Temperature Coefficient of Resistivity in Amorphous Semiconductors

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By invoking the microscopic response method in conjunction with a reasonable set of approximations, we obtain new explicit expressions for the electrical conductivity and temperature coefficient of resistivity (TCR) in amorphous semiconductors, especially a-Si:H and a-Ge:H. The predicted TCR for n-doped a-Si:H and a-Ge:H is in agreement with experiments. The conductivity from the transitions from a localized state to an extended state (LE) is comparable to that from the transitions between two localized states (LL). This resolves a long-standing anomaly, a “kink” in the experimental log_{10} \sigma vs. T^{−1} curve.

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The temperature coefficient of resistivity (TCR) in disordered systems is an important physical observable, is difficult to compute, and is of technological interest for micrometer materials for thermal imaging applications[1, 2]. Boltzmann or master equations are often used to calculate transport coefficients in crystalline semiconductors and semi-metals. The low carrier concentration in these materials results in a low kinetic energy of carriers. Thus the Landau-Peierls condition: the basic criterion for a kinetic approach \[\hbar/\tau < \max\{E_F, k_BT\}\] cannot be satisfied[3], where \(\tau\) is the time interval between two collisions (carrier with disorder and/or phonon), and \(E_F\) is the Fermi energy of a material. Then, neither the elastic scattering by disorder nor the inelastic scattering by a phonon has a well-defined transition probability per unit time. The situation for amorphous semiconductors (AS) is even more difficult. Due to the strong electron-phonon (e-ph) interaction for localized states, any transition involving localized state(s) requires a reorganization of the vibrational configuration[4–6]. Energy conservation between the initial and final electronic states[3] for these intrinsic multi-phonon transitions is violated more seriously than for the single-phonon processes. Thus the kinetic method is unjustified for AS[3].

In the kinetic approach[7], it is often supposed that (i) electrical conduction is fulfilled by the transition from a localized state to another localized state (LL) and the transition from an extended state to another extended state (EE)\[1, 2\]; (ii) the transition from a localized state to an extended state (LE) and the transition from an extended state to a localized state (EL) do not directly contribute to conduction; (iii) LE and EL transitions only maintain the non-equilibrium stationary distribution of carriers between localized states and extended states during a conduction process. Although phonon-assisted delocalization[8, 9] and photon-excited transient current[10] have been considered intuitively, rigorous expressions for LE and EL transition contributions to the conductivity are not yet available.

Because the interaction between the external electromagnetic field and an AS can be expressed with additional terms in the Hamiltonian, the transport coefficients can be expressed with transition amplitudes in the Microscopic Response Method (MRM)[5, 6]. Thus the long time limit required in the kinetic approach[3] is avoided. In addition, the MRM categorizes transport processes with diagrams computed to any given order of residual interactions[6]. We have seen that even to zero order in the residual interactions, LE and EL transitions contribute to conductivity[6]. Indeed, if one calculates the electrical conductivity of an AS from the full density matrix rather than its diagonal elements (master equation), one sees that LE and EL transitions contribute directly to electrical conduction. Since the MRM is equivalent to the density matrix method of Kubo[11], the two methods reach the same conclusion.

Disorder scattering in EE transitions driven by field has been treated in the coherent potential approximation. The conductivity from the EE transitions depends weakly on temperature[12], and is the same order of magnitude as that from LL transitions above room temperature[1, 2]. In this Letter we apply MRM[5, 6] to derive the contributions to conductivity from LL, LE and EL transitions solely drive by an external field. Two examples, the conductivity and TCR of a-Si:H and a-Ge:H are described.

An accurate conductivity calculation requires (i) the eigenvalues and eigenvectors of single-electron states and (ii) the eigenfrequencies and eigenvectors for each normal mode[3]. To express the conductivity in terms of accessible material parameters, we approximate the vibrations of an AS by a continuous medium. Although translational invariance is destroyed in AS, the standing wave modes are still well-defined. Because most amorphous materials are isotropic[1, 2] and only acoustic modes are important for the e-ph interaction in semiconductors[13], one can use \(\omega_k = \bar{c}_k\) for the vibrational spectrum, where \(\omega_k\) is the angular frequency for the mode characterized by wave vector \(k\). \(\bar{c}\) is the average speed of sound defined by \(3/\bar{c}^3 = 2/c_1^3 + 1/c_1^3\), where \(c_1\) and \(c_1\) are the speeds of transverse and lon-
gitudinal sound waves, determined by the bulk and shear modulus. The Debye cutoff wave vector \( k_D = (6\pi^2 n_0)^{1/3} \) is determined by the number density \( n_0 \) of atoms in an AS\(^{[13]}\). Because the displacements of atoms satisfy a wave equation, the transformation matrix \( \Delta \) between the vibrational displacements \( u_k \) at point \( R \) and the normal coordinates \( \Theta_k \) characterized by wave vector \( k \) is:

\[
\Delta_{Rk} = (2\pi)^{-3} V e^{i k \cdot R},
\]

where \( V \) is the volume of a sample. For a-Si\(^{[2]}\), \( \tau = 6.21 \times 10^3 \text{m/s} \) and \( k_D = 1.44 \times 10^9 \text{m}^{-1} \).

For simplicity, we take localized states to be spherically symmetric\(^{[14]}\). Following Mott, \( \xi_A \) is determined by the eigenvalue \( E \) of localized state \( \phi_A \): \( \xi_A \approx (c Z e^2/4\pi\epsilon_0\varepsilon) E^{-1} \), where \( Z \) is the effective nuclear charge of an atom core, \( \varepsilon \) is the static dielectric constant, \( E_c \) is the mobility edge of the conduction band, and \( c \) is a dimensionless constant. We will focus on n-doped material: transport in the conduction band, p-doped material may be treated analogously. For a-Si\(^{[2]}\), \( \varepsilon = 11.68, Z = 4 \) and the values of \( E_c \) are rather dispersed\(^{[15–17]}\). 0.2-2eV; we will take 1.44 0.5eV.

The most localized states are dangling bonds, they have the shortest possible \( \xi_{\text{min}} = 2.35/2\text{Å} \) (one half of a bond length). \( E = 0 \) for a dangling bond, then \( c = 0.121 \). For many AS\(^{[18]}\), in the range of conduction band tail, the density of localized states (DOS) satisfies

\[
N(E) = \left( n_{\text{loc}} / U \right) e^{-(E_c-E)/U},
\]

where \( U \) is the Urbach energy, \( n_{\text{loc}} \) is the total number of localized states per unit volume. For a-Si, \( U \approx 50\text{meV} \)\(^{[17–19]}\), the number density \( n_{\text{loc}} \) of localized conduction states is \( \approx \). \( n_{\text{loc}} = 5/(10.86\text{Å})^3 \). The exponential \( N(E) \) implies that most localized states in a-Si have a localization length in the range 6-12Å. Denote \( n \) as the carrier concentration, the Fermi energy \( E_F \) of a weakly doped AS is:

\[
E_F = E_c + U \ln(n/2n_{\text{loc}}),
\]

When \( n \leq 2n_{\text{loc}} \), all occupied states are localized at \( T = 0\text{K} \). Ansatz\(^{[3]}\) only characterizes the band tail states.

To describe dangling bonds, one can (i) introduce a reasonable DOS, e.g. a rectangle or a Gaussian; (ii) correspondingly modify \( E_L \) and energy zero-point for extended states; (iii) add the contribution from the dangling bonds to Eqs.\(^{[6–7]}\) in the summation(s) over localized states. In this paper we ignore the small contribution of dangling bonds to the conductivity.

In an AS, an extended state is a packet of Bloch waves of its reference crystal\(^{[21–22]}\), and is labeled by the wave vector of its principal Bloch wave, or more roughly by the momentum \( \mathbf{p} \) of a plane wave\(^{[11–12]}\). For an AS, for which the reference crystal does not exist, a wave packet constructed from plane waves is still a reasonable approximation for an extended state. We will use letter \( B \) with or without a natural number subscript to denote an extended state. Excepting EE transitions driven by an external field, we may approximate an extended state \( \chi_{\mathbf{B}}(\mathbf{r}) \) by a plane wave with certain momentum \( \mathbf{p} \), and its eigenenergy is that of the plane wave:

\[
\chi_{\mathbf{B}} = V^{-1/2} e^{i \mathbf{p} \cdot \mathbf{r} / \hbar}, \quad E_{\mathbf{B}} = p^2/2m,
\]

where the zero-point of energy for extended states is at the mobility edge \( E_c \). The attraction between an electron and an atom core may be approximated by a screened Coulomb potential\(^{[13]}\). For a-Si:H\(^{[2]}\), we approximate its Thomas-Fermi wave vector by the value\(^{[13]}\) for c-Si \( q_{TF} = 1.7\text{Å}^{-1} \).

With the foregoing approximations, the velocity matrix elements in the expressions of conductivity can be computed\(^{[23]}\). One can also obtain the static displacements of the atoms in a localized state induced by the e-ph interaction and the reorganization energy\(^{[14]}\) for transitions involving localized state(s)\(^{[23]}\), which are essential input for the conductivity.

![FIG. 1: (color online) log\(_10\)σ vs. 1/T in two n-doped a-Si:H samples at \( \omega = 0 \) with carrier concentration 10\(^{18}\) and 10\(^{19}\) cm\(^{-3}\). The unit of \( \sigma \) is ohm\(^{-1}\)cm\(^{-1}\).](Image)
spherical coordinate system with \( R_A \) as the origin and the wave vector direction \( \mathbf{k}/|\mathbf{k}| \) of the incident electromagnetic wave as polar axis (\( z \) axis)\(^{[23]}\). Because AS are isotropic, the angular part of the integral can be carried out. One can show that \( \sigma_{yy} = \sigma_{xx} = 0 \) and \( \sigma_{xy} = \sigma_{yx} = \sigma \). Because (i) the center \( R_A \) of \( \phi_A \) must be a neighbor of the observation point of current density, and (ii) the factors in the conductivity do not depend on \( R_A \),

\[
\Sigma_A \to \frac{4\pi}{3} \int_\infty^E dE N(E),
\]

where \( \Sigma = cZ^2/\left(4\pi\epsilon_0m^2\right) \) is the most probable localization length. For a-Si, \( \Sigma = 11.75\AA \), is quite close to the experimental value\(^{[23, 26]}\) 10\(\AA\). The conductivity from LE transitions is\(^{[23]}\):

\[
\left\{
\begin{array}{l}
\Re \sigma_A(\omega) = \frac{cZ^2}{\pi\epsilon_0U} \left[ 1 - f(E_B) \right] \\
\Im \sigma_A(\omega) = \frac{cZ^2}{\pi\epsilon_0U} \int_0^\infty d\xi f(E_A) \int \frac{\xi}{\xi_0} \\
\end{array}
\right.
\]

where \( \xi = \frac{\omega}{\sqrt{\hbar^2 \left[ (1 + h\omega_{BA}) \right]^2 - \left( \frac{\hbar}{2\kappa} \right)^2}} \). Equation (6) expresses conductivity and its associated temperature dependence upon several material parameters: \( n, n_{om}, \epsilon_0, \epsilon, \phi_T \), and \( \tau \). See Ref.\(^{[23]}\) for details.

Eqs. (6,7) express conductivity and its associated temperature dependence upon several material parameters: \( n, n_{om}, \epsilon_0, \epsilon, \phi_T \) and \( \tau \). See Ref.\(^{[23]}\) for details.

FIG. 2: (color online) TCR vs. \( T^{-2} \) in two n-doped a-Si:H samples at \( \omega = 0 \) Hz with carrier concentration \( 10^{18} \) and \( 10^{19} \) cm\(^{-3}\), experimental values are taken from Refs.\(^{[23, 24, 31]}\).

Eqs. (6,7) express conductivity and its associated temperature dependence upon several material parameters: \( n, n_{om}, \epsilon_0, \epsilon, \phi_T \) and \( \tau \). See Ref.\(^{[23]}\) for details.

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ity. If one forced a single Arrhenius fit to the overall conductivity, the formal activation energy would be different below and above \( T^* \). Thus one has a kink in the log\( \sigma (T) \) vs. 1/T curve. The non-exponential behavior as indicated in Eqs. (6,7) also has some role for the observed kink. For LL and LE transitions, we compute linear fits for the calculated log\( \sigma (T) \) vs. \( T^{-1} \), for which the norms of the residuals are 0.03 (LL) and 0.15 (LE) for 10\(^{18}\)cm\(^{-3}\), 0.05 (LL) and 0.20 (LE) for 10\(^{19}\)cm\(^{-3}\). This is consistent with the deviation from linear relation in the measured mobility vs. 1/T curve, cf. Fig. 7.10 of [2].

From Fig.1(a) and 1(b), we can see that T* decreases with n: T* =294K for 10\(^{18}\)cm\(^{-3}\), T* =286K for 10\(^{19}\)cm\(^{-3}\). This is consistent with the trend found in experiments: T* =400K for [PH\(_3\)]/[SiH\(_4\)]=10\(^{-6}\) and T* =333K for [PH\(_3\)]/[SiH\(_4\)]=10\(^{-2}\) cf. Fig. 3.1 of Ref.[3]. Fig. 3(a) and 3(b) plot log\( \sigma \) vs. log\( n \) at T=273K and 300K. We see that at T=273K (300K), the contribution from LL transitions is larger (smaller) than that from LE transitions for carrier concentration from 10\(^{15}\) to 10\(^{21}\)cm\(^{-3}\). For very different carrier concentrations (10\(^6\) times different), the kink temperatures fall near 273-300K, consistent with fact (ii). In Fig. 3(c) and 3(d) we plot log\( \sigma \) vs. log\( n \) for n-doped a-Ge:H at T=300K and 400K. T*’s fall between 300-400K, are higher than those for a-Si:H. It agrees with the observations, compare Fig. 3.1 and 3.6 of [30].

The compositional atomic orbital and/or their relative phases for the states close to Ef in the valence band (VB) are very different to those for states close to Ef in the conduction band (CB). Because \( U \propto \langle (|V_a - V_c)|)^2 \rangle_{av} \) and \( E_c \propto \langle (|V_a - V_c)|)_{av} \), where \( V_a \) and \( V_c \) are the potential of an AS and its reference crystal [21]. \( (|V_a - V_c)|)_{av} \) denotes configurational and state average in AS [22]. Larger \( U \) and \( E_c \) means stronger disorder, that implies smaller \( \xi \) or larger \( \lambda \), i.e. smaller \( \sigma \) and larger \( \kappa \).

Our approach is not restricted to one component systems with weak electronic correlation. If one has a reasonable single-electron DOS in which the correlation between electrons is already taken into account, it is not difficult to calculate the e-ph coupling in multi-component system, e.g. the e-ph interaction induced by the optical modes in VO\(_{1.83}\). The remaining procedure is exactly like here.

In conclusion, the microscopic response method expresses transport coefficients with transition amplitudes [5, 6] rather than transition probability per unit time, which enables the method to be used with amorphous semiconductors for which the Landau-Peierls condition is violated [3]. The conductivities from the three simplest transitions: LL, LE and EL transitions driven by field are expressed by several material parameters. The conductivity from LE transitions is as important as that from the LL transitions. The combination is responsible for the kink in the experimental log\( \sigma \) vs. \( T^{-1} \) curve. The LE transition is critical in determining the TCR.

This paper provides new analytical form for \( \sigma \) and \( \kappa \), suitable for amorphous semiconductors. A desirable extension would be a full \( \textit{ab initio} \) evaluation of all MRM diagrams using quantities from density functional theory. This complex task is underway.

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