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Connection between the Meyer-Neldel relation and multiple-trapping transport

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This paper shows that multiple-trapping-dominated transport quantities such as mobility and diffusion exhibit a Meyer-Neldel relation (MNR), an exponential relation between the prefactor of a thermally activated process and its activation energy. From these results, the Meyer-Neldel parameters can be related to the energy distribution of trapping sites and microscopic transport properties. The MNR for both the mobility of charge carriers and the annealing rate of metastable defects in hydrogenated amorphous silicon are quantitatively explained.

In the study of disordered materials, various properties, e.g., conductivity or diffusion, are found to exhibit exponential thermally activated (Arrhenius) behavior. Surprisingly, there is quite often an exponential relation between the activation energy and the preexponential factor for the various processes known as the Meyer-Neldel relation[1] (MNR). This relation has been observed in a wide variety of materials for a number of quantities. Examples of properties exhibiting the MNR include the electrical conductivity in powdered semiconductors[1] and hydrogenated amorphous silicon[2-6] (a-Si:H), trap emission rates for defects in binary and trinary alloys,[7] and the photocurrent in polycrystalline solar cells.[8] A typical example, presented in Fig. 1, is the annealing rates of metastable defects in a-Si:H for a large number of defects.[9,10] For properties exhibiting the MNR, the prefactor q_0 and activation energy E_a of the relevant property are related by a characteristic relation $q_0 = q_{00}\exp(E/E_0)$, where E_0 is remarkably constant between various material systems having a value of 0.03–0.1 eV and q_{00} is a constant. Although the MNR is similar in a variety of materials suggesting a common underlying mechanism, its origin is unclear. It is often associated with disorder of some form within the material. In the case of dc electrical conductivity in a-Si:H, a time-independent equilibrium process, the MNR is due to the statistical shift of the Fermi level.[5,11,12] However, the MNR is often observed for nonequilibrium time-dependent properties such as the mobility in time-of-flight experiments which do not depend on the equilibrium Fermi distribution or a statistical shift.[13]

Independently, significant progress has been made in understanding transport in disordered systems in terms of multiple trapping (MT) of mobile species.[14-16] The transport is dominated by frequent trapping into and thermal release from localized states. MT has been highly successful at explaining the time and temperature dependence of electrical transients,[13-16] photoinduced absorption,[17] etc., in many disordered materials[15,16] and explains transport by both drift and diffusion.

This paper demonstrates that there is a close connection between MT and the MNR for a certain class of quantities: namely, time-dependent transport properties. Whenever a MT-dominated transport process (i.e., time dependent) is observed over fixed distances as a function of temperature, a MNR should be observed for this transport quantity. This important result is first derived by considering dispersive diffusion of hydrogen and quantitatively predicts the MNR for the attempt-to-anneal frequency of light-induced metastable defects and the annealing activation energy (results in Fig. 1) due to hydrogen motion in a-Si:H. The connection between the MNR and MT is then further investigated by considering the field dependence of the drift mobility of carriers in a-Si:H.

Consider first the diffusion of hydrogen in a-Si:H. Recent measurements have demonstrated that hydrogen exhibits dispersive diffusion given by[18,19]

$$D(t) = D_{00}(\omega t)^{-\alpha}, \tag{1}$$

where D_{00} is a microscopic diffusion constant (weighted by a density-of-states ratio), ω is the hydrogen attempt frequency, and α is the temperature-dependent dispersion parameter which is given by $\alpha = 1 - \beta = 1 - T/T_0$. The quantity kT_0 is the characteristic energy of the exponential hopping distribution in dispersive transport, and T is

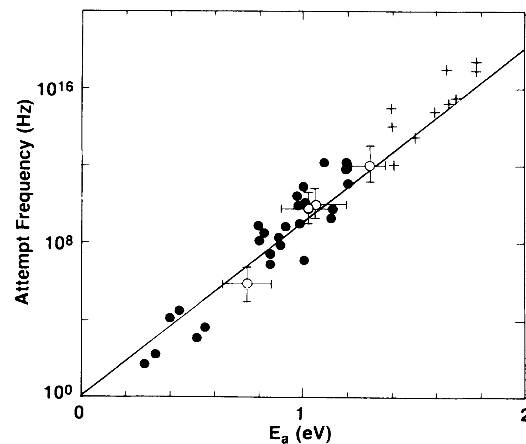

FIG. 1. The attempt frequency for annealing of various defects in a-Si:H vs the defect annealing energy from various sources. The crosses and solid dots represent electron and hole trapping defects, respectively, from Ref. 9 and the open circles represent the prefactors and annealing energies of dangling-bond defects in various films containing impurities from Ref. 10. The solid line represents the relation predicted by the hydrogen diffusion data of Ref. 18 into Eq. (8).

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the measurement temperature. Because of the limited spatial resolution to measure hydrogen diffusion ($\simeq 3$ nm) and finite annealing times, measurements of the temperature dependence of the diffusion must be performed such that the diffusion distance is kept nearly constant for the various annealing temperatures.[18] For time-dependent diffusion, the time t_L to diffuse a distance L is given by[20]

$$L^2 = \int_0^{t_L} D(t')dt' . \tag{2}$$

Solving Eq. (2) for t_L and substituting into Eq. (1) using the dependence of the dispersion parameter on temperature, the diffusion constant $D(T_L)$ can be written in the form

$$D(t_L) = D_0 \exp(-E_{\text{diff}}/kT) , \tag{3}$$

where $D_0 = L^2\omega(1-\alpha)/4$ and

$$E_{\text{diff}} = kT_0 \ln\{[L^2\omega(1-\alpha)]/(4D_{00})\}$$
$$= kT_0 \ln(D_0/D_{00}) \tag{4}$$

or

$$D_0 = D_{00}\exp(E_{\text{diff}}/kT_0) . \tag{5}$$

The relations given by Eqs. (3)–(5) are important because they demonstrate that the diffusion for a constant diffusion distance is activated with an activation energy E_{diff}. The prefactor for diffusion, D_0, depends exponentially on the activation energy according to the MNR where $E_0 = kT_0$ and the prefactor $q_{00} = D_{00}$ is the microscopic diffusion coefficient. The only assumption involved in the above derivation is that the motion is dispersive.

Physically, the origin of the MNR is as follows. The activation energy E_{diff} is the depth of the deepest trap visited during diffusion over a distance L.[16] The prefactor D_0 is the diffusivity for the hydrogen if the release time from these deepest traps is just the attempt frequency without any thermally activated waiting time, and D_0 depends inversely on the number of traps at this energy. For longer distances, the hydrogen transport is controlled by deeper traps causing E_{diff} to increase. Because the number of these traps decreases exponentially as the trap depth, the prefactor increases exponentially as a function of the controlling trap depth. The MNR between the prefactor and the activation energy follows immediately, demonstrating that the MNR and MT are manifestations of the same phenomenon.

These results can be quantitatively tested using defect annealing and creation kinetics[21] which requires the derivation of a relation between hydrogen diffusion and defect kinetics. Consider the case where defects of density, $n(t)$, are removed by conversion due to the diffusion of H to the defect. Examples include the conversion of dangling Si bonds to fourfold Si or fourfold donors to threefold nondoping donor.[21] The rate of change of the defect density is given by[19,22]

$$dn(t)/dt = -AD(t)n(t) , \tag{6}$$

where $A = 4\pi N r_0$, N is the density of diffusing hydrogen atoms, r_0 is the capture radius of the defect, and $D(t)$ is the diffusion coefficient which depends on time. Solving Eq. (6) using Eq. (1) yields the characteristic stretched exponential[19,22,23]

$$n(t) = n(0)\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{7}$$

where $\beta = T/T_0$ as before, $\tau = \tau_0\exp(E_\tau/kT)$, $\tau_0 = 1/\omega$, and E_τ is given by

$$1/\tau_0 = (AD_{00}/\beta)\exp(E_\tau/kT_0) . \tag{8}$$

Because the T dependence of β in the prefactor is small, Eq. (8) demonstrates that the parameter τ for defect annealing kinetics exhibits a MNR.

Equations (7) and (8) can now be quantitatively compared with the experimental data. The diffusion of hydrogen in 10^{-3} P-doped material from Ref. 18 is corrected to a constant diffusion distance using Eqs. (3) and (4). From this data, it is found that for $L = 100$ nm, and $T_0 = 600$ K, the activation energy is $E_{\text{diff}} = 1.4$ eV, and $D_0 = 0.03$ cm^2 sec^{-1}. For a 10^{-2} P-doped material, the activation energy is the same but the prefactor is approximately twice as large[18] so that $D_0 = 0.06$ cm^{2}sec^{-1}. Equation (5) yields a microscopic diffusion constant of $D_{00} = 5\times10^{-14}$ cm^2/sec. Using the relations $D_0 = L^2\omega/4$ and $\tau_0 = 1/\omega$, gives $\tau_0 = 4\times10^{-10}$ sec, comparing well with the observed value of 2×10^{-10} sec.[19,24] The capture radius of a diffusing H atom by a dangling bond is approximately the bond length of 0.2–0.3 nm, and the diffusing hydrogen density is approximately 10^{21} cm^{-3}, giving $A = 2.5\times10^{14}$ cm^{-2}. The resulting calculated activation energy for τ is $E_\tau = 0.95$ eV from Eq. (11) while the observed value is 0.93 eV.[19,24]

The previously unexplained MNR between annealing energy and attempt-to-anneal frequency of metastable defects shown in Fig. 1 can now be quantitatively derived from the hydrogen diffusion data using Eq. (8) which predicts that there is a MNR between the defect annealing energy and the prefactor. The exponential energy should be $E_0 = 0.05$ eV compared to the observed value of 0.05 eV.[9,10] Furthermore, the Meyer-Neldel prefactor is given by $q_{00} = AD_{00}/\beta$. From the data in Ref. 18, $D_{00} \approx 2\times10^{-15}$ cm^2/sec for undoped and the predicted Meyer-Neldel prefactor q_{00} is approximately between 1 sec^{-1} for undoped and 30 sec^{-1} for P-doped films using the value for A from above. The result of Eq. (8) (solid line Fig. 1) is in excellent agreement with the data.[9,10] Summarizing, dispersive diffusion quantitatively explains the MNR between the attempt frequency and anneal energy of metastable defects as well as the difference in the activation energy of the stretched exponential parameter τ (0.95 eV) and the apparent activation energy of hydrogen diffusion (1.4 eV).

The above arguments show that dispersive diffusion gives rise to the annealing MNR; they apply to other dispersive transport processes as well. As a further test of this connection, consider MT-dominated transport across a sample of thickness L. The mobility is dispersive and is given by relations quite similar to Eqs. (1) and (2): namely,[14,15]

$$\mu(t) = \mu_{00}(\omega t)^{-\alpha} \tag{9}$$

and

$$L=\int_0^{t_L}\mu(t')E\,dt' , \tag{10}$$

where t_L is the transit time, μ_{00} is the microscopic mobility (weighted by a density-of-states ratio), and E is the field. Because the carriers traverse a constant distance, the measured mobility will exhibit a MNR

$$\mu(t_L)=\mu_0\exp(-E_{\text{mobility}}/kT) \tag{11}$$

where

$$\mu_0=L\omega(1-\alpha)/E \tag{12}$$

and

$$E_{\text{mobility}}=kT_0\ln\{[L\omega(1-\alpha)]/(E\mu_{00})\}$$
$$=kT_0\ln(\mu_0/\mu_{00}) . \tag{13}$$

The hole drift mobility data presented previously in Ref. 13 are analyzed to test Eqs. (11)-(13). The hole mobility versus temperature for different fields on a single sample was fit to Eq. (11). A plot of μ_0 vs $1/E$ (Fig. 2) yields a reasonable straight line as expected from Eq. (12) with a slope of $L\omega=4.6\times10^7$ cm/sec or $\omega\simeq10^{11}$ Hz—a result in good agreement with $1-3\times10^{11}$ Hz obtained on the same sample from time-of-flight measurements.[13] The linear relation between E_{mobility} and $\ln E$ (inset, Fig. 2) expected from Eq. (13), yields $kT_0\simeq30$ meV compared with the 37 meV obtained on the same sample.[13] The derived value of μ_{00} (after inclusion of the appropriate density-of-states ratio) is consistent with the previously reported microscopic hole mobility of 1-10 $\text{cm}^2\text{V}^{-1}\text{sec}^{-1}$.[13,15] Although these mobility equations are implicit in the previous work on drift mobility,[13-16] Eqs. (9)-(13) demonstrate explicitly that a MNR follows immediately from MT for transport processes.

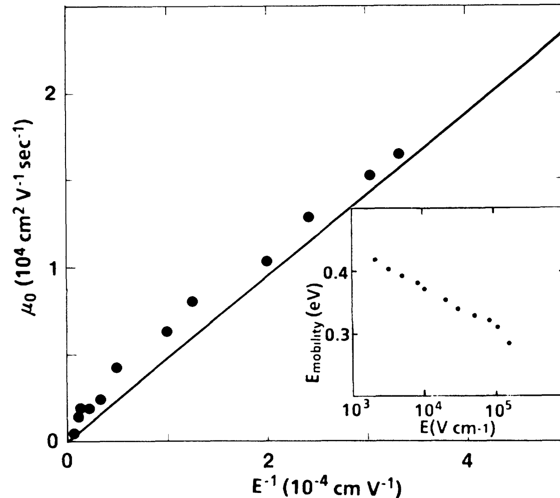

FIG. 2. The hole mobility prefactor vs electric field. Dots are data from dispersive transport of Ref. 13 and the solid line is predicted from Eq. (12). The inset represents the mobility activation energy vs electric field from the transport data of Ref. 13 and verifies the linear relation given by Eq. (13).

It is important to point out that the arguments in this paper demonstrate that the MNR follows from MT for fundamental quantities such as diffusion and mobility. Other quantities can depend on nontransport properties which may or may not exhibit a MNR. Conductivity, for example, depends on the density of carriers as well as the mobility. The conductivity in a-Si:H exhibits a MNR because the statistical shift causes the carrier density to follow a MNR as well as the mobility.[5,11,12] A different density of states could give rise to a non-MNR for the conductivity in other materials. Thus, while multiple trapping implies a MNR for time-dependent transport processes, the converse does not hold. It should be noted that experimentally the microscopic quantity μ_{00} (and D_{00} by the Einstein relation) are quite constant, independent of doping, deposition conditions, and even for different amorphous covalent materials.[15,25] Hence, the MNR holds for films deposited under different deposition conditions and doping.

In conclusion, this paper has demonstrated that there is a fundamental connection between time-dependent transport and the Meyer-Neldel relation for multiple trapping dominated processes. The energy factor of the MNR is related to the energy distribution of the traps while the prefactor is related to the microscopic transport properties. These results explain in a natural way the difference in the activation energy for hydrogen diffusion and the stretched exponential time constant for the decay of excess carriers as well as the time, temperature, and field dependence of carrier transport in disordered materials.

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