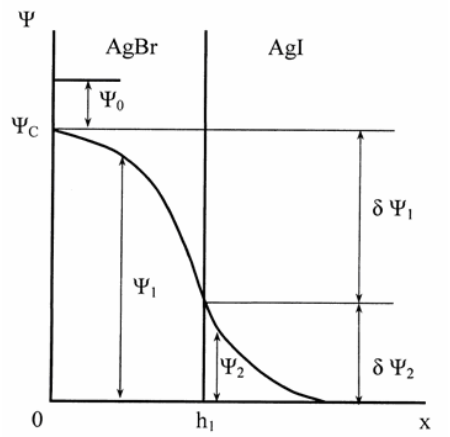

Fig. 1. Qualitative distribution of potential in AgBr-AgI heterojunction

Let us write the Poisson equations for the AgBr and AgI MC. The concentrations of electrons and holes in these compounds are small in comparison with the concentration of the Frenkel defects – interstitial silver cations and cation vacancies. The Frenkel defects in the electric field are distributed according to Boltzmann. Let us write the Poisson equations for the core and the shell in dimensionless variables

$$\Delta(\psi_c + \psi_0 - \psi_1) = \mathrm{sh}(\psi_c + \psi_0 - \psi_1), \qquad (1)$$

$$\Delta(\psi_2) = \mathrm{sh}(\psi_2), \qquad (2)$$

where

$$\Delta = \frac{1}{\xi_i^m}\frac{d}{d\xi_i}\left(\xi_i^m \frac{d}{d\xi_i}\right) \qquad i = 1, 2,$$

is the Laplacian. The $i = 1$ index is for the core and the i=2 index is for the shell. Here $\xi_i = x/l_i$ is the coordinate whose beginning is in the center of the "core-shell" system and normalized for the Debye length l_i:

$$l_i = \left(\frac{k_B \varepsilon_i \varepsilon_0}{2q^2 n_i}\right)^{1/2}, \qquad (3)$$

where ε_0 is the electric constant; n_i– the equilibrium concentration of defects in a infinitely large crystal. The parameters are equal to m=0, 1, 2 for planar, cylindrical and spherical systems, respectively. The equations (1–2) have the following boundary conditions: – in the center of the "core-shell" system by virtue of the symmetry of the equation

$$\xi_1 = 0, \ \frac{d\psi_1}{d\xi_1} = 0. \qquad (4)$$

– besides, according to Fig. 1

$$\psi_1(0) = \psi_c , \qquad (5)$$

– on the core-shell junction by virtue of a continuity of the potential

$$\psi_1(h_1/l_1) = \psi_2(h_1/l_2). \qquad (6)$$

Let us write the condition for a jog of electric induction on the interface of two phases with account of the expression (3) for the Debye length

$$2qn_1l_1 \frac{d\psi_1}{d\xi_1} = 2qn_2l_2 \frac{d\psi_2}{d\xi_2} - \sigma , \qquad (7)$$

where σ is the surface charge on the interface of two phases caused by the occurrence of torn off bonds due to the disorder of the lattices. The shell thickness is $\Delta h >> l_2$. Therefore, the boundary condition for the potential ψ_2 can be written as

$$\xi_2 = \infty . \ \psi_2 = 0 \qquad (8)$$

The characteristic sizes of the core are comparable with the Debye length. Therefore, analytical solutions to the Poisson equations are possible only in linear approximation. Let us write the equations (1), (2) in linear approximation

$$\Delta(\psi_c + \psi_0 - \psi_1) = \psi_c + \psi_0 - \psi_1 , \qquad (9)$$

$$\Delta(\psi_2) = \psi_2 , \qquad (10)$$

Let us consider the planar system. Let us imagine the core from AgBr as a planar infinitely large crystal with layers from AgI built up on lateral surfaces. For m=0 the equations (9), (10) can be written as

$$d^2(\psi_c + \psi_0 - \psi_1)/d\xi_1^2 = \psi_c + \psi_0 - \psi_1 , \qquad (11)$$

$$d^2\psi_2 / d\xi_2^2 = \psi_2 . \qquad (12)$$

Let us write the solution to the system of the equations (11, 12)

$$\psi_1 = \psi_c + \psi_0 - A_1 \exp\xi_1 - A_2 \exp(-\xi_1) , \qquad (13)$$

$$\psi_2 = B_1 \exp\xi_2 + B_2 \exp(-\xi_2). \qquad (14)$$

The constants of integration are calculated from the boundary conditions. Taking into account the boundary conditions (4), (5), we obtain

$$\psi_1(\xi_1) = \psi_c + \psi_0(1 - \operatorname{ch}\xi_1) . \qquad (15)$$

The ψ_2 potential at $\xi_2 \to \infty$ should be limited. Hence, B_1=0. Then

$$\psi_2(\xi_2) = B_2 \exp(-\xi_2) . \qquad (16)$$

The B_2 constant is determined from the boundary condition (6) and is equal to

$$B_2 = \{\psi_c + \psi_0[1 - \operatorname{ch}(h_1/l_1)]\}\exp(h_1/l_1) . \qquad (17)$$

Let us determine the band bendings of AgBr-AgI heterojunction

$$\delta\psi_1 = \psi_c - \psi_1(h_1/l_1) = \psi_0[\operatorname{ch}(h_1/l_1) - 1]. \qquad (18)$$

$$\delta\psi_2 = \psi_c - \delta\psi_1 . \qquad (19)$$

From the boundary condition (7), we obtain

$$-2qn_1l_1\psi_0 \operatorname{sh}(h_1/l_1) = $$

$$= -2qn_2l_2B_2 \exp(-h_1/l_2) - \sigma . \qquad (20)$$

Let us express ψ_0 from (18) through $\delta\psi_1$ and substitute it into equation (20). With account of $\delta\psi_2 = \psi_2(h_1/l_2)$ in (20) we obtain

$$-2qn_1l_1 \frac{\operatorname{sh}(h_1/l_1)}{\operatorname{ch}(h_1/l_1) - 1} \delta\psi_1 = -2qn_2l_2\delta\psi_2 - \sigma . \qquad (21)$$

Solving a system of the equations (19) and (21) relative to $\delta\psi_1$ and $\delta\psi_2$, we obtain

$$\frac{\delta\psi_1}{\psi_c} = \frac{\alpha\left(1 + \dfrac{\sigma}{2qn_2l_2\psi_c}\right)}{\alpha + \dfrac{n_1l_1}{n_2l_2}\operatorname{th}(h_1/l_1)} , \qquad (22)$$

$$\frac{\delta\psi_2}{\psi_c} = \frac{\dfrac{n_1l_1}{n_2l_2}\operatorname{th}(h_1/l_1) - \dfrac{\alpha\sigma}{2qn_2l_2\psi_c}}{\alpha + \dfrac{n_1l_1}{n_2l_2}\operatorname{th}(h_1/l_1)} , \qquad (23)$$

where α=1–1/ch(h_1/l_1). If the $h_1 >> l_1$ expressions for the band bendings on the heterojunction are simplified

$$\frac{\delta\psi_1}{\psi_c} = \frac{n_2l_2 + \dfrac{\sigma}{2q\psi_c}}{n_1l_1 + n_2l_2} , \ \frac{\delta\psi_2}{\psi_c} = \frac{n_1l_1 - \dfrac{\sigma}{2q\psi_c}}{n_1l_1 + n_2l_2} . \qquad (24)$$

The potential ψ_0 tends to zero. The relation of the band bendings for the ideal heterojunction (σ=0) is

$$\frac{\delta\psi_1}{\delta\psi_2} = \frac{n_2l_2}{n_1l_1} = \sqrt{\frac{\varepsilon_2n_2}{\varepsilon_1n_1}} . \qquad (25)$$

According to (22) and (23) relative changes of the band bendings are calculated with account of the core size and the charge σ. The calculations were carried out by using the following parameters: l_1=0,185 μm, l_2=0,019 μm, ε_1=12,5, ε_2=7,15, n_1=4,57·10^{14} cm^{-3} and n_2=4,25·10^{16} cm^{-3}. The results of the calculations are resulted in Fig. 2.

Let us consider the core as a flat disk with a layer of AgI built up on a lateral surface of a small cylinder. Let us write the Poisson equations at m=1

$$\xi_1^2 \frac{d^2}{d\xi_1^2}(\psi_c + \psi_0 - \psi_1) + \xi_1 \frac{d}{d\xi_1}(\psi_c + \psi_0 - \psi_1) -$$

$$-\xi_1^2(\psi_c + \psi_0 - \psi_1) = 0 , \qquad (26)$$

$$\xi_2^2 \frac{d^2\psi_2}{d\xi_2^2} + \xi_2 \frac{d\psi_2}{d\xi_2} - \xi_1^2\psi_2 = 0 . \qquad (27)$$

These equations are the Bessel equations and have the following solutions

$$\psi_1 = \psi_c + \psi_0 - A_1I_0(\xi_1) - A_2K_0(\xi_1) , \qquad (28)$$

$$\psi_2 = B_1I_0(\xi_2) + B_2K_0(\xi_2) , \qquad (29)$$

where $I_0(\xi_i)$, $K_0(\xi_i)$ are modified Bessel functions of the zero order of the first and second genera, respectively. Let us define the constants of integration A_1, A_2, B_1 and B_2. Given that $K_0(0)\infty$, we assume A_2=*0* when solving (28). Proceeding from the boundary condition (5) we obtain

$$\psi_1 = \psi_c + \psi_0[1 - I_0(\xi_1)] . \qquad (30)$$

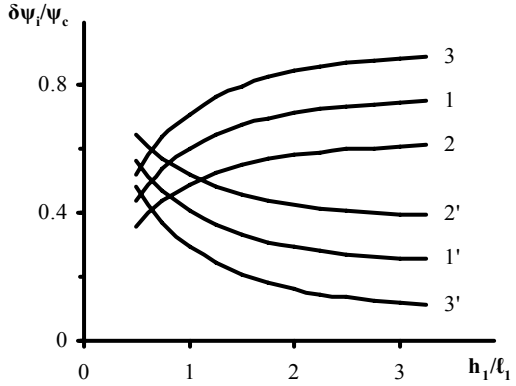

Fig. 2. Influence of the characteristic size of the flat "core" on the band bending on the boundary of the AgBr-AgI heterojunction: $\delta\psi_1/\psi_C$ – curves 1 – 3; $\delta\psi_2/\psi_C$ – curves 1' – 3' (curves 1, 1' – σ/ψ_C=0; curves 2, 2' – σ/ψ_C=–1,6·10^{-9} C/sm^2; curves 3, 3' – σ/ψ_C=1,6·10^{-9} C/cm^2)

The boundary condition (4), hitherto, is realized automatically, as $I_0'(0) = I_1(0) = 0$. The solution to ψ_2 should be limited at $\xi_2 \to \infty$; the function $I_0(\infty) = \infty$. From here, B_1=0. Thus

$$\psi_2 = B_2 K_0(\xi_2) \quad . \tag{31}$$

The constant B_2 according to the boundary condition (6), is equal to

$$B_2 = \{\psi_c + \psi_0[1 - I_0(r_1/l_2)]\} / K_0(r_1/l_2) , \tag{32}$$

where r_1 is the radius of a cylindrical core.

The equations for the band bendings are derived in the same way as for a flat disc and are defined by

$$\frac{\delta\psi_1}{\psi_c} = \frac{\dfrac{K_1(r_1/l_2)}{K_0(r_1/l_2)} + \dfrac{\sigma}{2qn_2l_2\psi_c}}{\dfrac{K_1(r_1/l_2)}{K_0(r_1/l_2)} + \dfrac{n_1l_1}{n_2l_2}\dfrac{I_1(r_1/l_1)}{I_0(r_1/l_1)-1}} , \tag{33}$$

$$\frac{\delta\psi_2}{\psi_c} = \frac{\dfrac{n_1l_1}{n_2l_2}\dfrac{I_1(r_1/l_2)}{I_0(r_1/l_2)-1} - \dfrac{\sigma}{2qn_2l_2\psi_c}}{\dfrac{K_1(r_1/l_2)}{K_0(r_1/l_2)} + \dfrac{n_1l_1}{n_2l_2}\dfrac{I_1(r_1/l_1)}{I_0(r_1/l_1)-1}} . \tag{34}$$

At $r_1 >> l_1, l_2$ the relations of the modified Bessel functions can be written as [6]

$$\frac{K_1(r_1/l_2)}{K_0(r_1/l_2)} \to 1, \frac{I_1(r_1/l_1)}{I_0(r_1/l_1)-1} \to 1 .$$

Equations (33) and (34) for the band bendings have the form of (24) for a flat disc. According to (33) and (34) relative changes of the band bendings are calculated with account of the core size and the charge o. Results of the calculations are resulted in Fig. 3.

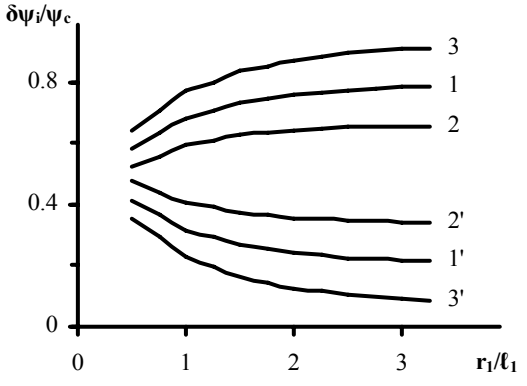

Fig. 3. Influence of the radius of the "core" in the form of a cylindrical disk on the band bending on the boundary of the AgBr-AgI heterojunction: $\delta\psi_1/\psi_C$ – curves 1 – 3; $\delta\psi_2/\psi_C$ – curves 1' – 3' (curves 1, 1' – σ/ψ_C=0; curves 2, 2' – σ/ψ_C=–1,6·10^{-9} C/sm^2; curves 3, 3' – σ/ψ_C=1,6·10^{-9} C/cm^2).

Let us consider the core as a spherical particle (radius r_1) with a built up layer of AgI. The Poisson equations at m=2 have the form of

$$\frac{1}{\xi_1}\frac{d^2}{d\xi_1^2}[\xi_1(\psi_c + \psi_0 - \psi_1)] = (\psi_c + \psi_0 - \psi_1) , \tag{35}$$

$$\frac{1}{\xi_2}\frac{d^2(\xi_2\psi_2)}{d\xi_2^2} = \psi_2 . \tag{36}$$

Let us write the solution to equations (35) and (36) with account of the boundary conditions (4) and (5)

$$\psi_1 = \psi_c + \psi_0\left(1 - \frac{1}{\xi_1}\operatorname{sh}\xi_1\right) , \tag{37}$$

$$\psi_2 = \frac{B_2}{\xi_2}\exp(-\xi_2) . \tag{38}$$

The constant B_2 is derived from the condition of the equality of potentials (6) on the boundary of two phases

$$B_2 = \left\{\psi_c + \psi_0\left[1 - \frac{l_1}{r_1}\operatorname{ch}(r_1/l_1)\right]\right\}\frac{r_1}{l_2}\exp(r_1/l_1) .$$

The equations for the band bendings are derived in the same way as for a flat disc and are defined by

$$\frac{\delta\psi_1}{\psi_c} = \frac{[\operatorname{sh}(r_1/l_1) - r_1/l_1][1 + \sigma/(2qn_2l_2\psi_c)]}{\operatorname{sh}(r_1/l_1) - r_1/l_1 + \beta} , \tag{39}$$

$$\frac{\delta\psi_2}{\psi_c} = \frac{\beta - \dfrac{\sigma}{2qn_2l_2\psi_c}[\operatorname{sh}(r_1/l_1) - r_1/l_1]}{\operatorname{sh}(r_1/l_1) - r_1/l_1 + \beta} , \tag{40}$$

where $\beta = \dfrac{n_1l_1}{n_2l_2}[\operatorname{ch}(r_1/l_1) - (l_1/r_1)\operatorname{sh}(r_1/l_1)]$.

At $r_1>>l_1$, l_2 expressions (39) and (40) for the band bendings assume the form of (24) for a flat disc. According to (39) and (40) relative changes of the band bendings are calculated with account of the core size and the charge σ. The results of the calculations are resulted in Fig. 4.

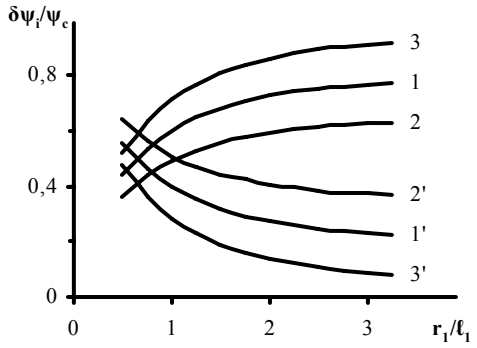

Fig. 4. Influence of the radius of the "core" in the spherical form on a band bending on the boundary of the AgBr-AgI heterojunction: $\delta\psi_1/\psi_C$ – curves 1 – 3; $\delta\psi_2/\psi_C$ – curves 1' – 3' (curves 1, 1' – $\sigma/\psi_C=0$; curves 2, 2' – $\sigma/\psi_C=-1{,}6\cdot10^{-9}$ C/cm^2; curves 3, 3' – $\sigma/\psi_C=1{,}6\cdot10^{-9}$ C/cm^2)

From Fig. 2–4 it is seen that increase in a characteristic size of the core results in band bendings' increase in AgBr and band bendings' decrease in AgI. At h_1, $r_1>3l_1$ the band bendings on the boundary of two silver halides practically do not change with increasing of a characteristic size of a core. The negative charge on the interface of the phases reduces the value of band bendings in AgBr and increases the one in AgI. The positive charge on the interface of the phases, alternatively, increases the value of band bendings in AgBr and reduces the one in AgI. The given effect is related to electroneutrality of the "core – shell" system.

Increase in band bendings in AgBr results in increase in the negative volume charge caused by cation vacancies. Increase in band bendings in AgI results in increase in the positive volume charge caused by interstitial silver cations. Alternatively, the band bendings on the AgBr-AgI heterojunction depends not only on the size of a core, but also on the geometry of the photosensitive "core – shell" system. It is necessary to note that the band bendings for planar and spherical heterojunctions are similar, and, hence, the photosensivities of these systems must be comparable. Therefore, changing the form and the sizes of the core, it is possible to change the band bending, and, hence, to govern the photosensivity of materials on the basis of silver halide microcrystals of a heterojunction type.

References

[1] S. Bando, Y. Shibahara, S. Ishimaru, Journal of Imaging Science. **25**, 193 (1985).

[2] E.I. Kagaкin, Yu.A. Breslav, T.A. Larichev, A.I. Mokhov, Zh. Nauchn. Prikl. Fotogr. Kinematogr. **36**, 353 (1991).

[3] F. Granzer, J.I.R.M. **29**, 109 (1992).

[4] F. Granzer, Journal of Imaging Science. **33**, 207 (1989).

[5] V.I. Il'in, S.F. Musikhin, A.Ya. Schik, *Varizonnye poluprovodniki u geterostpuktury,* Sankt-Peterburg. Nauka, 2000. 104 c.

[6] *Handbook of Mathematical Functions,* M. Abramowitz and J.A. Stegun, Eds., n.p.: NBS, 1964. Translated under the title *Spravochnik po spetcial'nym funktsiyam,* Moscow, Nauka, 1972, 872 p.