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Temperature Dependence of ac Hopping Conductivity*

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Previous work on ac hopping conductivity in semiconductors has shown that when the impurity concentration is relatively high, the temperature dependence of the conductivity is considerably more pronounced than the theory accounts for. At the same time, the frequency dependence becomes weakened at the higher temperatures. It is proposed that multiple hops can account for these phenomena. An approximate analysis of the effect of multiple hops on the conductivity is presented. The results of this analysis are compared with some experimental results and are found to be capable of explaining the observed deviations from previous theories.

THE conductivity due to hopping processes in germanium and silicon under nonsteady-state conditions has been the topic of several recent theoretical and experimental investigations.[1–5] These investigations were concerned with the frequency, temperature, and concentration dependences of the conductivity. On the whole, the theories based on the Conwell-Mott[6,7] model adequately explained the various dependencies of the conductivity and its magnitude. However, these theories do not adequately explain the temperature dependence of the conductivity for many samples. The characteristic of such samples is a relatively high-majority impurity concentration ($\sim 10^{17}$ cm^{-3} in silicon). The actual temperature dependence in such samples is always more pronounced than the temperature dependence suggested by theory [see, e.g., Eqs. (18a) and (18b) of Ref. 4 or Eq. (22) of Ref. 3]. Tanaka and Fan[3] attempted to explain the increased temperature dependence by pointing out that whenever two majority impurities are sufficiently close, the existence of the resonance energy between them will introduce traps. A different explanation of the temperature dependence is suggested here which is, for many cases, in better agreement with experimental data. Specifically, it is experimentally observed that the more pronounced temperature dependence is always associated with a weakened frequency dependence at higher temperatures. This is demonstrated in Fig. 10, Ref. 3, and in Figs. 5, 6, and, less distinctly, in Fig. 7, Ref. 1. The traps described by Tanaka and Fan do not explain this dependence between the variables T (temperature) and ω (frequency). As they point out, the frequency dependence should hardly be affected by the presence of traps. The explanation presented here, on the other hand, implies that an increased temperature dependence and a decreased frequency dependence always occur together. It is pointed out that the proposed mechanism does not explain the decrease of conductivity with majority concentration at very low temperatures (see Fig. 8, Ref. 3). The latter could be due either to configurations with $r_1 < \frac{1}{2} r_\omega$ (see Fig. 4, Ref. 4) or to the Tanaka-Fan traps. This paper thus does not exclude the existence of the traps. In fact, strong evidence for these can be found in the results of experiments with lithium-doped silicon.[8]

Previous theories[1–4] were based on the assumption that the ac current is restricted to hops between pairs of impurities only. It is suggested here that the unexplained temperature dependence is due to the breakdown of this assumption. Criteria had been established to decide whether single hops suffice to describe the conductivity at a given frequency. This was done on the following basis: Consider, in a random distribution of impurity atoms, all pairs which have a spatial separation of r_ω and an energy separation smaller than kT. There is a possibility that a third atom is so situated that its separations from both atoms are less than r_ω and less than kT. If this event is a very unlikely one, then the pair approximation is good and vice versa. The reason for this is that the presence of such an atom would shorten the time required for relaxation of the system and thus completely change the contribution to the conductivity at a given frequency. This criterion does not encompass the much more likely event that a third atom has a separation less than kT from both atoms, but less than r_ω from either atom. In such a case, the relaxation time of the system is very nearly unaffected by the third atom. Nevertheless, the conductance is increased because the charge transfer may be more extended. Furthermore, the probability of such configurations occurring increases with increasing kT. This is schematically illustrated in Fig. 1. Thus it is clear that this configuration will have an enhanced temperature dependence of the conductivity and that this effect will increase with increasing concentration.

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Furthermore, it is apparent that the likelihood of such multiplets will increase with increasing r_ω. Since an increased dependence of the conductivity on r_ω means a decreased dependence[1–4] on ω, the multiple hops will result in a decreased frequency dependence in addition to the increased temperature dependence. It may be noted that such a behavior is in qualitative agreement with the similarity relation described in Ref. 4, while these relations are not applicable to the behavior caused by Tanaka-Fan traps.

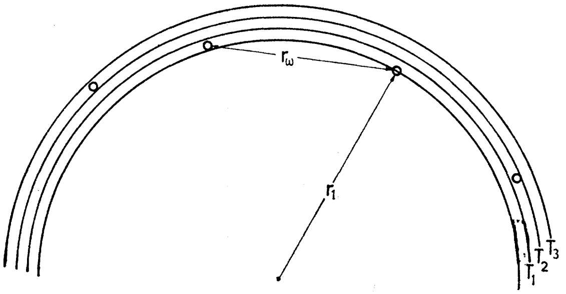

FIG. 1. An illustration of the suggested cause for the enhanced temperature dependence. The points represent a random arrangement of majority atoms, including the one nearest (at a distance r_1) to the minority impurity. The circles are equipotentials, with energy separations kT from the equipotential at r_1; $T_1<T_2<T_3$. At the temperature T_1 the carrier is restricted to a single hop. The hopping is gradually extended with increasing temperature.

In order to analyse approximately the effect of multiple-hop configurations we must estimate the conductance of any such configuration at a given frequency and the probability of its occurrence. (The notation used in the following analysis is the same as in Ref. 4.) We will assume that the conductance of the configuration can be described by means of a single relaxation time τ'. This assumption is good in the situation described below. Consider the various pairs that can be formed by the members of a configuration. There is a time τ (as defined on p. 1750, Ref. 1) corresponding to each such pair. If these times differ considerably from each other for the various pairs, then the configuration may be described approximately by a single relaxation time. Since the times τ for the pairs are exponential functions of the pair separations,[9] the conditions should apply with a high probability. The relaxation time which characterizes the whole configuration is the one given by the largest hop (say r') that the carrier must make to get from one end of the configuration to the other.[10] If now $d\sigma$ in Eq. (1), Ref. 4 stands for the conductivity of a given multiple-hop configuration and dp for its probability of occurence, the frequency-dependent term remains unchanged except that τ' replaces τ as specified above. Indeed, the only change necessary is to reinterpret r to mean the spatial extent of the configuration. This length will be denoted by $\bar{r}$. The function $\cosh^{-2}$ will be replaced by a step function, unity for $\Delta E<2.8kT$ and zero for $\Delta E>2.8kT$. The number 2.8 is determined by the point of steepest descent of the function $\cosh^{-2}$. Equation (1), Ref. 4 can now be written in the following form:

$$d\sigma(\bar{r},\Delta E,\omega)=\tfrac{1}{12}dp(\bar{r},\,\Delta E<2.8kT)\times N_A\bar{r}^2\omega\tfrac{1}{4}\pi a\delta(r'-r_\omega)4\pi\kappa r_T\,. \quad (1)$$

Use has been made here of the equation following Eq. (4), Ref. 4 and of the definition of r_T. The probability $dp(\bar{r},\,\Delta E<2.8kT)$ now represents the probability of finding a configuration with a spatial extent $\bar{r}$, with a relaxation time τ' given by r' and with all the atoms of the configuration being within an energy separation of $2.8kT$. The condition on the energy separation presents no analytical difficulty. For a configuration where the minority impurity has the nearest majority impurity at a distance r_1 from the latter, the condition $\Delta E<2.8kT$ corresponds to a spherical shell between r_1 and $r_1(1+2.8r_1/r_T)$ around the minority impurity atom. We thus restrict our attention to atoms within this shell. Since $r_1/r_T\ll1$, the shell will be a very thin one and we may replace it by a surface with a "surface impurity concentration" ν,

$$\nu=2.8(r_1^2/r_T)N_D\,. \quad (2)$$

The problem of finding $p(\bar{r},\,\Delta E<2.8kT)$ is still of a rather complicated nature. We shall resort to simplifying assumptions which, however, will still maintain the qualitative features of the problem. The assumptions made are as follows:

(1) The spherical shell is made planar. This assumption will be partially relaxed later.

(2) The question of finding the probability for a configuration with the longest jump r' will be simplified to the following problem.

Configurations with various numbers of atoms are considered. Bonds, between the atoms from left to right, are formed in such a way that every atom is connected with its nearest neighbor to the right. It is assumed that all configurations have the same spread in both dimensions. The number of bonds thus formed is counted and called n^2. The configuration is divided into n (or the next larger integer) equal parts from left to right. The procedure is illustrated in Fig. 2. A cut is made through each part and the number of bonds thus intersected is counted. For sufficiently large configurations this number is approximately n. It should be noted, however, that not all bonds will be necessarily intersected. Some bonds may escape intersection while others may be intersected by two cuts. Since neither possibility will occur frequently they are excluded from consideration. The shortest intersected bond is located on each cut. The longest of these (bond A in Fig. 2) is

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[10] A similar approach has been used for the calculation of steady-state conductivity in Ref. 9.

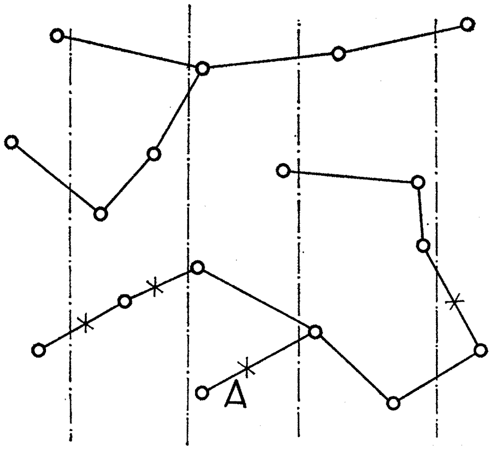

FIG. 2. An example of the bond-generating scheme. The points represent atoms of a configuration. Each atom is connected to its nearest right neighbor. The total number of bonds n^2 is counted (15 in this case). Since 4 is the integer closest to n from above, four cuts are made through the configuration (intermittent lines). Of all the bonds intersecting one cut, the shortest is selected (marked by crosses). The longest of the crossed bonds is bond A.

required to have the length r', since in most cases it is the longest bond which it will be necessary to cross in order to get from one end of the configuration to the other. Note that bond A is not necessarily a part of a continuous line of bonds which crosses the entire configuration (as, for example, in Fig. 2). However, the bonds indicated in Fig. 2 are not the only ones to be taken into account. While Fig. 2 contains only the shortest bond to the right of each site, all bonds which are shorter than r' may be included. These are shown in Fig. 3 for the same configuration as presented in Fig. 2. In this scheme of bonds it is quite likely that bond A is a part of a continuous path of bonds which spans the configuration.

(3) Consistent with the previous assumption that the configurations have a similar spread in both dimensions, it is assumed that all configurations of a given n contribute to the conductivity with the same $\bar{r}$. This average $\bar{r}$ is taken to be equal to nr'. The probability $p_\tau(r',n)dr'$ that the bond A is $r'\pm\frac{1}{2}dr'$ long is calculated in two steps. At first the probability $p'(r,n)dr$ that the shortest bond in one cut is of length $r\pm\frac{1}{2}dr$ is found. From $p'(r,n)$ the probability $p_\tau(r',n)dr'$ that this is the longest such bond among all cuts is calculated:

$$p'(r,n)dr=np(r)\left(\int_r^\infty p(\rho)d\rho\right)^{n-1}dr, \tag{3}$$

$$p_\tau(r',n)dr'=np'(r',n)\left(\int_0^{r'} p'(\rho,n)d\rho\right)^{n-1}dr'. \tag{4}$$

In Eq. (3) the probability $p(r)dr$ is the probability of finding a nearest neighbor within $\frac{1}{2}dr$ of the distance r. It is given by

$$p(r)dr=2\pi\nu r\exp(-\pi\nu r^2)dr. \tag{5}$$

By substituting Eq. (5) into Eq. (3), Eq. (3) into Eq. (4) and integrating, we obtain

$$p_\tau(r',n)dr'=2\pi n^2\nu r'\exp(-\pi\nu n r'^2)\times[1-\exp(-\pi n\nu r'^2)]^{n-1}dr'. \tag{6}$$

For $\pi n\nu r'^2<1$, Eq. (6) can be approximated by

$$p_\tau(r',n)dr'\cong 2n(\pi n\nu r'^2)^n dr'/r'. \tag{7}$$

The logical connection between the probability $p_\tau(r',n)dr'$ and the required probability $dp(\bar{r},\Delta E<2.8kT)$ is as follows: We select a group of n^2 majority impurities, as close as possible to the impurity at r_1, all of which lie on the spherical shell determined by $\Delta E<2.8kT$. Such a configuration has (within the above approximations) the probability $p_\tau(r',n)dr'$ that the "bond" which determines r' has the length r'. Next, an additional impurity atom, the one nearest to the configuration, is included. If the new configuration (of n^2+1 bonds) still has the characteristic bond of length r', it is counted in the larger configuration (i.e., of size n^2+1 or larger) since it will contribute to the conductivity with the largest possible r'. Thus the probability that a configuration will have the size n^2 is given by $p_\tau(r',n)$ multiplied by a conditional probability $\bar{p}(n)$. The latter is the probability that the configuration of size n^2+1 is characterized by an r' different from the one which characterized the configuration n^2. This conditional probability is equivalent to the probability that the added impurity atom is farther than r' from any atom present in the configuration and is approximately equal to $\exp(-2n\nu r'^2)$. A similar factor has been already assumed to be unity in Eq. (7) and will be again approximated by unity. Thus, if r_1 would be fixed, $dp(\bar{r},\Delta E<2.8kT)$ could be replaced by $p_\tau(r',n)dr'$. Since r_1 is not fixed and $p_\tau(r',n)$ depends on r_1 through

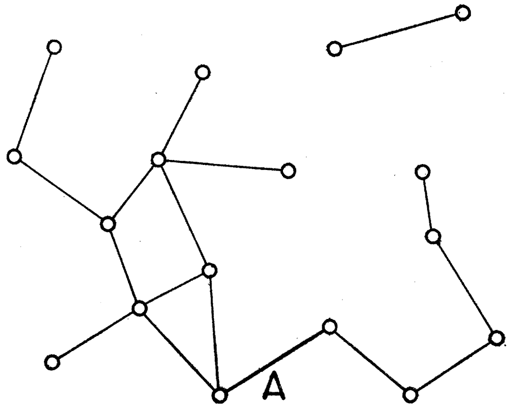

FIG. 3. The configuration of atoms is identical to that of Fig. 2. Here a bond is formed whenever the spacing between the atoms is less than r'.

Eq. (2), then

$$dp(\bar{r},\,\Delta E<2.8kT)=p_\tau(r',n)\bar{p}(n)dr'dp(r_1)$$
$$\cong p_\tau(r',n)dr'dp(r_1)\,, \quad (8)$$

where $dp(r_1)$ is given by Eq. (3a), Ref. 4. By substituting Eq. (2) into Eq. (7), Eq. (7) into Eq. (8), and Eq. (8) into Eq. (1), we obtain

$$d\sigma(\bar{r},\Delta E,\omega)=\tfrac{2}{3}\pi^2N_AN_Dn^2(2.8\pi nN_Dr_1^2r'^2/r_T)^n$$
$$\times r'\delta(r'-r_\omega)r_1^2r_T\exp(-\tfrac{4}{3}\pi r_1^3N_D)dr'dr_1\,. \quad (9)$$

To find the total conductivity from all possible configurations, Eq. (9) must be integrated over r_1 and r' and summed over n. The limits of integration over r_1 are discussed in Ref. 4. The variable r' can vary from zero to infinity, and thus the point where $\delta(r'-r_\omega)$ is different from zero is in the region of integration. In principle, n could vary from zero to infinity. However, we shall restrict n to rather small values in order to correct for the major exaggeration of assumption 1 above. The sphericity of the shell $\Delta E<2.8kT$ is taken into account by restricting the carrier to a maximum excursion of $2r_1$ around the minority impurity. This puts an upper limit on n: $n_{\max}=2r_1/r'$. This procedure also makes the transition from Eq. (6) to Eq. (7) more justifiable. We now obtain for the conductivity

$$\sigma(\omega)=\int_{\frac{1}{2}r_\omega}^{\infty}\sum_{n^2=0}^{(2r_1/r_\omega)^2}\tfrac{2}{3}N_D\pi^3r_\omega n^2(2.8\pi nr_1^2r_\omega^2N_D/r_T)^n$$
$$\times r_Ta\kappa\omega r_1^2\exp(-\tfrac{4}{3}\pi r_1^3N_D)dr_1\,. \quad (10)$$

It is interesting to apply Eq. (10) to the single-hop approximation, i.e., to permit n^2 to equal only zero or 1, and to compare the result with the more accurate theory for single hops of Ref. 4. To do this, we follow Ref. 4 and substitute $r_D=(\frac{4}{3}\pi N_D)^{-1/3}$ and $x_1=r_1^{-1}$. Equation (10) thus becomes

$$\sigma(\omega)=1.05\pi^2N_Ar_D^{-6}r_\omega^3a\kappa\omega\int_{2/r_\omega}^{0}x_1^{-6}\exp(-x_1r_D)^{-3}dx_1\,.$$

The last equation should be compared with Eq. (14) of Ref. 4. Since both the tanh term and $(1+\frac{1}{2}r_\omega x_1)$ are close to unity, the two equations differ by about 30%. More important, the functional dependence on the different variables agrees very well.

Using Eq. (10) it is possible to estimate when multiple hops will become important in the conductivity. This will happen when terms with $n>1$ become comparable to the term with $n=1$. Taking $n=2$ this yields the condition $N_D\sim0.07r_T/r_1^2r_\omega^2$. Since the value of r_1 is most likely to be approximately r_D this condition is equivalent to the condition $N_D\sim0.007r_T^3/r_\omega^6$. This corresponds, for the case of silicon at 10°K, to $N_D\sim4\times10^{16}$ cm^{-3}, which compares well with the experimentally found onset of the effect discussed [see, e.g., Fig. 10(a) and 10(b) in Ref. 3]. Since the concentration where the onset of the effect should begin is proportional to r_T^3, the effect around 1°K should disappear for all practical cases. This is well borne out by Fig. 10(b), Ref. 3 and by Fig. 6, Ref. 1. The following observations will ascertain that the functional dependence of Eq. (10) agrees qualitatively with the observations. As the concentration becomes higher, terms with $n>1$ become important. Those terms differ from the term with $n=1$ by the factor $n^{2+n}(2.8\pi r_1^2r_\omega^2N_D/r_T)^n$. Since r_T appears in negative powers and hence T appears in positive powers ($r_T\equiv e^2/4\pi\kappa kT$) they will account for an increased temperature dependence. Likewise, the frequency dependence will be decreased since r_ω appears in positive powers and r_ω is a decreasing function of frequency.

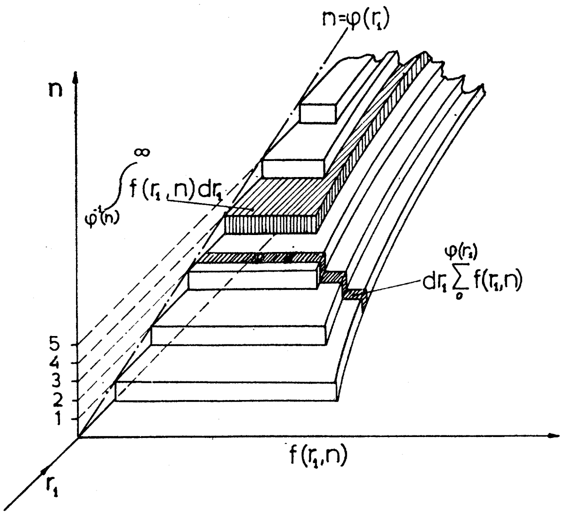

FIG. 4. A graphical indication of the change of the order of integration and summation between Eqs. (10) and (11). The volume under the steps can be written either as an integral over the differential sums or as a sum over the integrals.

It is possible to integrate Eq. (10) if we change the order of summation and integration. Some care is required in this procedure since the upper limit of the summation depends on the variable of integration. The procedure is indicated in Fig. 4. The result of this operation is as follows

$$\sigma(\omega)=\tfrac{2}{3}\pi^3N_Dr_\omega r_Ta\kappa\omega\sum_{n^2=0}^{\infty}n^2(2.8\pi nr_\omega^2N_D/r_T)^n$$
$$\times\int_{\frac{1}{2}nr_\omega}^{\infty}r_1^{2n+2}\exp(-\tfrac{4}{3}\pi r_1^3N_D)dr_1\,.$$

The integral is expressible by means of an incomplete Γ function. With the notation

$$\Gamma(\alpha,\,\beta+1)=\int_0^{\alpha}x^\beta e^{-x}dx\,,$$

we obtain

$$\sigma(\omega)=\tfrac{2}{3}\pi^3N_Dr_\omega r_Ta\kappa\omega\sum_{n^2=0}^{\infty}n^2(2.3\pi^{1/3}N_D^{1/3}nr_\omega^2/r_T)^n$$
$$\times[\Gamma(\tfrac{2}{3}n+1)-\Gamma(\tfrac{1}{6}\pi n^3N_Dr_\omega^3,\,\tfrac{2}{3}n+1)]\,. \quad (11)$$

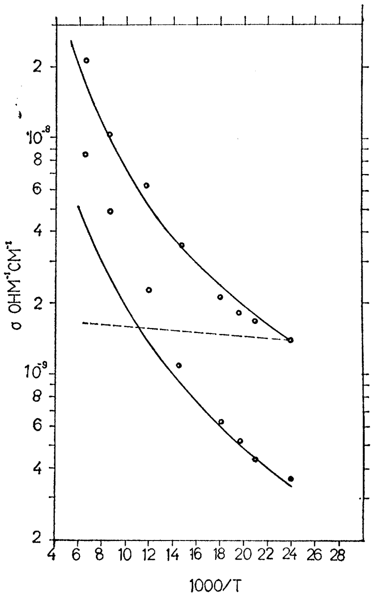

FIG. 5. A comparison between Eq. (11) and experimental results. The points are taken from Tanaka and Fan's (Ref. 3) Fig. 10(b) and the solid lines are an approximation to Eq. (11). In this approximation, the summation was carried to $n^2=9$, and the square brackets were approximated by unity. A more complete summation would improve the agreement. The curves were normalized to coincide with the value of the conductivity measured at 7×10^4 cps and 4.2°K. The intermittent line represents the pair approximation.

The term in the square bracket goes rapidly to zero with increasing n and is responsible for the convergence of the sum. It represents the statistical condition that it is very improbable for r_1 to become very large. To see somewhat more quantitatively whether the proposed explanation accounts for the observed behavior, Eq. (11) was used to evaluate $\sigma(\omega)$ for Tanaka and Fan's[3] sample $B4$ at 10^4 cps and 7×10^4 cps. The summation was carried out to $n^2=9$. For all these values of n, the brackets in Eq. (11) were approximated by unity. For the radius a we used 20 Å, according to the value suggested in Ref. 3. Since the minority impurity concentration is not known, and since we are interested primarily in the functional dependence, the calculations were normalized with respect to the experimental data at 7×10^4 cps and 4.2°K. The results of the comparison are shown in Fig. 5. Since with increasing temperature and decreasing frequency terms with larger n become more important, the agreement would improve if n^2 would not have been cut off at the value 9. It is apparent that in view of the rather severe approximation made in this treatment the results indicate that the multiple hops of the type suggested can certainly be responsible for the observed frequency and temperature dependencies in the more heavily doped samples.

It is interesting to inquire whether this effect of multiple hops is consistent with the similarity relations of Ref. 4. This may be answered by comparing Eq. (11) with Eq. (41) of Ref. 4, the latter being a consequence of the similarity relation. According to this, an increased power of r_ω must be associated with a decreased power of r_T. While this happens in Eq. (11) for every term $n>1$ in principle, the similarity relations are not obeyed exactly since every two increased powers in r_ω are associated with only one decreased power in r_T. It is possible that this imperfect obedience of the similarity conditions is responsible for the imperfections indicated in Fig. 9 of Ref. 4.

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