Unified percolation model for bipolaron-assisted organic magnetoresistance in the unipolar transport regime

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(Received 9 December 2015; revised manuscript received 10 July 2016; published 4 August 2016)

The fact that in organic semiconductors the Hubbard energy is usually positive appears to be at variance with a bipolaron model to explain magnetoresistance (MR) in those systems. Employing percolation theory, we demonstrate that a moderately positive U is indeed compatible with the bipolaron concept for MR in unipolar current flow, provided that the system is energetically disordered, and the density of states (DOS) distribution is partially filled, so that the Fermi level overlaps with tail states of the DOS. By exploring a broad parameter space, we show that MR becomes maximal around $U = 0$ and even diminishes at large negative values of U because of spin independent bipolaron dissociation. Trapping effects and reduced dimension enhance MR.

DOI: 10.1103/PhysRevB.94.075201

I. INTRODUCTION

In this paper, we examine the origin of magnetoresistance (MR) in an organic semiconductor (OSC) under the condition of unipolar current flow. In an OSC, charge carriers are usually injected from an electrode and migrate via incoherent hopping. If the counter charges, required to maintain overall charge neutrality of the device, are not incorporated in the bulk of transport material (e.g., at a gate electrode of a field effect transistor), MR must originate from the interaction between charge carriers of the same sign, which reduces to charge carrier scattering at the repulsive Coulomb potential unless bipolarons can be formed. This implies that the cost of Coulomb repulsion is overcompensated through the gain by coupling to phonons. However, the formation of bipolarons can lead to a spin blockade because the Pauli exclusion principle prevents double occupancy of two charge carriers of the parallel spin [1,2]. This spin blockade can be lifted by hyperfine interaction that can rotate a spin thus allowing for singlet-triplet interconversion of a charge carrier pair [3]. A sufficiently strong magnetic field can suppress this singlet-triplet mixing and restores spin blockade because only bipolarons in the singlet state can be formed. This gives rise to MR.

In OSCs there is usually a Coulomb penalty for adding two like charges on a given transport site because of insufficient phonon coupling. It is quantified in terms of the Hubbard energy U that is typically around 0.5 eV [4]. At first sight, one would expect that the MR be virtually negligible. However, the situation changes when an OSC is energetically disordered and/or when traps play a role [5–7]. In those cases, the energy released when a charge relaxes to a tail state of the density of states (DOS) distribution can overcompensate the Coulomb penalty, where there is a finite probability for bipolaron formation. The MR effect should therefore depend critically on the interplay between Hubbard repulsion and electronic localization due to energy disorder as a function of the Fermi level of the OSC.

Historically, the percolation treatment of low-field magnetoresistance of amorphous semiconductors has been discussed since the 1970s. By considering the conductance in the critical percolation path, Osaka [8] obtained an exponential dependence of MR on U. This monotonic increase of MR with U is unphysical. To avoid this problem, Harmon and Flatté developed a $U = 0$ model [2,7,9]. This raises the question of how the Hubbard energy can be incorporated in the percolation theory of MR. A related topic is spin relaxation and diffusion in the presence of bipolarons. In [10], Shumilin and Kabanov investigated the spin relaxation in a random magnetic field. In an earlier paper [11], we investigated the effect of spin diffusion after the injection of charge carriers from a ferromagnetic electrode into a disordered semiconductor. In both treatments, a finite value of U has been taken into account and the dynamics of spin polarization have been considered. However, these models are built for systems with substantial on-site magnetization, which is not the case for most MR experiments, where the Zeeman energy resulting from a typical magnetic field is negligible relative to kT [1,3]. For example, in [10], the magnetic field can affect the resistances only via nonzero on-site magnetization, and MR under typical experimental conditions cannot be explained. In [11], only the effects of bipolaron formation and spin exchange (which is unrelated to MR) are considered, thus even assuming zero magnetization, the model is insufficient to describe MR. Thus what is missing is a comprehensive treatment of the interdependent processes of generation, motion, and dissociation of bipolarons in a percolating network with zero on-site magnetization. In the current work, we developed a universal formalism for organic MR covering a broad parameter space using a percolation approach. It goes beyond the previous treatments and should lead to a deeper understanding of spintronics in organic systems [12,13].

II. THE MODEL

In a conventional hopping theory, it is assumed that charge carriers can only hop from a singly occupied site (S) i to an empty site (E) j. The hopping rate is usually described by the

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Miller-Abrahams relation [14]

$$\gamma_{ij}^{S\to E}(R_{ij},E_i,E_j) = \gamma_0 e^{-(2R_{ij}/R_0)-[\theta(E_j-E_i)/kT]}, \quad (1)$$

where γ_0 is the prefactor rate, R_{ij} is the distance between the two sites, R_0 is the localization length of the carrier's wave function, E_i and E_j are the energies of the sites i and j relative to the Fermi level, and $\theta(x) = x\varepsilon(x)$ with $\varepsilon(x)$ being the step function. Treating the external electric field as a perturbation [15], the hopping system can be modeled as a resistor network with the conductance between sites i and j to be $G_{ij} = G_0 e^{-s_{ij}}$ with $G_0 = e^2\gamma_0/kT$ and

$$s_{ij} = \frac{2R_{ij}}{R_0} + \frac{|E_i| + |E_j| + |E_j - E_i|}{2kT}. \quad (2)$$

The conduction can then be viewed as a percolation process: If setting a critical conductance G_c and disconnecting all bonds with conductance lower than G_c, the density of remaining bonds N_b divided by the total density of sites N_s should have the critical value B_c to allow for establishing an infinitely connected network. The conductance of the system is then approximately proportional to G_c, since it controls the most difficult transport path of the resistor network [16].

The above consideration neglects the possibility of double occupancy, i.e., $U = \infty$. If U is finite, there is a finite possibility of double occupancy. To consider this in theory, one should include additional carrier hopping processes such as from a singly occupied site to another singly occupied one (i.e., bipolaron formation), from a doubly occupied site to a singly occupied one (i.e., bipolaron motion) [17], and from a doubly occupied site to an empty one (i.e., bipolaron dissociation), as illustrated in Fig. 1(a). The corresponding hopping rates can be written as

$$\begin{aligned}
\gamma_{ij}^{S\to S}(R_{ij},E_i,E_j) &= p\gamma_{ij}^{S\to E}(R_{ij},E_i,E_j+U),\\
\gamma_{ij}^{D\to S}(R_{ij},E_i,E_j) &= \gamma_{ij}^{S\to E}(R_{ij},E_i,E_j),\\
\gamma_{ij}^{D\to E}(R_{ij},E_i,E_j) &= \gamma_{ij}^{S\to E}(R_{ij},E_i+U,E_j),
\end{aligned} \quad (3)$$

where D denotes the initial site i as being doubly occupied, and p is the probability that a bipolaron can form without spin blockade, implying that only carrier pairs with antiparallel spin can occupy the same site. The random hyperfine field rotates the spins and may convert triplet to singlet states, thus lifting spin blockade. A strong external magnetic field suppresses this singlet-triplet mixing, and restores the spin blockade.

It is not an easy task to calculate this probability rigorously without numerical methods. In this work, we adopt the treatment used in [3], where the long-time triplet-to-singlet transition probability is approximated as $p_{T\to S} \sim \sigma_h^2/(\sigma_h^2 + B^2)$. First consider the long waiting time case. According to [18], this $p_{T\to S}$ dominates for the bipolaron formation probability of random polaron pairs. For zero magnetic field, all three triplet states T_0, T_+, and T_- can transform into the singlet state S sooner or later, corresponding to $p = 1$, while for large magnetic fields, the parallelity of the z component of spin cannot be flipped, thus only the T_0 state can be transformed to a S state, corresponding to $p = 1/2$. To incorporate the short hopping time cases, an exponent factor [2] $1 - \exp(-\tau_h/\tau_s)$

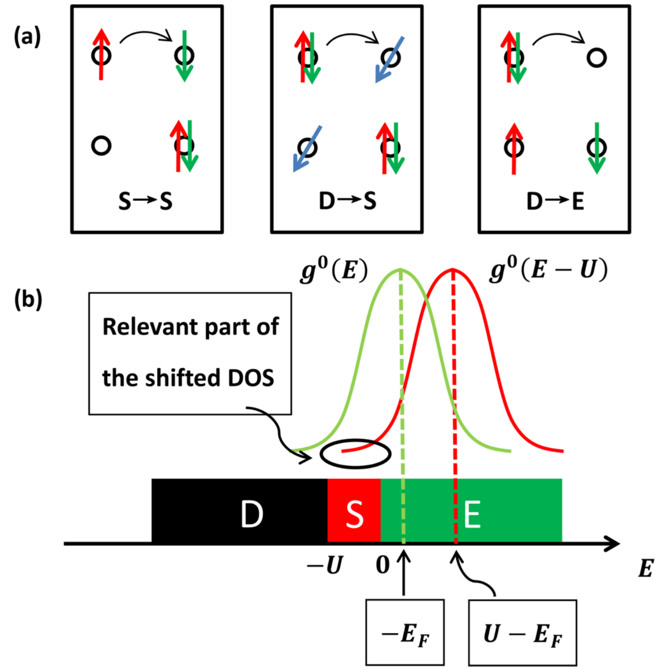

FIG. 1. (a) Carrier hopping processes including (left) bipolaron formation, (middle) bipolaron motion, and (right) bipolaron dissociation. Top row: spin configurations before hopping; bottom row: spin configurations after hopping. (b) Illustration of the effective DOS and the three occupancy ranges (D: double occupancy; S: single occupancy; and E: empty). Only the part of $g^0(E-U)$ that is inside the range $[-U,0]$ contributes to the MR.

should be multiplied on $p_{T\to S}$, so finally we have

$$p = \left(\frac{1}{2} + \frac{1}{2}\frac{\sigma_h^2}{\sigma_h^2 + B^2}\right)(1 - e^{-e\tau_h\sigma_h/\pi m}), \quad (4)$$

where σ_h is the standard deviation of the hyperfine field, B is the external magnetic field, m is the carrier mass, e the elementary charge, and $\tau_h = 1/(\nu_0 e^{-s_{ij}})$ is the hopping waiting time [19,20].

To incorporate these processes into percolation theory, it is convenient to introduce an equivalent treatment: the singly occupied sites in a finite U system can be considered as empty in a $U = \infty$ system with the probability p for bipolaron formation process, except that their corresponding site energies should be raised by U. Similarly, the doubly occupied sites can always be considered as singly occupied in the bipolaron motion and dissociation process. Thus, the system can still be approximated as a $S \to E$ percolating process, only with the original DOS $g^0(E)$ replaced by an effective DOS

$$g(E) = g^0(E) + [f_D(E) + pf_S(E)]g^0(E-U), \quad (5)$$

where f_S and f_D are the probabilities of a site to be singly and doubly occupied, respectively. Neglecting intersite correlations, each site is a separate thermodynamic system in contact with the reservoir, and forms a grand canonical ensemble [8]. The four microstates available are empty, singly occupied with spin up, singly occupied with spin down, and doubly occupied microstates. The grand canonical partition function is then

$Z = 1 + 2\exp(-E/kT) + \exp[-(2E + U)/kT]$, and thus

$$f_E(E) = \frac{1}{1 + 2\exp(-E/kT) + \exp[-(2E + U)/kT]},$$
$$f_S(E) = \frac{2\exp(-E/kT)}{1 + 2\exp(-E/kT) + \exp[-(2E + U)/kT]}, \quad (6)$$
$$f_D(E) = \frac{\exp[-(2E + U)/kT]}{1 + 2\exp(-E/kT) + \exp[-(2E + U)/kT]},$$

where f_E is the probability of a site to be empty.

The percolation problem can then be directly calculated using this effective DOS. As a function of s_c, the density of bonds is [16]

$$N_b(G_c) = N_s B_c = \int d\boldsymbol{R}_{ij} dE_i dE_j g(E_i) g(E_j) \varepsilon \left[\ln\left(\frac{G_0}{G_c}\right) - s_{ij} \right]. \quad (7)$$

The solution of Eq. (7) gives the critical conductance G_c, and MR can be evaluated by introducing the external magnetic field as a parameter.

III. MR IN IDEAL OSCs

In an ideal amorphous organic semiconductor, the DOS can be well described by a Gaussian distribution [21],

$$g^0(E) = \frac{N_s}{\sqrt{2\pi}\sigma} e^{-(E+E_F)^2/2\sigma^2}, \quad (8)$$

where σ is the disorder width, and E_F is the Fermi level. Substituting this DOS into Eqs. (5) and (7), we can numerically calculate the OMR: guessing an initial G_c at first, the corresponding N_b is obtained by numerical integration. Then a binary search algorithm is used to repeatedly generate a new G_c until N_b equals $N_s B_c$. Here we use the definition of MR as

$$MR(B) = \frac{R(B) - R(0)}{R(0)} = \frac{G(0) - G(B)}{G(B)}, \quad (9)$$

where $G(B)$ $[R(B)]$ is the conductance (resistance) at external magnetic field B, and $G(0)$ $[R(0)]$ is the conductance (resistance) at zero magnetic field. A typical MC curve for a three-dimensional (3D) system with $B_c = 2.8$ [16,22], $\sigma = 0.15$ eV, $U = 0.5$ eV, $R_0 = 0.45$ nm $E_F = -0.1$ eV, $N_s = 10^{21}$ cm^{-3}, $\sigma_h = 5$ mT, and $T = 300$ K is shown in Fig. 2(a). It can be fitted well by a Lorentzian line shape $B^2/(B^2 + B_0^2)$ [23]. It is also noted that the temperature dependence of the conductance exhibits an Arrhenius-like

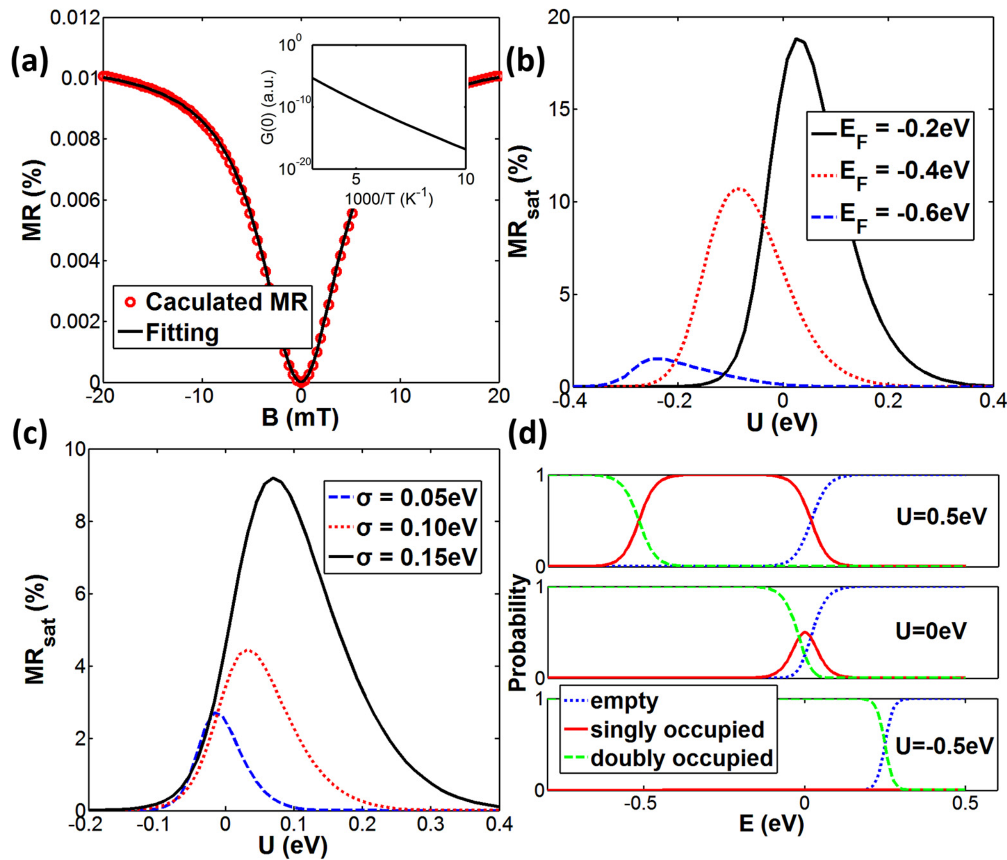

FIG. 2. (a) The MR curve as a function of external magnetic field in a 3D system. Circular marks: MR values calculated using Eq. (7). Solid curve: fitting of the calculated data using a Lorentzian line shape. Inset: the temperature dependence of the conductance at zero magnetic field. (b) Saturated MR as functions of the bipolaron formation energy parametric in the Fermi level. (c) Saturated MR as functions of the bipolaron formation energy parametric in the disorder width. The parameters in (b) and (c) are the same as in (a) except for varying E_F in (b) and varying σ in (c). (d) Probability of a site to be empty, singly occupied, and doubly occupied at 300 K.

relationship, as shown in the inset of Fig. 2(a). This is a consequence of thermally activated hopping in a Gaussian DOS rather than long-range hopping in the spirit of Mott's variable range hopping concept [24]. Setting MR(50 mT) as the saturated magnetoconductance MR_{sat}, we calculated MR as a function of the Hubbard energy U, parametric in the Fermi level E_F and disorder width σ in Figs. 2(b) and 2(c), respectively. It shows that raising the Fermi level as well as the disorder width increases the MR effect in the $U > 0$ regime. This is a plausible result because as the DOS is being filled up and/or the DOS widens, the probability of bipolaron formation increases. Remarkably, after reaching the maximum around $U = 0$, the MR deceases as U becomes more negative. Note that our results contradict Osaka's claim that magnetoresistance increases monotonically with U.

To explain these results, we first investigate the occupation probabilities f_E, f_S, and f_D according to Eq. (6). At zero temperature and for positive U, it is easy to prove that $f_E(E) = \varepsilon(E)$, $f_D(E) = \varepsilon(-U - E)$, and $f_S(E) = \varepsilon(E + U) - \varepsilon(E)$. The full energy range thus divides into three parts: the interval $[-U,0]$ is singly occupied, and the other two ranges $[0,\infty]$ and $[-\infty,-U]$ are empty and doubly occupied, respectively. Raising the temperature has only a small effect except that there is a smearing of the boundaries between the domains, as shown in Fig. 2(d). For negative U, both boundaries tend to merge. Therefore the interface between empty and double occupancy lies at $E = -U/2$. An external magnetic field enters into the percolation problem through the bipolaron formation probability p. Therefore, only the term proportional to $f_S(E_j)$ in Eq. (5) determines the MR. This explains why a large negative U leads to a vanishing MR. The reason is that when the sites are almost either empty or doubly occupied, the external magnetic field has little effect on the percolation process, because bipolaron dissociation is spin independent. Another important aspect in the effective DOS [Eq. (5)] is the energy shift U. This can be illustrated in Fig. 1(b), where only the $U > 0$ case is considered and the three energy ranges are colored by black (doubly occupied), red (singly occupied), and green (empty), respectively. The original DOS is shifted to the right by U, and then multiplied by $f_S(E_j)$. Thus, only the part of the shifted DOS within the range $[-U,0]$ contributes substantially to the MR. The larger U is, the wider will be the single occupancy range, but the relevant DOS will be located in the deeper tail. Remembering that the energy E is measured from the Fermi level E_F, to get a large MR, it is thus beneficial to raise the Fermi level. Larger disorder width also helps to relax the requirement concerning the value of U. To shift the $n\sigma$ tail of the DOS into the singly occupied range, the inequality $U - E_F < n\sigma$ should be satisfied. This explains the change of MR_{sat} curves in Figs. 2(b) and 2(c). We note that this rise of MR with the Fermi level has been demonstrated in a recent experiment performed with a thin-film field transistor (TFT) structure [25], where the MR increases with the gate voltage. In typical experiments [25], it is nontrivial to obtain high E_F and low U, so that only deep tails of the DOS can contribute. This leads to a small value of MR. When optimizing the Fermi level and disorder in some unipolar devices, it is possible to have large MR, as predicted in Figs. 2(b) and 2(c). In a two-terminal device, on the contrary, the hopping waiting time τ_h decreases, leading to a smaller p according to Eq. (4), although the carrier concentration increases with larger voltage.

The $U = 0$ case was discussed in detail previously [2]. Here we note that a system with small Hubbard energy can indeed exhibit a substantial MR effect, because on the one hand, the single occupancy around $E = 0$ is still not completely suppressed [Fig. 2(d)]. On the other hand, reducing U will shift the DOS toward the singly occupied range. $U \approx 0$ roughly provides a balance between these two effects.

IV. THE EFFECT OF TRAPS

In real world OSCs there are always physical and/or chemical defects. In the bipolar transport regime, it has been experimentally suggested that the existence of traps should facilitate MR [6]. Here we show this is also valid for unipolar transport cases. The DOS including deep traps can be modeled as a double Gaussian function

$$g^0(E) = \frac{N_s - N_t}{\sqrt{2\pi}\sigma} e^{-(E+E_F)^2/2\sigma^2} + \frac{N_t}{\sqrt{2\pi}\sigma_t} e^{-(E+E_t+E_F)^2/2\sigma_t^2}, \tag{10}$$

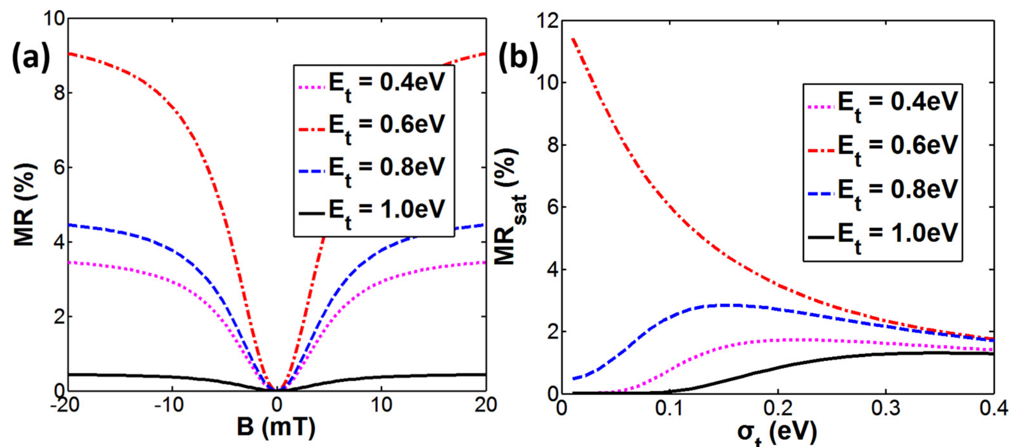

FIG. 3. (a) MR as functions of external magnetic field at different trap depths. (b) Saturated MR as functions of the width of the trap distribution at different trap depths.

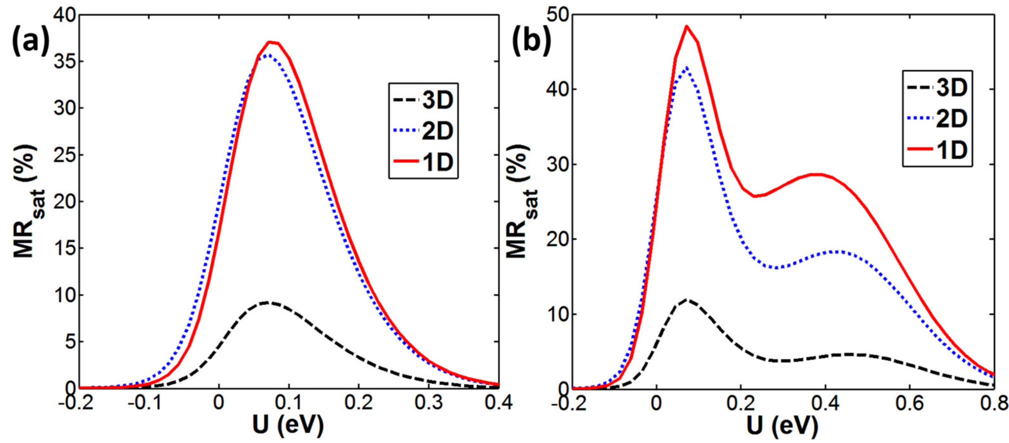

FIG. 4. Effect of dimensionality of MR in a trap-free system (a) and a system containing traps (b).

where N_t is the density of trapping sites, E_t is the trapping depth, and σ_t is the trapping width. From an intuitive point of view, the additional trapping term in Eq. (10) alleviates the requirement to shift the DOS to the singly occupied domain [Eq. (5)], and the inequality now becomes $U - E_F < n\sigma_t + E_t$. It is even possible to shift the peak of the DOS into the range $[-U,0]$, which requires $U \approx E_F + E_t$. To verify this argument, we calculate the MR curves of a two-component system with the same parameters used in Fig. 2(a), together with $N_t = 0.1N_s$, $\sigma_t = 0.15$ eV, and varying E_t. The results are presented in Fig. 3(a). As expected, a concentration of 10% trappings sites greatly enhances the MR values. Their optimal depth is ~0.6 eV, which is comparable to the difference between U and E_F. The dependence of $\mathrm{MR_{sat}}$ on the variance of the trap distribution is plotted in Fig. 3(b). On one hand, if the center of trap distribution is far from $E = 0$, an increase of the trap depth would pull more trapping states inside the single occupancy range, thus increasing the MR. This is the case for $E_t = 0.4$ and 1.0 eV. On the other hand, if the center of trap distribution is already inside the single occupancy range and near the $E = 0$ point, which is the case for $E_t = 0.6$ eV, a narrower trap distribution would ensure that more trapping states would participate in the MR effect. If the trapping distribution is sufficiently wide, it does not matter where the center is located, and the four curves in Fig. 3(b) would coincide. The enhancement of MR with traps agrees with previous experiments [25], where TFTs fabricated on both bare SiO_2 and HMDS-treated SiO_2 were investigated. The former has a larger trap density, and exhibits a larger MR effect. Here we show that to further increase the MR amplitude, both the trap depth and width can be tailored.

V. THE EFFECT OF DIMENSIONALITY

Another aspect that influences the MR effect is dimensionality [5]. In TFT structures, the system can often be considered two dimensional (2D), and a nanowire represents a one-dimensional (1D) system. There are two mechanisms that might lead to larger MR in lower dimensional systems. The first one is the geometric restriction. It tends to force the carriers to hop to already occupied sites, thus forming bipolarons. Using the same parameters as in Fig. 2(a), we recalculate the corresponding $\mathrm{MR_{sat}} - U$ curves in 3D, 2D, and 1D cases. In the 3D case, the density of sites was chosen to be $10^{21}\,\mathrm{cm}^{-3}$, equivalent to a lattice constant of 1 nm. This corresponds to site densities of $10^{14}\,\mathrm{cm}^{-2}$ and $10^{7}\,\mathrm{cm}^{-1}$ in 2D and 1D, respectively. The respective percolation thresholds are chosen to be 4.48 [22] and 2 [26] for 2D and 1D systems, respectively. Both trap-free systems [Fig. 4(a)] and systems containing traps with $N_t = 0.1N_s$, $\sigma_t = 0.15$ eV, and $E_t = 0.6$ eV [Fig. 4(b)] are calculated. The MR indeed increases with decreasing dimensionality, for the same Hubbard energy $U = 0.5$ eV.

The second possible mechanism is that systems with lower dimensionality might have lower U. This can be rationalized in terms of a scaling argument in which the 3D treatment given in [27] can be extended to 1D and 2D systems. As derived in the Appendix, the bipolaron energy E_2 and the energy of two polarons, $2E_1$, as functions of their size L can be expressed as

$$E_2 \sim \frac{A^{(\mathcal{D})}}{\kappa L^2} + \frac{B^{(\mathcal{D})}}{\varepsilon_r L} - \frac{2\lambda^{(\mathcal{D})}}{L^{\mathcal{D}} + \eta^{\mathcal{D}}},$$
$$2E_1 \sim \frac{C^{(\mathcal{D})}}{\kappa L^2} - \frac{\lambda^{(\mathcal{D})}}{L^{\mathcal{D}} + \eta^{\mathcal{D}}}, \tag{11}$$

where $\mathcal{D}$ denotes the dimensionality, $A^{(\mathcal{D})}$, $B^{(\mathcal{D})}$, and $C^{(\mathcal{D})}$ are dimensional dependent constants, κ is the ratio between the carrier effective mass and the electron mass, ε_r is the dielectric constant, η is a cutoff length, and $\lambda^{(\mathcal{D})}$ a normalized coupling strength between the electron and lattice. Qualitatively speaking, the lower the dimensionality, the slower the term $1/(L^{\mathcal{D}} + \eta^{\mathcal{D}})$ in Eq. (11) will decrease with L and will facilitate bipolaron formation. This lowering of U could contribute to MR enhancement much more than geometric restriction, since the latter only enhances MR on the same order, while the former can be an order of magnitude effect, as revealed by Figs. 4(a) and 4(b).

VI. CONCLUSIONS

In summary, by employing a unified percolation model, we demonstrate that a moderately positive Hubbard energy is compatible with a bipolaron mechanism to rationalize MR in an OSC under unipolar current flow. However, this is only valid if (i) the DOS distribution of the semiconductor

energetically broadened and (ii) tail states of the DOS are filled and a Fermi level is established. The sign of MR is negative because a magnetic field eliminates spin mixing due to hyperfine interaction and therefore prevents the formation of bipolarons. The Fermi level and trap dependences of MR agree with previous experiments, and the treatment and results also have general implications for charge and spin transport in disordered systems.

ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China (China) (Grants No. 61505243, No. 61574166, and No. 61306117), Youth Innovation Promotion Association CAS (Grant No. 2015095), Beijing Training Project for the Leading Talents in S&T (Grant No. Z151100000315008), the Opening Project of Key Laboratory of Microelectronic Devices and Integrated Technology, Institute of Microelectronics of Chinese Academy of Sciences, and the CAEP Microsystem and THz Science and Technology Foundation under Grant No. CAEPMT201504.

APPENDIX

Similar to [27], the bipolaron energy can be expressed as

$$E_2 = \langle H_{el}\rangle + E_s \int d^{\mathcal{D}}r_1 d^{\mathcal{D}}r_2 |\psi(\boldsymbol{r}_1,\boldsymbol{r}_2)|^2[\Delta(\boldsymbol{r}_1)+\Delta(\boldsymbol{r}_2)] + \frac{1}{2}K\int d^{\mathcal{D}}r\,\Delta^2(\boldsymbol{r}). \tag{A1}$$

By assuming symmetric wave function: $\psi(\boldsymbol{r}_1,\boldsymbol{r}_2) = \psi(\boldsymbol{r}_2,\boldsymbol{r}_1)$, and minimizing E_2 with respect to $\Delta(\boldsymbol{r})$, one gets

$$2E_s\Delta(\boldsymbol{r})\int d^{\mathcal{D}}r_1|\psi(\boldsymbol{r}_1,\boldsymbol{r})|^2 + K\Delta(\boldsymbol{r}) = 0. \tag{A2}$$

Thus, $\Delta(\boldsymbol{r}) = -2E_s\int d^{\mathcal{D}}r_1|\psi(\boldsymbol{r}_1,\boldsymbol{r})|^2/K = -2E_s\rho(\boldsymbol{r})/K$ with $\rho(\boldsymbol{r}) = \int d^{\mathcal{D}}r_1|\psi(\boldsymbol{r}_1,\boldsymbol{r})|^2$. So

$$E_2 = \langle H_{el}\rangle - \left(2E_s^2/K\right)\int d^{\mathcal{D}}r\,\rho^2(\boldsymbol{r}). \tag{A3}$$

Using the definition that $\int d^{\mathcal{D}}r\,\rho^2(\boldsymbol{r}) = L^{-\mathcal{D}}$, one has $E_2 = \langle H_{el}\rangle - 2E_s^2/KL^{\mathcal{D}}$. From a dimensional analysis, it is easy to see that $\langle H_{el}\rangle = \langle T_2\rangle + \langle V_2\rangle$, and

$$\langle T_2\rangle = -2\times\frac{\hbar^2}{2m^*}\int d^{\mathcal{D}}r_2\psi(\boldsymbol{r}_1,\boldsymbol{r}_2)\nabla_2^*\psi(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{\hbar^2}{m^*}\int d^{\mathcal{D}}r_2|\nabla_2\psi(\boldsymbol{r}_1,\boldsymbol{r}_2)|^2 \sim \frac{A^{(\mathcal{D})}}{\kappa L^2} \tag{A4}$$

$$\langle V_2\rangle = \int d^{\mathcal{D}}r_1 d^{\mathcal{D}}r_2 V(\boldsymbol{r}_1,\boldsymbol{r}_2)|\psi(\boldsymbol{r}_1,\boldsymbol{r}_2)|^2 = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r}\int d^{\mathcal{D}}r_1 d^{\mathcal{D}}r_2\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}|\psi(\boldsymbol{r}_1,\boldsymbol{r}_2)|^2 \sim \frac{B^{(\mathcal{D})}}{\varepsilon_r L}. \tag{A5}$$

Similarly, two-polaron energy can be obtained to be

$$2E_1 = 2\langle T_1\rangle - 2\frac{E_s^2}{2K}\int d^{\mathcal{D}}r\,\rho^2(\boldsymbol{r}) = 2\langle T_1\rangle - \frac{E_s^2}{KL^{\mathcal{D}}} \sim \frac{C^{(\mathcal{D})}}{\kappa L^2} - \frac{E_s^2}{KL^{\mathcal{D}}}. \tag{A6}$$

Defining $E_s^2/K = \lambda$, and adopting the cut off length η according to [27], one finally obtains Eq. (11) in the main text.

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