High-temperature conductivity with variable hopping length

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A conductivity with a variable hopping length has been observed in Si with a degree of compensation $K \approx 10^{-3}$–10^{-5} in a temperature range in which a saturation of the ϵ_3 conductivity should be observed, according to the general understanding.

The static conductivity of a large number of Si:B and Si:P samples, with concentrations (N) of the major dopant ranging from 1.6×10^{16} to 1.2×10^{17} cm^{-3}, has been studied experimentally ($N \ll N_M$, where N_M is the concentration corresponding to the metal-semiconductor transition). The equilibrium conductivity of a sample was measured as a function of the temperature, $\sigma(T)$ ($T = 4.2$–18 K), and the magnetic field, $\sigma(H)$ ($H = 0$–30 kOe). Results on three of the samples are reported in this letter. At $T < 15$ K their conductivity is a hopping conductivity. The values of the degree of compensation K are so low $K \approx 10^{-5}$–10^{-3} that one might expect the theory of hopping conductivity at small values of K (Ref. 1) to give a fairly good description of our results, in both the qualitative and quantitative senses.

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According to that theory, at very low values of T there should be a conductivity with a variable hopping length (VLHC) ($\ln \sigma = \text{const} - (T_0/T)^{1/4}$, at intermediate T a conductivity with a constant activation energy $\epsilon_3 = 0.61\epsilon_D$ (1–0.29 $K^{1/4}$) or "ϵ_3 conductivity" ($\epsilon_D = e^2/\kappa r_D$, $r_D = 0.62\, N^{-1/3}$ is the average distance between atoms of the major dopant), and at high T, specifically, at $T > T_s$, where $T_s = K^{-1}\epsilon_3(\ln K^{-1})$, a saturation of the ϵ_3 conductivity.

This is indeed the situation for samples 2 and 3 [Fig. 1(a)]. Our measurements correspond to the region of intermediate and high values of T. The calculated values of ϵ_3 for these samples agree in a completely satisfactory way with the experimental values.

For sample 1, in contrast, the expected behavior was not found: There was no region with a constant activation energy, and there was no hint of saturation [Fig. 1(a)]. It was found that this plot becomes quite linear in the coordinates $\ln \sigma = f(T^{-1/4})$ [line 1 in Fig. 1(b)].

Note that sample 1 has the smallest values of N and K. A behavior $\ln \sigma \sim T^{-1/4}$ is observed at $T > T_s$ at sufficiently small values of N and at $K < 10^{-3}$ in a number of n- and p-type Si samples with various impurities. This behavior seems to be a common property of these samples. We will refer to it as the "high-temperature conductivity with a variable hopping length" (HTVLHC). It was also found that with increasing K at $N \sim$ const, or with increasing N at $K \sim$ const, the VLHC gives way to the ϵ_3 conductivity. To illustrate the point, we selected samples in such a way that the first and

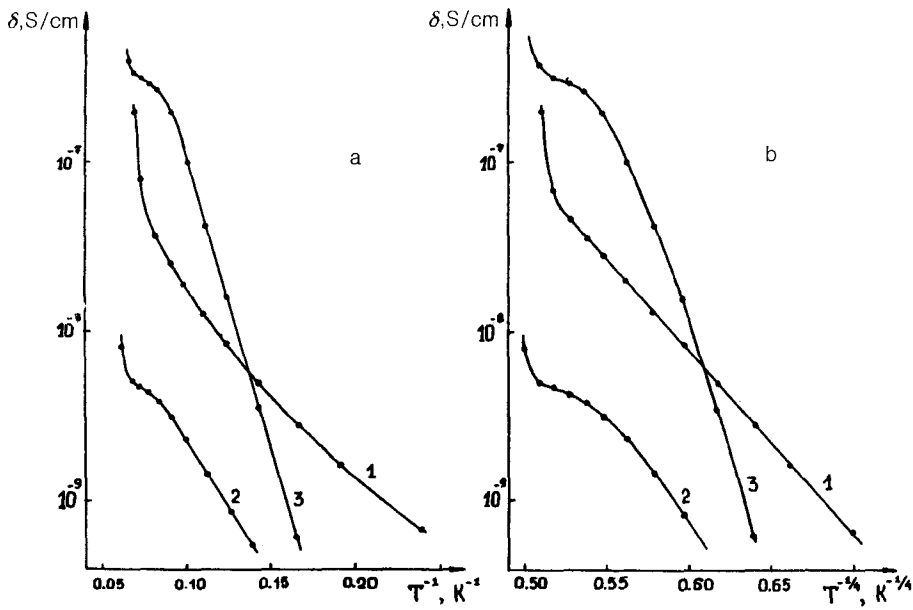

FIG. 1. Plots of (a) $\log \sigma = f(T^{-1})$ and (b) $\log \sigma = f(T^{-1/4})$ for Si:B samples. 1—$N = 4.5\times10^{16}$ cm^{-3}, $K = 6.7\times10^{-4}$; 2—$N = 5.3\times10^{16}$ cm^{-3}, $K = 10^{-2}$; 3—$N = 1.2\times10^{17}$ cm^{-3}, $K = 2.8\times10^{-4}$.

second differed more in term of K than in terms of N, while the opposite was true for the first and third samples.

There thus exists a certain curve $f(N,K) = 0$ which partitions the first quadrant of the N, K plane into two regions: one, adjacent to the origin, which corresponds to the HTVLHC, and an outer region corresponding to the ϵ_3 conductivity ($N \ll N_M$).

In the standard theory of hopping conductivity in crystalline semiconductors it is assumed that the impurity band is formed as a result of fluctuations caused in the potential by charged centers which exist at $K \neq 0$. At $T = 0$ and small values of K, the width of this "classical" band, Δ_{cl} ($T = 0$), is determined by the size of the large-scale fluctuations,[1] γ: $\Delta_{\rm cl}$ ($T = 0$) $= \gamma = 0.26\epsilon_D K^{1/4}$. As T increases, $\Delta_{\rm cl}$ decreases as a result of a strengthening of the screening as the number of (unoccupied) vacancies increases.

In the absence of compensation, on the other hand, the width of the band is set by a quantum splitting of the levels of a resonant pair of centers at a distance $r < r_D$. For short-range centers at large values of r_D, the width $\Delta_{\rm qu}$ is determined by the energy overlap integral I (the Lifshitz model[2]). For Coulomb centers we would find $\Delta_{\rm qu} = I = (2/3)(e^2/\kappa a)(r_D/a)\exp(-r_D/a)$. For our samples we find $\Delta_{\rm qu} \approx \Delta_{\rm cl}(T = 0)$.

We suggest that the HTVLHC which we observe is a consequence of the appearance of a quantum structure in the impurity band at very small values of K. This structure, as in the Lifshitz model, is determined by the spectrum of excitations of the resonant pair of centers when they close to a distance $r < r_D$. This spectrum, however, has a shape quite different from that which would prevail in the case of short-range centers. Consequently, the structure of the impurity band formed by hydrogen-like atoms at very small values of K requires a special study.

We cannot at this point offer a systematic explanation for the HTVLHC. We can only point to a circumstance which we consider important: A close resonant pair of hydrogen-like centers is an analog of the hydrogen molecule H_2. The first ionization potential of the H_2 molecule, $\epsilon_i(r)$, is not a monotonic function of the distance (R) between the protons. At a certain $r = r_m \approx 4a_0$ the quantity $\epsilon(r) = \epsilon_1 - \epsilon_i(r)$ goes through a maximum (ϵ_1 is the Rydberg): $\epsilon(r_m) = \epsilon_1 - \epsilon_i(r_m)$. Figure 2 shows the dependence of $\epsilon(r)$ found from the data of Ref. 3; the energy ϵ_m is 0.05–0.06 of ϵ_1.

If these results are extended to small impurities in Si:B or Si:P, it turns out that ϵ_m is slightly smaller than the calculated value of the energy ϵ_3 in our samples. Consequently, there is a certain density of states $g_i[\epsilon(r)] = 2\pi N^2 r^2 (dr/d\epsilon)$ of excitations just below the Fermi energy which correspond to a decay of the H_2 molecule into an ion H_2^+ and a free electron. Since we have a derivative $dr/d\epsilon \to \infty$ as $r \to r_m$, the density of states $g_i(\epsilon_m)$ may be substantial.

Clearly, the existence of a substantial density of states near the Fermi energy should promote the appearance of a VLHC. In addition, the approximate equality of the energies ϵ_m and ϵ_3 means that the amplitude for the scattering of a tunneling electron of energy $\approx \epsilon_m$ by a pair with $r \approx r_m$ becomes large. Since the concentration of such pairs is substantial ($\approx 0.05N$ in our samples), this scattering might substantially increase the electron localization radius, which determines the amplitude of the wave

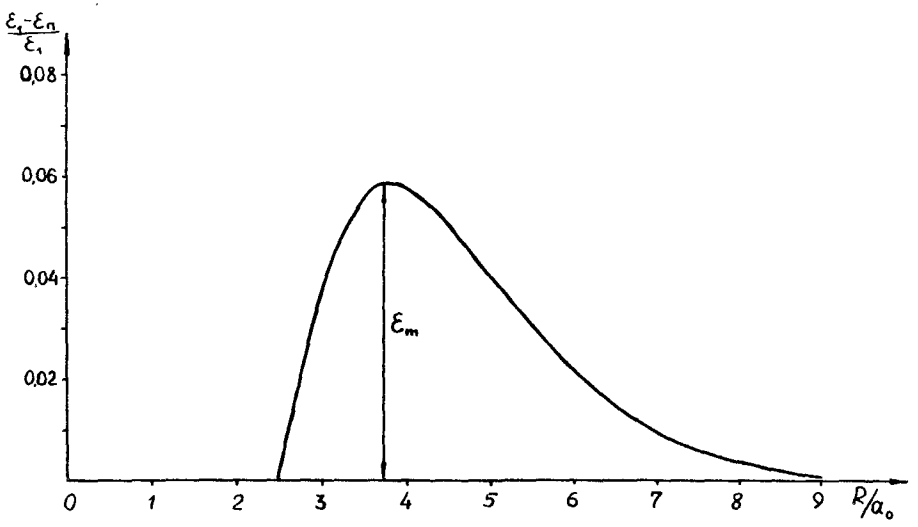

FIG. 2. First ionization potential of the H_2 molecule as a function of R/a_0.

function at large distances from the localization center.[4] This circumstance should also stimulate a VLHC. Further evidence for a substantial localization radius comes from the anomalously large positive magnetoresistance which we observed in samples with a HTVLHC.

As K or N is increased, the HTVLHC should evidently disappear. An increase in K will cause greater fluctuations in the potential, with the result that pairs will cease to be resonant. An increase in N will increase the gap between ϵ_3 and ϵ_m, with the result that the scattering of a tunneling electron would be weakened, and the localization radius reduced.

The existence of a substantial density of states at $\epsilon \approx \epsilon_m$ could also affect the position of the Fermi energy in semiconductors with small values of K.

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