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SEMICONDUCTOR STRUCTURES, INTERFACES, AND SURFACES

Dependence of the Band Bending at the AgBr–AgI Microcontact Interface on the Shape and Size of the Heterogeneous System

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Abstract—The nonideal AgBr–AgI heterocontact has been considered. The Poisson equations for this heterocontact are solved in the linear approximation for planar, spherical, and cylindrical geometric layouts. Expressions for the band bending at the interface are obtained. The dependence of the band bending on the core size and shape and the surface charge at the interface is calculated. It is shown that the band bending at the AgBr–AgI interface depends not only on the core size but also on the geometric characteristics of the photosensitive core–shell system.

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1. INTRODUCTION

To increase the light energy conversion efficiency to latent image centers, it is necessary to separate electrons and holes, i.e., decrease their recombination rate. To solve this problem, some methods of synthesis of silver halide microcrystals of heterocontact (core–shell) type have been developed on the basis of the AgBr–AgI system [1–6]. Upon illumination, silver particles in such systems are formed at the interface. Silver halides are known to be wide-gap, Frenkel disordered ionic semiconductors. AgI belongs to the class of superionic conductors. The thickness of the AgI shell is about 0.12 μm. The AgBr core size is about 0.25–0.4 μm, a value that is comparable with the Debye length of point defects. In the interface region of AgBr, the band bending is downward, while in the interface region of AgI, the band bending is upward [5]. The relations between the band bendings at the AgBr/AgI interface were derived in [5] on the assumption of equal distances from the interface to the points where electric field is zero in these crystals. However, this assumption is invalid since the screening (Debye) lengths of these two compounds are determined by Frenkel defects, whose concentrations are, first, different for AgBr and AgI, and, second, exceed the electron and hole concentrations in them by several tens of orders of magnitude. Note that the contact potential difference between ionic crystals depends not only on the difference between the electron work functions but also on the difference between the work functions of ions.

The value of the band bending at the interface depends not only on the core size but also on the heterostructure shape. Therefore, changing the shape and sizes of a core–shell heterostructure, one can deliberately control its photosensitivity.

2. STATEMENT OF THE PROBLEM

Let us solve the problem of the effect of the shape and size of a core–shell heterostructure on the band bending near the contact. According to [7], if the lattice mismatch for a contact between two crystals exceeds 0.5%, such a heterojunction is nonideal. The lattice constants a of AgBr and AgI are 5.77 and 6.74 Å, respectively; i.e., this heterojunction is nonideal. In this case, a surface charge may be induced by dangling bonds at the interface. The band bending is determined from matching of the solutions to the Poisson equations for each phase. Figure 1 shows a qualitative pattern of the potential (potential energy of an electron) distribu-

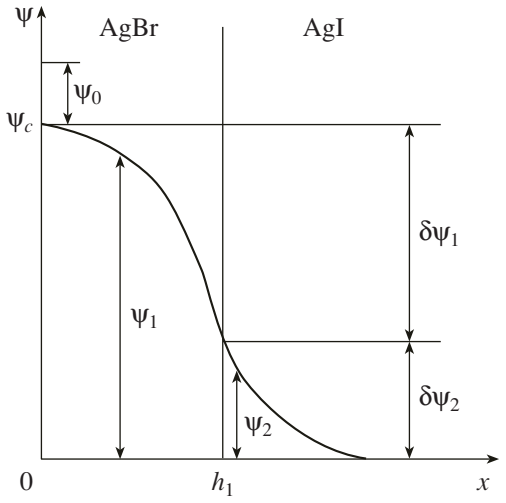

Fig. 1. Qualitative pattern of potential distribution in an AgBr–AgI heterojunction.

tion in the AgBr–AgI heterojunction. Here, ψ_c is the contact potential difference, $\delta\psi_1$ is the band bending in AgBr at the interface with AgI, $\delta\psi_2$ is the band bending in AgI at the interface with AgBr, ψ_1 is the potential distribution in AgBr, ψ_2 is the potential distribution in AgI, ψ_0 is the potential induced at the center of an AgBr microcrystal by the nonzero (for microcrystals comparable in size with the Debye length) space charge at the microcrystal center, and h_1 is the characteristic size of AgBr microcrystals. The potentials ψ_c, $\delta\psi_1$, $\delta\psi_2$, ψ_1, ψ_2, and ψ_0 are normalized to k_BT/q, where k_B is the Boltzmann constant and q is the elementary charge.

Let us write the Poisson equations for AgBr and AgI microcrystals. The electron and hole concentrations in these compounds are low in comparison with the concentrations of Frenkel defects: interstitial Ag cations and cation vacancies. The distribution of Frenkel defects in the electric field is of the Boltzmann type. The Poisson equations for the core and shell in dimensionless variables have the form

$$\Delta(\psi_c + \psi_0 - \psi_1) = \sinh(\psi_c + \psi_0 - \psi_1), \quad (1)$$

$$\Delta\psi_2 = \sinh(\psi_2), \quad (2)$$

where

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

is the Laplace operator. The subscripts $i = 1$ and 2 refer to the core and shell, respectively. Here, $\xi_i = x/l_i$ is the coordinate counted from the center of the core–shell system and normalized to the Debye length l_i:

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

Here, ε_0 is the dielectric constant, ε_i is the relative permittivity of a crystal, and n_i is the equilibrium concentration of Frenkel defects in an infinite crystal. The parameter $m = 0$, 1, and 2 for planar, cylindrical, and spherical systems, respectively.

Equations (1) and (2) have the following boundary conditions. At the center of the core–shell system, in view of the symmetry of the problem,

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

In addition, according to Fig. 1,

$$\psi_1(0) = \psi_c. \quad (5)$$

At the core–shell interface, in view of the continuity of the potential,

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

The condition for the electric displacement jump at the interface between two media, with due regard to expression (3) for the Debye length, has the form

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

where σ is the surface charge density at the interface, which is caused by the formation of dangling bonds due to the lattice mismatch. The shell thickness $\Delta h \gg l_2$. Therefore, the boundary condition for the potential ψ_2 can be written as

$$\xi_2 = \infty, \quad \psi_2 = 0. \quad (8)$$

3. THEORETICAL ANALYSIS

The characteristic core sizes are comparable with the Debye length. Therefore, analytical solutions to the Poisson equations can be obtained only in the linear approximation. Let us write Eqs. (1) and (2) in this approximation:

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

$$\Delta\psi_2 = \psi_2. \quad (10)$$

We will consider a planar system. Let the AgBr core have a shape of a planar infinite crystal with AgI layers on its lateral surfaces. For $m = 0$, Eqs. (9) and (10) will take the form

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

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

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

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

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

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

$$\psi_1(\xi_1) = \psi_c + \psi_0(1 - \cosh\xi_1). \quad (15)$$

The potential ψ_2 should be limited at $\xi_2 \longrightarrow \infty$; therefore, $B_1 = 0$. Hence,

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

The constant B_2 is determined from boundary condition (6):

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

Let us determine the band bending at the AgBr–AgI interface:

$$\delta\psi_1 = \psi_c - \psi_2(h_1/l_1) = \psi_0[\cosh(h_1/l_1) - 1], \quad (18)$$

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

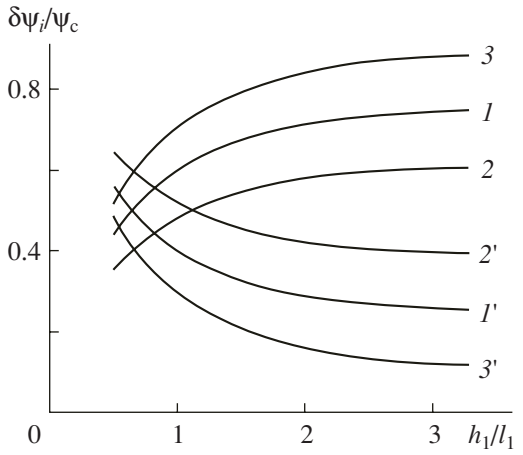

Fig. 2. Effect of the characteristic size of the planar core on the band bending at the AgBr–AgI interface: (*1*–*3*) $\delta\psi_1/\psi_c$ and (*1'*–*3'*) $\delta\psi_2/\psi_c$; σ/ψ_c = (*1*, *1'*) 0, (*2*, *2'*) -1.6×10^{-9}, and (*3*, *3'*) 1.6×10^{-9} C/cm^2.

From boundary condition (7), we have

$$\begin{aligned} &-2qn_1l_1\psi_0\sinh(h_1/l_1) \\ &= -2qn_2l_2B_2\exp(-h_1/l_2) - \sigma. \end{aligned} \tag{20}$$

Let us express ψ_0 from (18) in terms of $\delta\psi_1$ and substitute it into Eq. (20). Then, we will take into account in formula (20) that $\delta\psi_2 = \psi_2(h_1/l_2)$ and, as a result, obtain

$$\begin{aligned} &-2qn_1l_1\frac{\sinh(h_1/l_1)}{\cosh(h_1/l_1)-1}\delta\psi_1 \\ &= -2qn_2l_2\delta\psi_2 - \sigma. \end{aligned} \tag{21}$$

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

$$\frac{\delta\psi_1}{\psi_c} = \frac{\alpha[1+\sigma/(2qn_2l_2\psi_c)]}{\alpha+(n_1l_1/n_2l_2)\tanh(h_1/l_1)}, \tag{22}$$

$$\frac{\delta\psi_2}{\psi_c} = \frac{(n_1l_1/n_2l_2)\tanh(h_1/l_1)-\alpha\sigma/(2qn_2l_1\psi_c)}{\alpha+(n_1l_1/n_2l_2)\tanh(h_1/l_1)}, \tag{23}$$

where $\alpha = 1 - 1/\cosh(h_1/l_1)$. If $h_1 \gg l_1$, the expressions for the band bending at the interface are simplified:

$$\begin{aligned} \frac{\delta\psi_1}{\psi_c} &= \frac{n_2l_2+\sigma/(2q\psi_c)}{n_1l_1+n_2l_2}, \\ \frac{\delta\psi_2}{\psi_c} &= \frac{n_1l_2-\sigma/(2q\psi_c)}{n_1l_1+n_2l_2}, \end{aligned} \tag{24}$$

and the potential ψ_0 tends toward zero. The ratio of the band bendings for an ideal contact ($\sigma = 0$) is

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

Formulas (22) and (23) were used to calculate the relative changes in the band bendings as functions of the core size and the charge σ. Calculations were carried out with the following parameters: $l_1 = 0.185$ μm, $l_2 = 0.019$ μm, $\varepsilon_1 = 12.5$, $\varepsilon_2 = 7.15$, $n_1 = 4.57 \times 10^4$ cm^{-3}, and $n_2 = 4.25 \times 10^{16}$ cm^{-3}. The results of the calculations are shown in Fig. 2.

Let us consider a core in the form of a planar disk with an AgI layer on its lateral surface. Let us write the Poisson equations at $m = 1$:

$$\begin{aligned} &\xi_1^2\frac{d^2}{d\xi_1^2}(\psi_c+\psi_0-\psi_1)+\xi_1\frac{d}{d\xi_1}(\psi_c+\psi_0-\psi_1) \\ &-\xi_1^2(\psi_c+\psi_0-\psi_1) = 0, \end{aligned} \tag{26}$$

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

These are Bessel equations. Their solutions are

$$\psi_1 = \psi_c+\psi_0-A_1I_0(\xi_1)-A_2K_0(\xi_1), \tag{28}$$

$$\psi_2 = B_1I_0(\xi_2)+B_2K_0(\xi_2), \tag{29}$$

where $I_0(\xi_i)$ and $K_0(\xi_i)$ are modified zero-order Bessel functions of the first and second kind, respectively. Let us determine the integration constants A_1, A_2, B_1, and B_2. Since $K_0(0) = \infty$, we will assume that $A_2 = 0$ in solution (28). On the basis of boundary condition (5), we obtain

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

In this case, boundary condition (4) is satisfied automatically, since $I_0'(0) = I_1(0) = 0$. The solution for ψ_2 should be limited at $\xi_2 \longrightarrow \infty$. The function $I_0(\infty) = \infty$. Hence, $B_1 = 0$. Thus,

$$\psi_2 = B_2K_0(\xi_2). \tag{31}$$

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

$$B_2 = \{\psi_c+\psi_0[1-I_0(r_0/l_2)]\}/K_0(r_1/l_2), \tag{32}$$

where r_1 is the cylindrical core radius.

The equations for the band bending are derived in the same way as for the planar case; they have the form

$$\frac{\delta\psi_1}{\psi_c} = \frac{K_1(r_1/l_2)/K_0(r_1/l_2)+\sigma/(2qn_2l_2\psi_c)}{K_1(r_1/l_2)/K_0(r_1/l_2)+\gamma}, \tag{33}$$

$$\frac{\delta\psi_2}{\psi_c} = \frac{\gamma-\sigma/(2qn_2l_2\psi_c)}{K_1(r_1/l_2)/K_0(r_1/l_2)+\gamma}, \tag{34}$$

where

$$\gamma = \frac{n_1l_1}{n_2l_2}\frac{I_1(r_1/l_1)}{I_0(r_1/l_1)-1}.$$

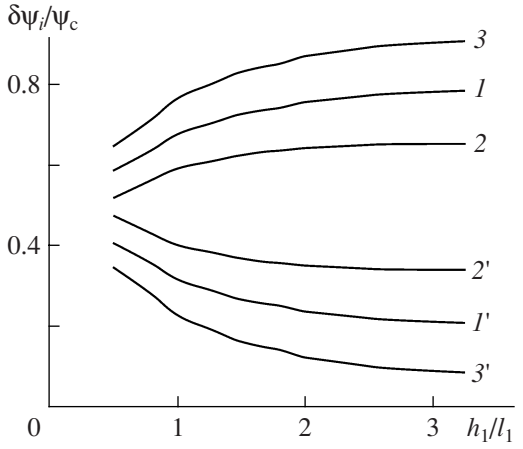

Fig. 3. Effect of the radius of the cylindrical disk-shaped core on the band bending at the AgBr–AgI interface: (*1–3*) $\delta\psi_1/\psi_c$ and (*1'–3'*) $\delta\psi_2/\psi_c$; $\sigma/\psi_c = (1, 1')\ 0, (2, 2') -1.6 \times 10^{-9}$, and $(3, 3')\ 1.6 \times 10^{-9}$ C/cm^2.

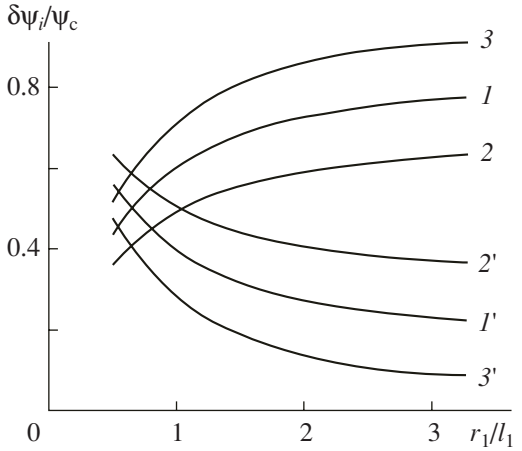

Fig. 4. Effect of the radius of the spherical core on the band bending at the AgBr–AgI interface: (*1–3*) $\delta\psi_1/\psi_c$ and (*1'–3'*) $\delta\psi_2/\psi_c$; $\sigma/\psi_c = (1, 1')\ 0, (2, 2') -1.6 \times 10^{-9}$, and $(3, 3')\ 1.6 \times 10^{-9}$ C/cm^2.

At $r_1 \gg l_1, l_2$, the ratios of the modified Bessel functions [8] tend toward unity:

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

Formulas (33) and (34) for the band bending pass to formulas (24) in the planar case. Expressions (33) and (34) were used to calculate the relative changes in the band bending as functions of the core size and the charge σ.

The results of the calculations are shown in Fig. 3.

Let us now consider a core in the form of a spherical particle of radius r_1 with an AgI layer. The Poisson equations at $m = 2$ have the form

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

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

Let us write the solutions to Eqs. (35) and (36), taking into account boundary conditions (4) and (5):

$$\psi_1 = \psi_c + \psi_0\left(1 - \frac{1}{\xi_1}\sinh\xi_1\right), \quad (37)$$

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

The constant B_2 is found from the condition of equality of potentials (6) at the interface:

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

The equations for the band bending are derived in the same way as in the planar case; they have the form

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

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

where

$$\beta = \frac{n_1l_1}{n_2l_2}[\cosh(r_1/l_1) - (l_1/r_1)\sinh(r_1/l_1)].$$

At $r_1 \gg l_1, l_2$, formulas (39) and (40) for the band bending pass to formulas (24) describing the planar case. Expressions (39) and (40) were used to calculate the relative changes in the band bending as functions of the core size and the charge σ. The results of the calculations are shown in Fig. 4.

4. RESULTS AND DISCUSSION

The results of the calculation (Figs. 2–4) suggest that an increase in the characteristic core size leads to an increase in the band bending in AgBr and a decrease in the band bending in AgI. At $h_1, r_1 > 3l_1$, the band bendings at the interface between two silver halides almost do not change with an increase in the characteristic core size. A negative charge at the interface decreases the band bending in AgBr and increases it in AgI. A positive charge at the interface between the two media, vice versa, increases the band bending in AgBr and decreases it in AgI. This effect is related to the electroneutrality of the core–shell system. An increase in the band bending in AgBr leads to an increase in the negative space charge, which is due to cation vacancies. An increase in the band bending in

AgI leads to an increase in the positive space charge, which is due to interstitial silver cations. And vice versa.

The band bending at the AgBr–AgI interface depends not only on the core size but also on the geometric layout of the photosensitive core–shell system. It should be noted that the band bending for planar and spherical heterocontacts are similar, and, therefore, the photosensitivities of these systems should be comparable.

Thus, changing the core shape and size, one can change the band bending and, therefore, deliberately control the photosensitivity of materials based on silver halide microcrystals of heterocontact type.

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