Conduction anisotropy in layered semiconductors

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We present a simple theoretical model for the diffusion of free carriers in layered semiconducting compounds, for which a small concentration of dopants (guest layers) disturb the system conductance, resulting in a strong anisotropy across and along the layers, which depends on the temperature of the system, as well as on the barrier lowering caused by the applied voltage. This model is based on diffusion via random walks of free particles, with the guest layers acting as barriers hindering free motion. By considering the probability of overcoming the barriers, we derive a formula for the current in terms of the guest concentration, barrier height, and temperature. Experimental results from previous studies for the system $ZnIn_2S_4$:$Zn_2In_2S_5$ concerning the anisotropic conductivity, its temperature and voltage dependence, as well as computer simulations are in excellent agreement with this model.

In layered semiconducting compounds the electrical conductivity perpendicular to the layers is often severely influenced either by a slipping of successive layers with respect to each other,[1] or by the presence of layers which have a different stoichiometry than the host compound.[2] These planar defects are termed compositional faults. In Fig. 1 such a case is shown with guest layers presented by thick planes between the layers of the host compound, which are presented by thin planes. The guest layers generally possess a different structure than the host planes. Therefore, the lattice periodicity is disturbed along the z axis, and they act as potential barriers, limiting the motion of the free carriers in the space between them.[2–5] Such a schematic is given in Fig. 2, with the guest layers shown as barriers. The barriers are characterized by their height H and thickness b. Electrical conductivity in the range of moderate and high temperatures is achieved by thermal activation of the free carriers, i.e., carriers possessing a thermal energy higher than H can overcome the barriers, thus contributing to the electrical conductivity. In the low temperature region, almost all carriers can be considered as "frozen," i.e., they do not have enough thermal energy to overcome the barriers. In this case, the main mechanism to pass through these barriers is quantum mechanical tunneling. The main difference between these two mechanisms is that tunneling does not depend on the temperature T, while thermal activation depends exponentially on T. In the low temperature region, where only tunneling contributes to the electrical conductivity, a significant anisotropy ratio α of the conductivities $\sigma_\perp$ and $\sigma_\parallel$ across and along (perpendicular and parallel) the layers has been observed.[2] Here α is defined as the ratio $\sigma_\parallel/\sigma_\perp$.

In the case of the layered semiconductor $ZnIn_2S_4$, which includes compositional faults in the form of guest layers $Zn_2In_2S_5$, the anisotropy ratio α has been estimated to have a value of $\simeq 10^3$,[2] and to be, at low temperatures, temperature independent. In order to measure the conductivity $\sigma_\perp$ a voltage V has to be applied on the upper and lower surfaces of the crystals. This voltage mainly drops on the N potential barriers formed by the compositional faults, because they represent the high resistivity regions of the crystal, consequently lowering the barrier height by an amount V/N. For small applied voltages this lowering is negligible, but for moderate and high applied voltages the lowering leads to a

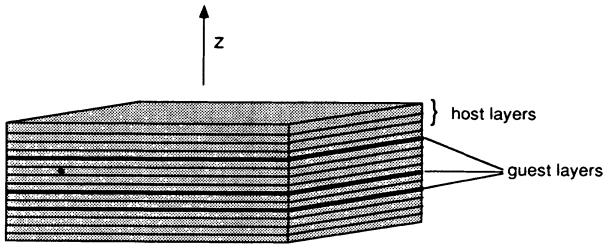

FIG. 1. Compositional faults (thick planes) between the ordinary layers (thin planes) of the host compound. Note that the lattice periodicity is severely disturbed along the z axis.

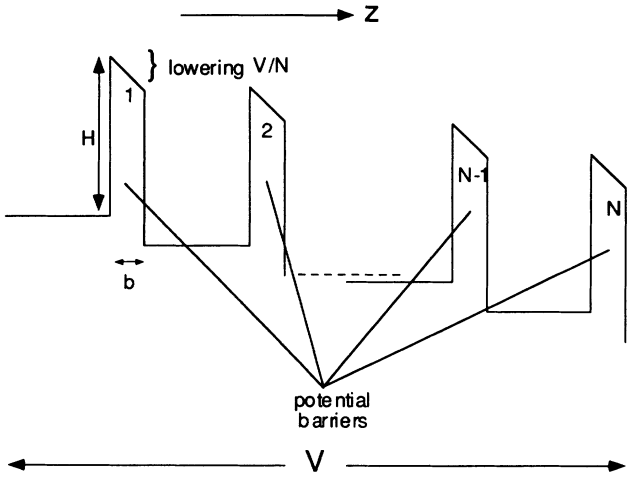

FIG. 2. Potential barriers created by the N stoichiometric faults (guest layers), with a thickness b and height H. For an applied voltage V the lowering of each barrier corresponds to V/N.

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considerable raise of the conductivity $\sigma_\perp$, thus decreasing the anisotropy ratio α. In the moderate and high temperature region more and more free carriers gain the required thermal energy to pass over the barriers. When the mean thermal energy approaches the barrier height H almost all carriers contribute to the conductivity $\sigma_\perp$. When this happens the anisotropy ratio α approaches unity.

In the present work, we present a procedure to estimate the anisotropy ratio α, its dependence on the temperature T, and finally, the influence of the applied voltage V on α. Moreover, with this model we can predict the I-V characteristic of the crystal, doped with the impurity. We consider that the undisturbed host layers (between successive potential barriers formed by the compositional faults) act as traps for the free carriers, which, for simplicity, are supposed to be free electrons. Only the carriers that have enough thermal energy to overcome the barriers are considered capable of contributing to the conductivity of the semiconductor along the z axis. Since the guest layers are randomly distributed in the crystal, our model also assumes a random distribution of the barriers.

The experimental data obtained in the past[2–4] for the case of the layered semiconductor $ZnIn_2S_4$ containing stoichiometric faults (i.e., $Zn_2In_2S_5$ layers) between its host layers can be summarized as follows.

(i) In the low temperature region the anisotropy ratio α has a temperature independent value of about 10^3.[2] As the voltage increases the anisotropy ratio α decreases, as shown in Fig. 3 (circles).[4]

(ii) In the high temperature region the anisotropy ratio α depends exponentially on the temperature T, decreasing with increasing T, and for k_BT values approaching the barrier height H the anisotropy ratio α approaches a constant value.[2]

(iii) The I-V characteristic of the semiconductor is a straight line for small values of the applied voltage V, but its slope shows an abrupt increase for high values of V (Fig. 4, circles).[4]

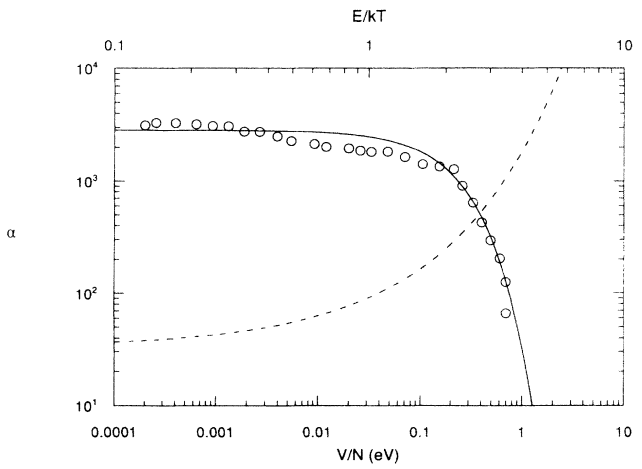

FIG. 3. Log-log plot of the measured (circles) and theoretically predicted (full line) anisotropy ratio α as a function of the applied voltage V/N (lower x axis), and as a function of $[H-(V/N)]/k_BT$ (upper x axis, dotted line). The experimentally measured points are for the $ZnIn_2S_4$:$Zn_2In_2S_5$ system. Note that for $H-(V/N) \simeq k_BT$ the shift d approaches a constant value, of about $\simeq 35$.

Similar experimental results have been reported for the case of other layered compounds.[1,6,7] In the following we will try to interpret the above results using a simple diffusion model of the carriers performing random walk motion.[8] Thus, the structure of the compound is represented by a three dimensional lattice. Random layers of this lattice along the z axis are designated as barriers, with concentration c. These barriers represent the compositional faults. A large number of particles, typically of the order of 10^4, with randomly chosen initial positions, diffuse on this lattice via symmetric random walks. In practice, only the coordinates in the z axis are monitored, and in essence the problem is a one-dimensional one. When a particle encounters a barrier it has a probability p to pass over the barrier, which depends on the height of the energy barrier H, the applied voltage per barrier V/N, and the temperature T, while it has a probability $1-p$ to remain on the same site. The probability p is given by a Boltzmann factor e^{-E/k_BT}, where $E = H - (V/N)$ is the height of the barrier after the lowering caused by the applied voltage.

During a walk of n steps, a particle succeeds to overcome a barrier n_b times. The number of the successful passes n_b is monitored as a function of the total steps (time) n. In this way, we estimate the number of carriers that contribute to the conductivity of the crystal in the perpendicular direction ($\sigma_\perp$). To estimate the quantity n_b, we observe that after a walk of n steps, a particle meets nc barriers. Since it has a probability $p = e^{-E/k_BT}$ to overcome these barriers we conclude that

$$n_b = nce^{-E/k_BT}. \tag{1}$$

Several curves based on Eq. (1) are shown in Fig. 5 (full lines) for different values of E/k_BT. The symbols in this figure are results of simulation calculations after averaging over 10^4 independent walks. A much larger number of walks, of the order of 10^7, were used for the first 100 steps, for low values of the ratio E/k_BT (lower lines in Fig. 5), due to large fluctuations in this region. The upper line in the figure corresponds to $n_b = n$, i.e., the case

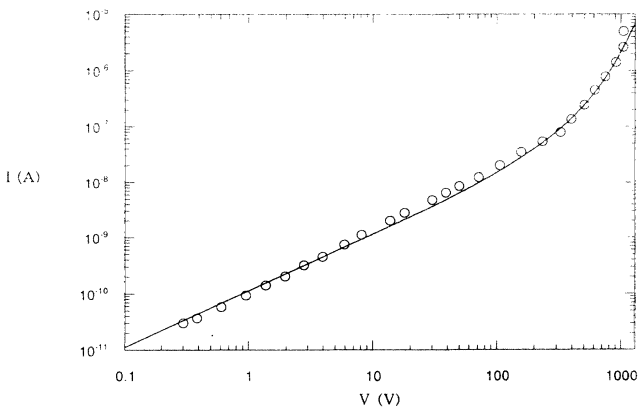

FIG. 4. The I-V characteristic of the compound. The open circles in this plot represent the experimentally measured points for the $ZnIn_2S_4$:$Zn_2In_2S_5$ system, while the full line is the theoretically predicted from Eq. (6).

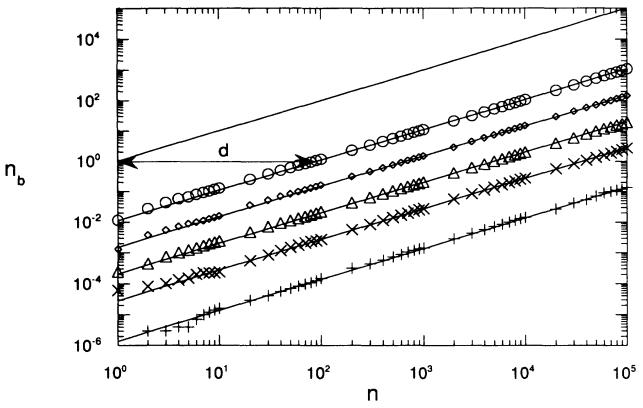

FIG. 5. Log-log plot of the number of successful passes n_b as a function of the total number of steps n, with E/k_BT as a parameter, for the following values of E/k_BT: 0, 1, 3, 5, 7, and 10, respectively (top to bottom). For these calculations a concentration of $c = 3 \times 10^{-2}$ was used. The lines represent the behavior predicted by Eq. (1), and the symbols are results of computer simulations.

that there are no barriers and all carriers contribute to the conductivity of the crystal. This is considered as the "reference" line. The other lines have a horizontal shift d from this line, and we observe that d is getting larger as the ratio E/k_BT increases.

When $E/k_BT = 0$, then n_b practically is equal to n (slope of 1), because either E is very low or k_BT is large, thus enabling all free carriers to contribute to $\sigma_\perp$. As the exponent E/k_BT grows larger the $n_b - n$ lines shift to the right by an amount d. This deviation d corresponds to the anisotropy ratio α measured at low temperatures.

It is now simple to calculate the shift d of the lines of Fig. 5, using Eq. (1). d is found to be a function of E/k_BT and c, i.e.,

$$d = \ln n - \ln n_b = \frac{E}{k_BT} - \ln c. \tag{2}$$

The shift d represents in fact the logarithm of the anisotropy ratio α, since by definition

$$\alpha = \frac{\sigma_\parallel}{\sigma_\perp} = \frac{ne\mu}{n_b e \mu_b}, \tag{3}$$

and

$$\ln \alpha = \ln n - \ln n_b + \ln \frac{\mu}{\mu_b}, \tag{4}$$

where μ represents the mobility of the carriers for zero barrier height, and μ_b is the mobility of the carriers for a crystal which contains barriers. The mobility is known to be, in general, structure dependent. Thus, the ratio μ/μ_b represents the structure induced mobility anisotropy. Since the concentration of barriers in the crystal is indicative of the structure of the crystal the term $\ln(\mu/\mu_b)$ will correspond to the term $-\ln c$ of Eq. (2). In Fig. 3 α is plotted as a function of V/N (full line) and also as a function of E/k_BT (dotted line). Both lines are based on Eq. (2). The points are the results of the experimental measurements. Note that for E/k_BT equal or less than unity (in other words the thermal energy of the carriers is equal to or higher than the barrier height) the anisotropy ratio α does not equal unity, but rather tends to a constant value. This discrepancy can be explained in terms of the mobility anisotropy, which as seen from Eqs. (2) and (4), always adds a constant background value to α, of the order of 10–100, as already reported.[1]

From Fig. 3, where α is plotted as a function of E/k_BT we can make the following conclusions:

(a) Considering T constant, the rapid decrease of a at $E/k_BT \simeq 1$ is caused by the corresponding lowering of H due to the deformation of the potential barriers by the applied voltage.

(b) Considering H constant, this decrease of $[H - (V/N)]/k_BT \simeq 1$ is due to the gain of sufficient thermal energy by the free carriers to overcome the barriers.

Since we are interested in the dependence of the anisotropy ratio on the applied voltage, we can consider that a measure of the anisotropy ratio is the resistance of the crystal at a specific value of voltage, i.e.,

$$\alpha = \lambda \frac{V}{I}, \tag{5}$$

where λ is a constant taking care of the proper units. Thus, using Eq. (2), we can convert the $\alpha - V$ curve (Fig. 4) to an I-V characteristic by use of the following equation:

$$I = c\lambda V \exp\left(\frac{V/N - H}{k_BT}\right). \tag{6}$$

The predicted I-V characteristic of the crystal, Eq. (6), is in excellent aggreement with the experimentally measured characteristic as shown in Fig. 4.

Summarizing, we have shown that a simple random walk model in a system where the guest layers act as barriers can adequately explain the strong conductivity anisotropy that had been repeatedly observed experimentally in the past, both in the case of $ZnIn_2S_4$:$Zn_2In_2S_5$ examined in the present report, as well as in the very similar cases of $Zn_2In_2S_5$:$ZnIn_2S_4$, $Zn_3In_2S_6$:$Zn_2In_2S_5$, and $Zn_5In_2S_8$:$Zn_2In_2S_5$:$Zn_3In_2S_6$.[9–12] The anisotropy ratio α can be easily derived, as a function of both the applied voltage and the system temperature.

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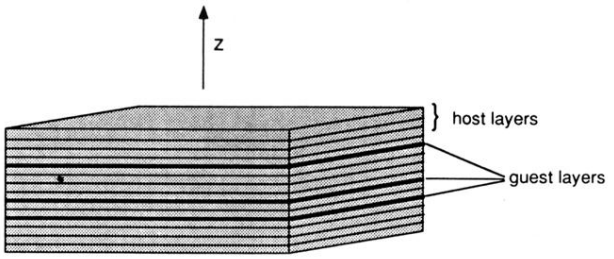

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