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Electronic Properties of Doped Semiconductors

Springer-Verlag Berlin Heidelberg New York Tokyo 1984



Lecture 1

Topics:

- 1. Impurity states in semiconductors
- 2. Basic experimental facts
- 3. Impurity band structure
- 4. Electron transition between two localized states
- 5. Mott's law
- 6. Miller-Abrahams random resistor network
- 7. Percolation treatment
- 8. Spin relaxation in the hopping regime

Impurity levels inside a forbidden gap



Table 1.2. Donor ionization energies in Ge and Si. Theoretical values were calculated in the effective-mass approximation. Experimental values correspond to the impurities indicated in parentheses. Energies of all s-state levels, split due to the chemical shift, are listed separately

Electrical Properties of Germanium Semiconductors at Low Temperatures*

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The resistivity can be described approximately by the equation¹⁰

$$1/\rho = C_1 e^{-\epsilon_1/kT} + C_3 e^{-\epsilon_3/kT},$$

with $\epsilon_1 \approx 1 \times 10^{-2}$ ev and $\epsilon_3 \approx 2 \times 10^{-3}$ ev.



The explanation of these observations due to Hung, who assumed that the localized impurity states interact and form a conduction band, seems plausible for the following reasons. The width of the impurity band should drastically decrease with increasing separation between the impurity atoms. Therefore one would expect the mobility of the charge carriers in the impurity band to decrease rapidly with decreasing concentration of impurities. This effect is demonstrated by the

21 August 1972

Anisotropic Electrical Properties of Amorphous Germanium



FIG. 1. Temperature dependence of the planar resistance for films deposited at and above 300°K. Ge_{0.99}-Ga_{0.01} sample No. 1, $d=5.8 \ \mu$ m, $\rho_{\rm RT}=600 \ \Omega$ cm; Ge sample No. 1, $d=3.5 \ \mu$ m, $\rho_{\rm RT}=1500 \ \Omega$ cm; Ge sample No. 9, $d=2.86 \ \mu$ m, $\rho_{\rm RT}=600 \ \Omega$ cm.

$$\rho = \rho_0 \exp[(T_0/T)^{1/4}]$$

$$\approx 40$$



Mott-Anderson Localization in the Two-Dimensional Band Tail of Si Inversion Layers

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Experimental evidence for a transition from localized to extended states in a two-dimensional band tail is obtained by measuring the conductivity in n- and p-type inversion layers in Si as a function of electron density and temperature (4.2 to 0.4°K). A transition from metallic to thermally activated conductivity is observed as a function of electron density, while the temperature dependence at electron densities below the transition shows both thermally activated nearest-neighbor hopping and variable-range hopping as proposed by Mott.



FIG. 2. $\ln\rho$ versus $(1/T)^{1/3}$ at $n_s = 6.4 \times 10^{11}/\text{cm}^2$. The slope of the solid line gives the parameter $T_0 = 177^{\circ}\text{K}$. The inset shows the activation energy W as a function of n_s .



In Fig. 2, the data for $n_s = 6.4 \times 10^{11}/\text{cm}^2$ are replotted on a $\ln\rho$ -versus- $(1/T)^{1/3}$ scale. It is clear that ρ follows the $\exp[(T_0/T)^{1/3}]$ dependence on T for $T \leq 1^{\circ}$ K. However, the temperature range is much too limited to determine unambiguously the correct power of 1/T.

The parameter T_0 deduced from our data is 500° K for $n_s = 5.2 \times 10^{11}/\text{cm}^2$ and 180° K for $n_s = 6.4$ $\times 10^{11}/\text{cm}^2$. According to Mott's argument, T_0 $\approx 27 \alpha^2 / \pi k \eta$ in the case of a 2D system. Here k is the Boltzmann constant and α^{-1} is the range of the localized state. Our data yield $\alpha^{-1} \approx 110$ Å for $n_s = 5.2 \times 10^{11}/\text{cm}^2$ and ≈ 180 Å for $n_s = 6.4$ $\times 10^{11}/\text{cm}^2$. We can also estimate α^{-1} from⁴ $\alpha(E_F) \approx [2m^*(E_c - E_F)/\hbar^2]^{1/2}$. Using $m^* = 0.2m_0$ and $E_F = n_s / \eta$, we obtain $\alpha^{-1} \approx 80$ Å for $n_s = 5.2$ $\times 10^{11}/\text{cm}^2$ and $\alpha^{-1} \approx 100$ Å for $n_s = 6.4 \times 10^{11}/\text{cm}^2$.

Lightly doped



Typically, an empty donor is the nearest neighbor of an acceptor



Some acceptors empty two donors

in their neighborhood- 2 complex



Positive energy shift by acceptor overweighs negative energy shift by second donor

Some acceptors do not have a donor in the neighborhood- 0 complex

Neutrality condition:

 $N_0(\mu) = N_2(\mu)$ decréases increases

For 0-comlex to exist there must be no donors in a sphere

with radius
$$\mathbf{r}_{\mu} = e^{2/\kappa\mu}$$
 around a fixed acceptor

$$N_{0}(\mu) = N_{\mathcal{A}} \exp\left[-\frac{4\pi}{3} \frac{e^{6}N_{D}}{\kappa^{3}\mu^{3}}\right]$$
Shift by acceptor Shift by donor
2-comlexes
 $\epsilon_{1} = \frac{e^{2}}{\kappa|\mathbf{r}_{1}|} - \frac{e^{2}}{\kappa|\mathbf{r}_{1} - \mathbf{r}_{2}|}$

$$\int_{\Theta \to -r} A \int_{\Gamma} \int_{\Theta} e^{2} \epsilon_{2} = \frac{e_{2}}{\kappa|\mathbf{r}_{2}|} - \frac{e^{2}}{\kappa|\mathbf{r}_{1} - \mathbf{r}_{2}|}$$

$$(\mu) = N_{\mathcal{A}}N_{D}^{2} \int d\mathbf{r}_{1} \int_{r_{2} > r_{1}} d\mathbf{r}_{2} \Theta[\epsilon_{1}(\mathbf{r}_{1}, \mathbf{r}_{2}) - \mu] \Theta[\epsilon_{2}(\mathbf{r}_{1}, \mathbf{r}_{2}) - \mu]$$

probability that two donors are the nearest neighbors of the acceptor

 $N_2^>$

$$N_2^{<} = N_A N_D^2 \int d\mathbf{r}_1 \int_{\mathbf{r}_1 < \mathbf{r}_2} d\mathbf{r}_2 \exp\left[-\frac{4\pi}{3} N_D r_2^3\right] \Theta\left[\epsilon_1(\mathbf{r}_1, \mathbf{r}_2) - \mu\right] \Theta\left[\epsilon_2(\mathbf{r}_1, \mathbf{r}_2) - \mu\right]$$

$$N_0(\mu) = N_2(\mu)$$
 \longrightarrow $\mu = 0.61\epsilon_D = 0.99 \ e^2 N_D^{1/3}/\kappa$

0-comlexes constitute 1.3% of the acceptor concentration

Temperature dependence of the *nearest-donor* hopping conductivity

$$\exp\left(-\frac{\mu}{T}\right) = \exp\left(-\frac{0.99e^2 N_D^{1/3}}{\kappa T}\right)$$
probability that at $T \ll \mu$ a donor is empty
condition $N_D a^3 \ll 1$ ensures that $\mu \ll \frac{\hbar^2}{ma^2} \Longrightarrow$ impurity band is narrow
Width of the density-of-states peak
is determined by long-range fluctuations
 $\gamma = 2\sqrt{2\pi} \frac{e^2}{\kappa r_0} (N_0 r_0^3)^{1/2} = 0.26\epsilon_D (N_d/N_D)^{1/4}$
 $r_0 = 0.58 N_d^{-1/2} N_D^{1/6}$
These figures may tempt one to think that in the first approximation be
0- and 2-complexes can be ignored. However, this would be incorrect.

These figures may tempt one to think that in the first approximation both 0- and 2-complexes can be ignored. However, this would be incorrect. If every acceptor produced a 1-complex, such complexes would include configurations where the nearest donor is far from its acceptor. The site energy ϵ for such a donor is almost zero. But this donor must be ionized, since we are dealing with a 1-complex, and hence we would have $\mu=0$ rather than $0.61\epsilon_D$. Thus it is not permissible to neglect the 0- and 2-complexes in calculating the Fermi level.



At T=0 electrons tend to occupy states of lowest energy. Therefore they will move into regions with a positive impurity charge. If the excess impurity density ΔN is lower than the average electron density n, then the fluctuations will be completely neutralized by a small variation in the electron density. If, on the other hand, $\Delta N >> n$, the fluctuations cannot be neutralized by electrons at all. Indeed, even if all electrons moved from negative regions, their density in the positive regions would only double, still remaining small compared to the impurity charge.



Fig. 3.5. Energy diagram of a highly compensated semiconductor, taking the long-range potential relief into account. Meandering lines (solid and dashed) represent the bottom of the conduction band and the impurity ground-state energy, both following the behavior of the potential energy $V(\mathbf{r}) = -e\phi$. The straight solid line on the top and dashed line correspond to these unperturbed energies. The Fermi level is shown by a solid line at the bottom. Also shown is the local density of states at some point in space. The region of occupied states is shaded. The dash-dotted lines correspond to the percolation levels (Sect. 5.2); ε_1 and ε_2 are the activation energies (Sect. 8.2)

Phonon-assisted transition between two sites:



Hopping Conductivity in Disordered Systems

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and

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average occupation



Resistance corresponding to a single hop



Mott's law



Transport resulting from energy levels within the strip

constant density of states within the strip

$$|\varepsilon_i - \mu| \leq \varepsilon_0$$

concentration of sites within the strip

 $N(\varepsilon_0) = 2g(\mu)\varepsilon_0$



Numerical factor in log-resistance from percolation theory

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 $-(N_D a^3)$

 \boldsymbol{a}

Impurity Conduction at Low Concentrations*†

Allen Miller[‡] and Elihu Abrahams Physics Department, Rutgers University, New Brunswick, New Jersey (Received June 23, 1960)

Nearest-neighbor hopping: tunneling dominates over activation

ка

 $\ln R_{ii}$

 $\ln R$



Numerical factor in log-resistance from percolation theory: Variable-range hopping

Bonding criterion

Dimensionless concentration of sites within energy strip

$$\mid\!\Delta_i\mid<\!1$$

$$n(\xi) = 2g\varepsilon_{\max}r_{\max}^{3} = \frac{gTa^{3}}{4}\xi^{4}$$

Infinite cluster appears at $n(\xi) = n_{c} = 5.3$
$$\ln R = \left[\frac{14}{ga^{2}T}\right]^{1/3}$$
$$\ln R = \left[\frac{21}{ga^{3}T}\right]^{1/4}$$

Mott's law with numerical factor

So far we have been dealing with an example of a very complicated anisotropy, namely that of a four-ellipsoid donor state. Another example of an anisotropic wave function whose shape is provided by donor states is germanium subjected to a large uniaxial stress. It is well known [6,17] that $\xi_{ij} = 2 \left[\frac{x_{ij}^2 + y_{ij}^2}{a^2} + \frac{z_{ij}^2}{b^2} \right]^{1/2}$ germanium subjected to a large uniaxial stress. It is well known [6.17] that under uniaxial compression in the {111} direction, the energy of one of the conduction band minima goes down, while that of the other three minima goes up. At pressures of order 109 dyne/cm2 this splitting becomes so large that the electron ground state on a donor is no longer associated with all four ellipsoids as it is in the absence of pressure, but with one ellipsoid only. Further increases in pressure essentially produce no new change in the wave function. Therefore the value of order 109 dyne/cm2 can be called the limiting or "maximal" pressure. At the "maximal" pressure only one term corresponding to a selected ellipsoid remains in the expressions (6.2.1), (6.2.2), and (6.2.7). As a result we obtain an expression of the form (6.2.10) with \$ii given by

Near the percolation threshold

Hopping transport in amorphous film of a thickness d

$$d \ll a\xi_c = \bar{r}$$

2D Mott's law with

$$T_0 = \frac{\beta}{\left[g\,d\right]a^2}$$

$$d >> \overline{r}$$

 $L_c \sim a \xi_c^{\nu+1}$

Fig. 9.4. The relation of bulk and film infinite clusters. Dashed lines show the film boundaries, solid lines the parts of the bulk infinite cluster lying within the film. L is the correlation radius, dthe film thickness

$$\delta \varphi = \Omega_{so} \tau$$

$$\tau_{s} = \frac{1}{\Omega_{so}^{2} \tau}$$

$$l_s = rac{v}{\Omega_{so}}$$

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Dyakonov-Perel spin relaxation near the metal-insulator transition and in hopping transport

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For localized electron the dominant mechanism of spin relaxation is interaction with random hyperfine field created by nuclei inside the donor orbit

the initial spin orientation is "forgotten" at distances less than $L_c \sim a \xi_c^{\nu+1}$

If $\delta \varphi_c << 1$ initial spin orientation will be "forgotten" at the diffusion stage

$$l_s = \frac{L_c}{\delta \varphi_c} \sim \frac{L_c \exp(-\xi_c)}{\omega^N \tau_0}$$

spin diffusion length contains correlation radius of infinite cluster