

Schottky barriers and their properties in superionic crystals

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The phenomena of Schottky barrier creation in RbAg_4I_5 are studied. Luminescence with high spatial resolution is used as a tool for investigation of the process on the blocking-electrode–solid-electrolyte boundary. The profile of the distribution of electronic centers near the contact region is measured. The presence of electrons and ions in the depletion region at the interface between the RbAg_4I_5 and the graphite electrode is established and interpreted within the framework of the modified Schottky model. It is shown that the small concentration of electrons determines the extent of the depletion region. The kinetics of the creation of Schottky barriers is measured and described by taking into account the presence of self-trapped electrons and mobile silver ions in RbAg_4I_5 . It is shown that the small value of the self-trapped electron diffusion coefficient ($D_{st} \approx 1 \times 10^{-8} \text{ cm}^2/\text{sec}$) limits the kinetics of the process of creation of Schottky barriers.

I. INTRODUCTION

The history of attempts to explain Schottky barrier formation is very complex. One of the main problems is the reduced range of barrier heights available at metal-semiconductor interfaces^{1–3} as compared with a simple Schottky model.⁴ The “Fermi level pinning” is the main problem in studies of Schottky barriers.^{1–3} There are many instances in which the Fermi level position determines the site occupied by a dopant, and instances in which the Fermi level position determines the density of vacancies present within the material.⁵ In this paper, Schottky barrier formation is measured and described in superionic crystals, taking into account the presence of mobile silver ions.

Superionic conductor heterojunction research is a new and important area of research of solid state ionics. One form of heterojunction considered here, namely, the metal–superionic-conductor Schottky barrier junction, is most important for solid electrolytes. Superionic conductors and their applications are of interest primarily because of the enormously high value of their ionic conductivity, amounting to $\sigma_i \approx 0.01\text{--}0.3 \text{ ohm}^{-1} \text{ cm}^{-1}$. The electronic conductivity σ_e in superionic crystals is known to be several orders of magnitude lower than the ionic conductivity.^{6–8} However, electron processes play an important role, because the properties of the electron subsystem determine the processes occurring at the electronic-conductor–superionic-conductor boundary, which in the end determine the extent of practical application of superionic crystals.

It is well known that photoluminescence is a sensitive tool for investigation of the electronic subsystem and the profile of distribution of electronic centers in solid electrolytes.^{9,10} In the present work, with the aim of studying the process at the interface between a solid electrolyte and an electrode and the kinetics of creation of Schottky barriers, an investigation of photoluminescence with high spatial resolution was carried out.

II. EXPERIMENT

Investigations were carried out on polycrystalline RbAg_4I_5 , grown by fusion of a mixture of RbI and AgI of stoichiometric composition. The RbAg_4I_5 crystals obtained are rather stable and can be kept in air for a long time without noticeable changes. Samples with 8 mm length and $3 \times 4 \text{ mm}^2$ cross section were cut from an ingot just before each experiment. The front surfaces of the sample ($3 \times 4 \text{ mm}^2$) were covered by deposited graphite. The samples were mounted in a helium refrigerator. With the aim of studying the kinetics of creation of Schottky barriers, the photoluminescence was measured at 13 K as a function of time at room temperature. The photoluminescence studies were made in the near-electrode region with high spatial resolution. For excitation of the photoluminescence, we used a xenon lamp and a monochromator. By means of an optical system, the light beam was focused to an area of $150 \times 100 \mu\text{m}^2$. The luminescence was analyzed with a double grating monochromator and detected by a photomultiplier. The signal was counted with a photon counter and stored in a computer.^{11,12}

III. FUNDAMENTALS OF THE SCHOTTKY MODEL IN SOLID ELECTROLYTES

It is well established that at metal-semiconductor interfaces the Fermi level position during growth may well control the chemistry occurring during growth.⁵ At metal–superionic-crystal interfaces the situation is more complicated, due to the presence of the mobile ionic subsystem. To describe the specific features at the metal–superionic-crystal interfaces, let us assume the Schottky model for Schottky barrier heights⁴ at the electronic-conductor–nonsuperionic-phase RbAg_4I_5 interface. For highly ionic materials such as this, a simple Schottky model assumption is reasonable. Consider a

contact between an electronic conductor (graphite) and RbAg_4I_5 solid electrolyte.

A. Nonsuperionic phase

Let us first consider the contact between an electronic conductor and the nonsuperionic phase of RbAg_4I_5 . When the electronic conductor and solid electrolyte are brought into contact, a redistribution of charge occurs and finally a new equilibrium condition is reached in which the Fermi levels of the two substances are equal. As a result of the redistribution of charge, a dipole layer is formed at the contact.⁴ The work function of the graphite ($\Phi_C \simeq 4.7$ eV) (Ref. 4) is higher than the work function of RbAg_4I_5 ($\Phi_{SE} \simeq 4.44$ eV) (Ref. 13) ($\Phi_C > \Phi_{SE}$). The situation before contact is shown in Fig. 1(a). It is seen that the Fermi level of RbAg_4I_5 is then above the Fermi level in graphite by the amount $(\Phi_C - \Phi_{SE})$. After contact, a redistribution of charge occurs. Electrons from the near-surface region of RbAg_4I_5 will diffuse to the boundary and enter the graphite, leaving ionized donors behind in that near-surface region. After the redistribution of charge is completed, the Fermi levels in both materials are at the same position; this means that the energy levels in the bulk RbAg_4I_5 are lowered by the amount $(\Phi_C - \Phi_{SE})$. As a consequence a potential barrier is formed at the surface, as shown in Fig. 1(b). On the RbAg_4I_5 side, the height of this barrier is thus $(\Phi_C - \Phi_{SE})$, as shown in Fig. 1. Expressed in volts, the height of the barrier is

$$eV_d = (\Phi_C - \Phi_{SE}), \quad (1)$$

where V_d is known as the diffusion or contact potential.¹⁴

This potential difference is due to the electric dipole layer at the contact. The positive charge at RbAg_4I_5 is caused by ionized donors and this charge does not occur as a surface charge but as a distributed charge in the near-contact region [Fig. 1 (b)]. For this reason in the nonsuperionic phase of RbAg_4I_5 the layer near the sur-

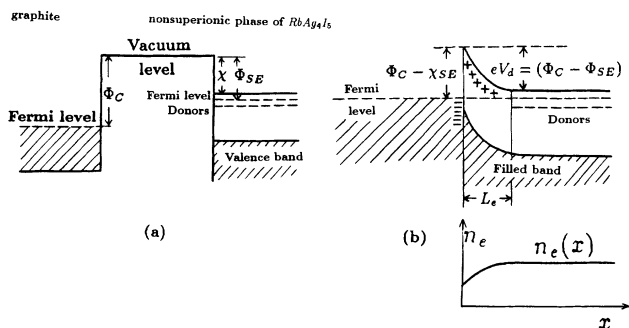


FIG. 1. Energy level diagram of the contact between an electronic conductor (graphite) and nonsuperionic-phase RbAg_4I_5 with $\Phi_C > \Phi_{SE}$, where $\Phi_C = 4.7$ eV and $\Phi_{SE} = 4.44$ eV are the work functions of graphite and RbAg_4I_5 , respectively, and χ_{SE} is the electron affinity. Energy level diagram (a) before and (b) after contact.

face is a space-charge layer. Inside this near-contact region the concentration of mobile electrons is smaller than that in the bulk [Fig. 1(b)]. There is internal electric field and voltage distribution in the space-charge layer. The thickness L_e of this layer depends upon the concentration of mobile electrons in the conduction band (n_e) and is of the order of the Debye screening radius for electrons in the nonsuperionic phase of RbAg_4I_5 :

$$L_e \simeq \sqrt{\epsilon kT / e^2 n_e}, \quad (2)$$

where ϵ is the dielectric constant of the nonsuperionic phase of RbAg_4I_5 , e is the electronic charge, k is Boltzmann's constant, and T is the sample temperature. According to the simple model,¹⁴ the Schottky barrier acts as a capacitor with a value of the potential V_d . The capacitance C per unit area of the double charge layer is the same as for a plane capacitor of unit area and plate distance L_e [$C = \epsilon / (4\pi L_e)$]. Due to this a value of charge Q_{non} per unit area of surface of the space-charged layer is

$$Q_{\text{non}} \simeq \frac{\epsilon(\Phi_C - \Phi_{SE})}{4\pi e L_e}, \quad (3)$$

for the nonsuperionic phase of RbAg_4I_5 .

B. Superionic α phase of RbAg_4I_5

The situation before contact between the electronic conductor and $\alpha\text{-RbAg}_4\text{I}_5$ is the same as for the nonsuperionic phase of RbAg_4I_5 [Fig. 1(a)]. The Fermi level for electrons in $\alpha\text{-RbAg}_4\text{I}_5$ is above the Fermi level for electrons in graphite by the amount $(\Phi_C - \Phi_{SE})$. After the contact, a redistribution of charge occurs. In our previous study of the process of ambipolar diffusion,¹⁰ it was shown that the mobile electrons in $\alpha\text{-RbAg}_4\text{I}_5$ are self-trapped and move together with the surrounding ions. If the self-trapped electron in $\alpha\text{-RbAg}_4\text{I}_5$ diffuses to the boundary and enters the graphite, then there is silver ion near the surface of the solid electrolyte. Due to charge neutrality, the charge of the ionized donor is screened by the redistribution of mobile ions in its immediate surroundings and by movement of the ion from the position surrounding the donor together with the electron from this ionized donor. There is no distributed charge in the near-contact region since the charges of ionized donors are screened. On the solid electrolyte side the charge will occur as a surface charge (Fig. 2). There are an internal electric field and a voltage distribution in a thin layer with a thickness

$$L_i = \sqrt{\epsilon kT / e^2 n_i} \simeq 5 \text{ \AA}, \quad (4)$$

where $n_i \simeq 10^{22} \text{ cm}^{-3}$ is the concentration of mobile ions in $\alpha\text{-RbAg}_4\text{I}_5$.

Due to this, the barrier capacitance in $\alpha\text{-RbAg}_4\text{I}_5$ ($C_{\text{sup}} \simeq \epsilon / 4\pi L_i$) is much higher than in a nonsuperionic crystal and it needs many more electrons per unit area of surface,

$$Q_{\text{sup}} \simeq \frac{\epsilon(\Phi_C - \Phi_{SE})}{4\pi e L_i}, \quad (5)$$

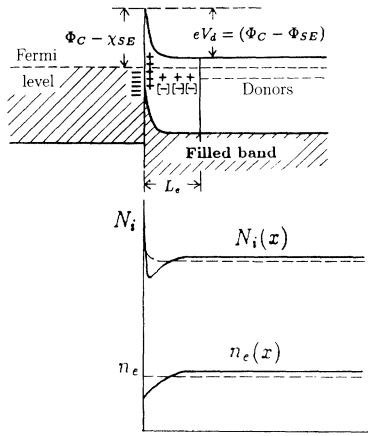


FIG. 2. Energy level diagram of the graphite- α -RbAg₄I₅ contact and a profile of the concentration of silver ions and electrons ~ 30 – 100 h after contact. N_i and n_e are the concentrations of ions and electrons. The new equilibrium concentration of electrons and ions in the sample with graphite contact after finishing the process of diffusion is shown by the dashed curve.

and a longer time for formation of the diffusion potential V_d .

To create the diffusion potential the self-trapped electrons together with the ions come from the near-contact region. Outside the thin surface-charge layer there is an area of the near-contact region in which the concentration of electrons and silver ions is smaller than in the bulk (Fig. 2). For electrical neutrality, the change of the concentration of silver ions is the same as the change of the concentration of electrons (Fig. 2). Due to this the small concentration of electrons determines the extent and time dependence of formation of the depletion region.

As mentioned above, after the contact, the self-trapped electrons diffuse to the boundary and enter the graphite. In accordance with this, the creation of the near-contact depletion region can be described by the process of one-dimensional diffusion of self-trapped electrons and the surrounding silver ions to the boundary from the bulk. In the present work photoluminescence was used as a tool to determine the concentration profile of silver in the depletion region. The calculation of the diffusion coefficient from the concentration profile was carried out by using Fick's second law,¹⁵ which in one dimension is

$$\frac{dC}{dt} = \frac{d}{dx} \left[D \frac{dC}{dx} \right], \quad (6)$$

where C is the concentration of the diffusing atoms, x the diffusion distance, and D the diffusion coefficient. The analytical solution of this one-dimensional diffusion equation (6) for a thin film of tracer is

$$C(x, t) = C_0 + C_1 \exp \left[-\frac{x^2}{4Dt} \right], \quad (7)$$

where C_0 is the background concentration in the sample

and t is the diffusion time. The diffusion coefficient was determined by fitting the analytical equation (7) to the experimental data of the profile of silver concentration.

To confirm our model of Schottky barrier formation in α -RbAg₄I₅ an investigation was made of the photoluminescence with high spatial resolution in the near-contact region.

IV. RESULTS AND DISCUSSION

With the aim of studying the mechanism of Schottky barrier formation in superionic crystals and the influence of a blocking electrode on the properties of the electronic subsystem in RbAg₄I₅, an investigation of photoluminescence was made. Previous studies showed that the photoluminescence of the low-temperature γ phase of RbAg₄I₅ comes from luminescence centers.^{9,10,16} In the photoluminescence spectrum of RbAg₄I₅ there are luminescence bands with wavelength maxima at $\lambda_{p11}=387$, $\lambda_{p11.1}=397$, $\lambda_{p12}=437$, $\lambda_{p13}=450$, and $\lambda_{p14}=462$ nm. In accordance with the results obtained in Ref. 9 the emission bands at $\lambda_{p11}=387$ nm and $\lambda_{p11.1}=397$ nm may be attributed to centers involving silver vacancies, and the emission bands at $\lambda_{p12}=437$ nm and $\lambda_{p14}=462$ nm are associated with centers whose composition involves interstitial silver. Analysis of the distribution of the photoluminescence band intensity along the sample length will allow us to get information about the profile of distribution of luminescence centers and of the silver cation concentration.^{9,10}

To get information about the mechanism and time dependence of Schottky barrier formation, the photoluminescence spectra were measured with high spatial resolution in the near-contact region of RbAg₄I₅. For this experiment graphite was deposited on the end face of a sample with 8 mm length and 3×4 mm² cross section. Figure 3 shows the photoluminescence spectra 65 h after graphite deposition measured at different distances from the contact. From Fig. 3, it is seen that the intensity of the luminescence bands at $\lambda_{p11}=387$ nm and $\lambda_{p11.1}=397$ nm increases in the near-contact region. The intensity of

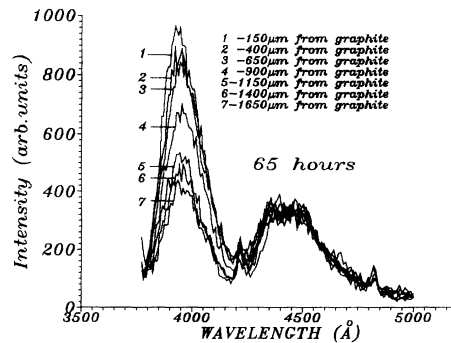


FIG. 3. Photoluminescence spectra 65 h after electronic conductor deposition as measured at distances 150 (curve 1), 400 (curve 2), 650 (curve 3), 900 (curve 4), 1150 (curve 5), 1400 (curve 6), and 1650 μ m (curve 7) from the contact.

these luminescence bands decreases as a function of distance from the contact and at a distance $1650 \mu\text{m}$ the photoluminescence spectrum looks like the spectrum from the primary sample. In our previous study⁹ it was shown that the photoluminescence in the spectral region $3800\text{--}4150 \text{ \AA}$ is associated with luminescence centers whose composition involves silver vacancies, and the integrated intensity in this spectral region is proportional to the lack of silver. In accordance with this the integrated intensity in the spectral region $3800\text{--}4150 \text{ \AA}$ at some distance from the contact is proportional to the lack of silver (or to the concentration of silver vacancies at this distance). The dependence on the distance from the contact gives the profile of relative concentration of silver vacancies in the RbAg_4I_5 sample after graphite deposition. Figure 4 shows the experimental results for the distance dependence of the relative concentration of silver vacancies in the RbAg_4I_5 sample 65 h after graphite deposition at temperature 295 K, and also the fit of the analytical curve (7) to the experimental data. To get a value of the diffusion coefficient of the self-trapped electrons and surrounding silver ions, the calculated curve for solution of the diffusion equation (7) is fitted to the experimental data by using D as the fitting parameter. From this procedure the value of the self-trapped electron diffusion coefficient is obtained as $D_e = 0.96 \times 10^{-8} \text{ cm}^2/\text{sec}$ at temperature 295 K.

To get information about the kinetics of the creation of the Schottky barrier and near-electrode depletion region in $\alpha\text{-RbAg}_4\text{I}_5$, measurements of the distribution of the photoluminescence band intensity in the near-contact region were done as a function of time from graphite deposition. Figure 5 shows the experimental results for the distance dependence of the relative concentration of silver vacancies, 6, 27, 65, and 102 h after graphite deposition (curves 1, 2, 3, and 4, respectively). The fitting of the curve calculated by equation (7) to the experimental data gives a value of the diffusion coefficient of

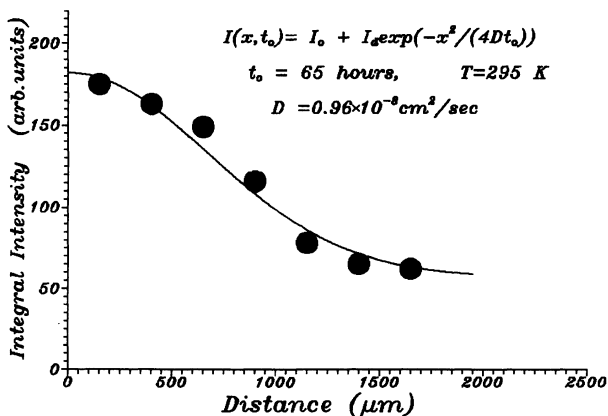


FIG. 4. Integrated intensity in the spectral region $3800\text{--}4150 \text{ \AA}$ as a function of distance from the contact (solid circles) 65 h after graphite deposition. The solid line is the fit of the analytical solution of the one-dimensional diffusion equation (7) to these data.

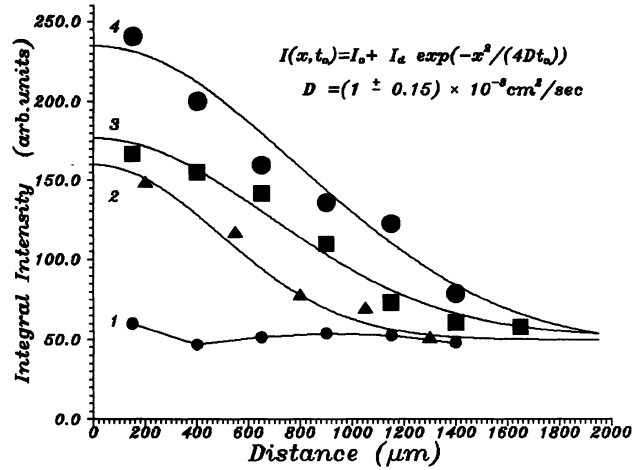


FIG. 5. Relative concentration of silver vacancies as a function of distance from contact as measured 27, 65, and 102 h after graphite deposition. The solid lines show the fit of the analytical solution of the one-dimensional diffusion equation (7) to the data (curves 2, 3, and 4). Curve 1 shows the relative concentration of silver vacancies 6 h after graphite deposition.

$D_e = (1 \pm 0.2) \times 10^{-8} \text{ cm}^2/\text{sec}$ for the process of one-dimensional diffusion of self-trapped electrons in $\alpha\text{-RbAg}_4\text{I}_5$ at 295 K (Fig. 5). This value is in good agreement with the value of the self-trapped electron diffusion coefficient $D_e = (1.7 \pm 0.7) \times 10^{-8} \text{ cm}^2/\text{sec}$ measured in our previous work.¹⁰

In accordance with this, the creation of the Schottky barrier and of the depletion near-contact region in $\alpha\text{-RbAg}_4\text{I}_5$ takes place due to the diffusion of self-trapped electrons from solid electrolyte into graphite. A redistribution of charge and diffusion take place until the Fermi levels in both materials are at the same position. As a consequence, a potential barrier $eV_d = (\Phi_C - \Phi_{SE})$ is formed at the surface. The value of this potential barrier is due to the difference in the values of the work function for electrons in graphite and RbAg_4I_5 , but the properties of the barrier are determined by the presence of mobile silver ions. Really, there is no distributed charge in the near-contact region of $\alpha\text{-RbAg}_4\text{I}_5$, since the charge of the ionized donors is screened by the redistribution of mobile silver ions. On the solid electrolyte side the charge appears as a surface charge (Fig. 2). Due to this in $\alpha\text{-RbAg}_4\text{I}_5$ the barrier capacitance ($C_{\text{sup}} \approx 10^{-5} \text{ F}$) (Ref. 17) is much higher than in semiconductors and in the nonsuperionic phase of RbAg_4I_5 . In this case many more electrons are needed for formation of the diffusion potential ($V_d \approx 0.25 \text{ V}$),

$$Q_{\text{sup}} \approx V_d C_{\text{sup}} \approx 2.5 \times 10^{-6} q / \text{cm}^2 \approx 2 \times 10^{13} e / \text{cm}^2. \quad (8)$$

V. MODEL OF SAMPLE DEPLETION

If we deal with a semi-infinite medium of $\alpha\text{-RbAg}_4\text{I}_5$ after finishing the process of diffusion there is internal electrical field and voltage distribution in a thin layer with a thickness $\sim 5\text{--}10 \text{ \AA}$ and there is no deviation from

the properties of bulk RbAg_4I_5 outside the Schottky barrier. But for a real sample, the deposition of an electronic conductor on the surface of $\alpha\text{-RbAg}_4\text{I}_5$ will change the properties of the sample drastically. For the formation of the diffusion potential it needs about 10^{13} electrons per cm^2 to diffuse from the bulk to the boundary and enter the electronic conductor. At the same time, the electronic conductivity of $\alpha\text{-RbAg}_4\text{I}_5$ is small ($\sigma_e \approx 3 \times 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$),⁷ and the concentration of mobile electrons is small ($n_{st} \sim 10^{15} - 10^{16} \text{ cm}^{-3}$), too.¹⁰ In accordance with this if the thickness of the sample L_{sample} is small, the order of Q_{sup}/n_{st} ($L_{\text{sample}} \leq 0.1 \text{ mm}$), then it needs approximately all the mobile electrons to diffuse from the bulk to the boundary for formation of the diffusion potential. In this case the deposition of an electronic conductor leads to depletion of the sample by mobile electrons and ions and to a shift of the position of the Fermi level.

To describe this phenomenon let us consider the process of screening of ionized donors in $\alpha\text{-RbAg}_4\text{I}_5$. As pointed out earlier, the charge of the ionized donors is screened by ions leaving positions surrounding the donor together with the electrons from this donor. But this is the same as a transformation of the structure of the donor centers and the same as a decrease of the concentration of donors in the sample. If N_e is the amount of electrons which leave $\alpha\text{-RbAg}_4\text{I}_5$ for formation of the diffusion potential, then the average decrease of the concentration of donors in the sample is N_e/L_{sample} , and the average concentration of donors (N_D) in the sample is

$$N_D = N_D^0 - N_e/L_{\text{sample}} = N_D^0 - \frac{V_d C_{\text{sup}}}{eL_{\text{sample}}}, \quad (9)$$

where N_D^0 is the initial concentration of donors. Let us propose that there is only one type of donor in $\alpha\text{-RbAg}_4\text{I}_5$ with the depth of the donor level E_D . In this approach the position of the Fermi level (μ) and the value of the work function (Φ_{SE}) are the following functions of N_D and E_D :

$$\mu = \frac{1}{2}E_D - \frac{kT}{2} \ln \left[\frac{N_D^0 - \frac{V_d C_{\text{sup}}}{eL_{\text{sample}}}}{P_e} \right], \quad (10)$$

and

$$\Phi_{\text{SE}} = \chi_{\text{SE}} + \mu = \chi_{\text{SE}} + \frac{1}{2}E_D - \frac{kT}{2} \ln \left[\frac{N_D^0 - \frac{V_d C_{\text{sup}}}{eL_{\text{sample}}}}{P_e} \right], \quad (11)$$

where $P_e = 2(2\pi m_e kT/h^2)^{3/2}$ is the density of electronic states in the conduction band and χ_{SE} is the value of the electron affinity.

It is seen that the new position of the Fermi level (μ) and the value of the work function (Φ_{SE}) depend on the sample size L_{sample} and on the value of the diffusion potential (V_d). At the same time, the value of the diffusion potential depends on the value of the work function of RbAg_4I_5 [Eq. (1)]. Due to this, a new equilibrium condition is reached in the $\alpha\text{-RbAg}_4\text{I}_5$ sample after the contact

deposition. The position of the Fermi level shifts and the value of the work function increases with respect to the initial sample. It is possible to obtain the new equilibrium values of the work function and the diffusion potential and the position of the Fermi level, as well as their general dependence on the sample size, by self-consistent solution of Eqs. (1), (10), and (11). Let us consider a simple approach when the sample depletion and the decrease of the concentration of donors (9) in the sample is small, $V_d C_{\text{sup}}/eL_{\text{sample}} \ll N_D^0$. Then the corrections to the value of the diffusion potential (V_d) and to the position of the Fermi level (μ) are small, too. From a simple calculation it follows that the new value of the position of the Fermi level is

$$\mu = \mu_0 + \frac{kT}{2} \left[\frac{V_d^0 C_{\text{sup}}}{eL_{\text{sample}} N_D^0} \right] - \frac{kT}{2} \left[\frac{V_d^0 C_{\text{sup}}^2 (eV_d^0 + kT)}{e(eL_{\text{sample}} N_D^0)^2} \right], \quad (12)$$

where the quantities

$$\frac{kT}{2} \left[\frac{V_d^0 C_{\text{sup}}}{eL_{\text{sample}} N_D^0} \right]$$

is of the same order of magnitude as the correction of the concentration of donors, and

$$\frac{kT}{2} \left[\frac{V_d^0 C_{\text{sup}}^2 (eV_d^0 + kT)}{e(eL_{\text{sample}} N_D^0)^2} \right]$$

is a second-order correction. Thus the first-order correction gives the shift of the position of Fermi level in RbAg_4I_5 after the deposition of an electronic conductor. It is seen that the shift of the Fermi level and the sample depletion are proportional to the value of the diffusion potential and are inversely proportional to the thickness of the sample. But for quantitative analysis of the dependence of Φ_{SE} , μ , and V_d on the sample size (L_{sample}) it is necessary to know the real dependence of the position of the Fermi level on the concentration and on the depth of donor levels in RbAg_4I_5 .

VI. CONCLUSION

The formation of a depletion zone ($\sim 0.1 - 1 \text{ mm}$) near the contact region in RbAg_4I_5 has been investigated. It is found that blocking electrode deposition on the surface of the sample leads to a change in concentration and structure of the luminescence centers and to a decrease of the concentration of mobile silver ions and electrons in parallel in the near-surface region. If the size of the sample is smaller than the size of the depletion region in RbAg_4I_5 ($\sim 1 \text{ mm}$) then the deposition of an electronic conductor leads to depletion of the sample by mobile electrons and ions and to a shift of the position of the Fermi level. It is shown that the small concentration of electrons determines the size and time dependence of formation of depletion region. The value of the self-trapped electron diffusion coefficient is obtained as $D_e = (1 \pm 0.2) \times 10^{-8} \text{ cm}^2/\text{sec}$.

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