Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Organic Electronics 6 (2005) 137–141
Organic Electronics
www.elsevier.com/locate/orgel

Trap states as an explanation for the Meyer–Neldel rule in semiconductors

P. Stallinga *, H.L. Gomes

Universidade do Algarve, Optoelectronics, UCEH, FCT, Campus de Gambelas, Faro 8000, Portugal

Received 19 October 2004; accepted 14 March 2005
Available online 19 April 2005

Abstract

It is shown that whenever traps, distributed exponentially in energy, are governing the conduction in electrical materials, a Meyer–Neldel observation is expected. This is a direct result of the model incorporating a high density of traps by Shur and Hack. Since this type of conduction is common for low mobility materials, such as organic semiconductors or amorphous silicon, they are therefore likely to obey the Meyer–Neldel rule.

PACS: 72.80.Le; 73.50.−h; 72.20.Jv

Keywords: Meyer–Neldel rule; Electronic transport; Traps; Semiconductors

The Meyer–Neldel rule (MNR) [1] is observed in many processes in nature. Applied to semiconductor materials, the Meyer Neldel rule states that the prefactor of the thermally activated mobility increases exponentially with the activation energy. What this means is that (1) the activation energy of current or carrier mobility depends on the bias conditions, (2) there exists a temperature, known as the isokinetic temperature T_{MN}, where the dependence on bias disappears. In other words, when presented in an Arrhenius plot (logarithm of the measured quantity vs. reciprocal temperature), the curves of current or mobility are straight lines that pass through or converge to a common point not coinciding with infinite temperature. The MNR is frequently observed in low-conductivity disordered materials. As examples: porous and amorphous silicon [2,3], microcrystalline silicon films [4], ionic conductivity [5], glassy materials [6] and organic materials [7]. The common factor to all these materials is the existence of a large density of localized states with high activation energy (traps). In this article we discuss the link between trap states and the Meyer–Neldel rule

* Corresponding author. Tel.: +351 969541198; fax: +351 289800030.
E-mail address: pjotr@ualg.pt (P. Stallinga).

1566-1199/$ - see front matter
doi:10.1016/j.orgel.2005.03.008

using a model of Shur and Hack [8]. As an example we show results of thin-film field-effect-transistors of α-sexithiophene (α-T6), although the idea is equally well applicable to other low mobility materials.

In the standard model for field effect transistors, the current in the linear region ($V_{ds} \ll V_g - V_t$) is of the form

$$I_{ds} = \frac{W}{L}\mu C_{ox} V_{ds}(V_g - V_t). \quad (1)$$

Here W and L are the source and drain electrode length and distance respectively, μ is the carrier mobility, C_{ox} is the insulator capacitance density and V_{ds} and V_g the drain–source voltage and gate–source voltage respectively. V_t is the voltage needed at the gate to open the channel. The above equation allows for a definition of the as-measured mobility via the derivative of a transfer curve (I_{ds} vs. V_g):

$$\mu = \frac{L}{W C_{ox} V_{ds}} \frac{\partial I_{ds}}{\partial V_g}. \quad (2)$$

Actually, this is the de facto standard used for determining the carrier mobility in field effect transistors and is also sometimes called the field effect mobility, μ_{FET}, to distinguish it from mobilities measured by other techniques such as time-of-flight or Hall effect. For various reasons, this mobility can still depend on the bias conditions and the temperature.

In the multi-trap-and-release model, the charges spend most of their time on localized trap states, where the mobility is zero. To contribute to conduction, a charge first has to be (thermally) excited to a delocalized band where the mobility is high. The field-effect mobility now, by the way it is measured, is a weighed average of the trap states and the conduction bands and is not the intrinsic mobility of free carriers. Since the thermal equilibrium of the distribution over the levels depends on the temperature, the as-measured mobility depends on the temperature. Parameters in this are the band state density and the trap state density and depth. Poole and Frenkel [9] have shown that the effective trap depth can be lowered by the application of an in-plane field. This makes the as-measured mobility also field (drain–source voltage) dependent. Many authors have shown that non-crystalline low-conductivity materials such as most organic materials or amorphous silicon are well described by this Poole–Frenkel conduction model [10], thereby showing that traps is the limiting factor in the conductivity. In a recent publication we have shown this to be true for α-sexithiophene [11].

As shown by Shur and Hack, a high density of trap states also causes the mobility to depend on the gate voltage [8,12]. Because the ratio of free-to-trapped charges increases with the gate voltage, the transfer curves are supra-linear [8,11]. They present a model with a density of traps that is exponentially decreasing with depth. Their model dictates that the drain–source current is of the form [8, Eq. 53]

$$I_{ds} = \frac{q\mu_0 W}{L} f(T, T_2)[C_{ox}(|V_g - V_t|)]^{(2T_2/T-1)} V_{ds} \quad (3)$$

with

$$f(T, T_2) = N_V \exp\left(\frac{-E_{F0}}{kT}\right) \frac{kT\epsilon}{q} \left(\frac{\sin(\pi T/T_2)}{2\pi\epsilon T_2 kT g_{F0}}\right)^{T_2/T}. \quad (4)$$

Here T_2 is a parameter describing the slope of the distribution of deep trap states in a logarithmic energy diagram: $d\ln(N_T)/dE = 1/kT_2$. N_V is the effective density of band states which is considered independent of temperature (assuming a more accurate slowly-varying function, such as $N_V \propto T^{3/2}$ [9], does not change the analysis). g_{F0} is the density of deep localized states at the Fermi level E_{F0}, which can be as large as N_V. μ_0 is the band mobility, ϵ the semiconductor permittivity, q the elementary charge and k the Boltzmann constant. Note that a factor q has been removed from the last term of the original form of Eq. (4) in order to make the units correct.

Eq. (3) directly predicts the second part of the Meyer–Neldel observation, namely a temperature where the current does not depend on the gate voltage:

$$T_{MN} = 2T_2. \quad (5)$$

In other words, the Meyer–Neldel temperature is a direct measure of the distribution of deep trap states and this temperature can rapidly be determined by taking temperature-scanned-current curves at different biases.

For temperatures well below T_2, the approximation $\sin(\pi T/T_2) \approx \pi T/T_2$ can be made and, together with the relation $a^x = \exp(x\ln(a))$ it is easily shown that the Arrhenius plots of current are linear and the effective activation energy depends on the gate bias (demonstrating the first part of the Meyer–Neldel rule):

$$E_A = E_{F0} - kT_2\left[\ln\left(\frac{1}{2\epsilon(kT_2)^2 g_{F0}}\right) - 2\ln(C_{ox}(|V_g - V_t|))\right]. \quad (6)$$

This activation energy can thus substantially deviate from the depth of the traps at the Fermi level, E_{F0}. Moreover, because of the linearity of the Arrhenius plots, one can easily make the mistake of assuming a single discrete trap level to be responsible for the activation of the current.

Eq. (6) also shows that the activation energy depends on the bias condition V_g. Fig. 1 shows a simulation of a temperature-dependent-current (*I–T*) experiment of a system with deep traps with the parameters as of Table 1. In the inset, the as-measured activation energy is shown as a function of bias, $|V_g - V_t|$. This is indeed very similar to the Meyer–Neldel observation seen in a wide variety of materials. (Note: Since the parameters are interdependent, the same results can be obtained for other combinations of E_{F0} and g_{F0}.)

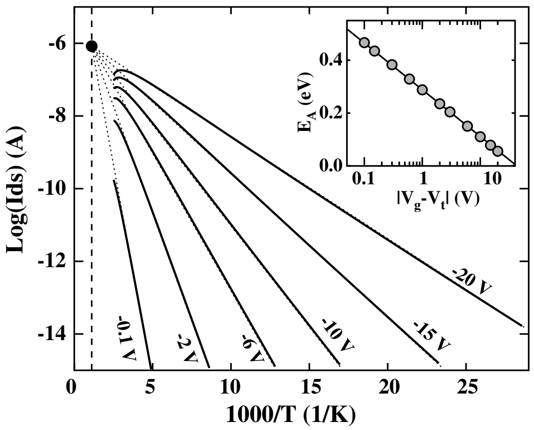

Fig. 1. Simulation of temperature-dependent currents (*IT*) based on parameters of Table 1, with gate biases from 0.1 V to 20 V as indicated. The solid dot (●) represents the Meyer–Neldel point (T_{MN}, I_{MN}). The inset shows the effective activation energy as a function of bias.

Table 1
Simulation parameters used to generate Fig. 1

Parameters	Value	Unit
N_V	10^{19}	cm^{-3}
C_{ox}	1.92×10^{-4}	F/m^2
E_{F0}	484	meV
V_{ds}	-0.1	V
g_{F0}	10^{16}	$cm^{-3}\,eV^{-1}$
T_2	450	K
W	1	cm
L	30	μm
μ_0	3	$cm^2\,V^{-1}s^{-1}$
ϵ	$5\epsilon_0$	

Applying Eq. (2) for the as-measured mobility to Eqs. (3) and (4) we find that the observed mobility has a similar behavior but becomes gate-voltage independent at a Meyer–Neldel temperature of $T_{MN} = T_2$. Moreover, the as-measured mobility is much smaller than the band conduction mobility μ_0. As an example, for the parameters of Table 1 and $|V_g - V_t| = 6$ V and $T = 300$ K, the measured mobility is 8.0×10^{-3} cm^2/Vs—three orders of magnitude below the band mobility μ_0.

For a specific α-sexithiophene p-channel FET, with geometric parameters W, L and C_{ox} as given in Table 1, *I–T* scans were made for various bias conditions [11]. An example of an *I–T* curve for $V_g = -10.5$ V and $V_{ds} = -0.5$ V, together with a simulation on basis of Eq. (3) is shown in Fig. 2. A summary of the measured activation energies of current as a function of gate bias is given in Fig. 3. Unfortunately, in these experiments, the scanning had to be limited to below 210 K to avoid the phenomenon known as stress [14], substantial shifts of the threshold voltage V_t with time and upon changes of bias. This is especially pertinent because the effect of bias on the measured activation energy is expected to be largest for V_g close to V_t, as predicted by Eq. (6). Thus, small changes of V_t influence the results dramatically. Recently, Gomes et al. [13] have shown that α-sexithiophene also suffers from this phenomenon for higher

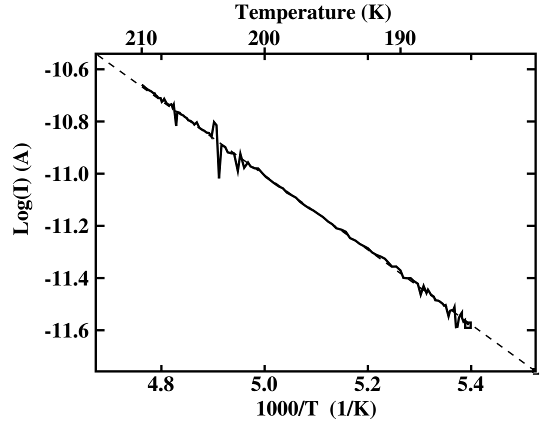

Fig. 2. Arrhenius plot of the current of an FET based on sexithiophene with bias $V_{ds} = -0.5$ V and $V_g = -10.5$ V. The dashed line shows a simulation with $E_{F0} = 535$ meV, $N_V = 1.7 \times 10^{19}/\mathrm{cm}^3$, $V_g - V_t = -2$ V and other parameters as of Table 1. The slope of the curve yields an effective activation energy of 296 meV.

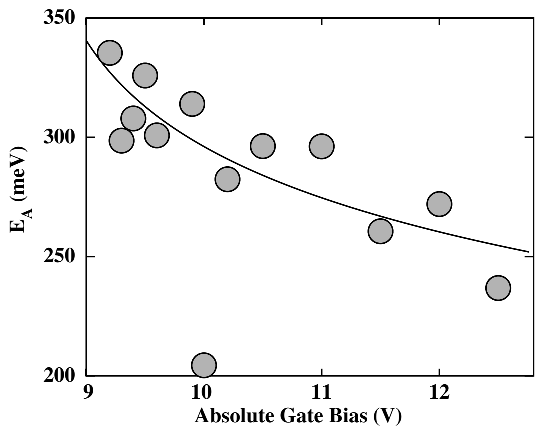

Fig. 3. Measured activation energy as a function of bias of an FET based on sexithiophene. The solid line is a fit to the data yielding $T_2 = 250 \pm 200$ K and $V_t = -8.5 \pm 1.4$ V. To avoid systematic error, the measurements were carried out in random order. Each point represents a curve such as shown in Fig. 2.

temperatures and we expected to obtain distorted results when stressing becomes important above 210 K. Even in the low temperature range chosen for the experiment, we cannot exclude small changes of V_t. However, it is clear from Fig. 3 that the activation decreases with V_g as predicted by the above theory. Moreover, to avoid systematic errors in the measurement caused by stress, the experiments were carried out in random order.

In another experiment [11], measuring the mobility of the carriers as a function of temperature, Meyer–Neldel temperatures ($T_{MN} = T_2$) were found to vary from sample to sample and different T_2's were sometimes found in the high and low temperature range, sometimes with an abrupt change at around 200 K [11]. Using the above theory this implies a change in the energetic distribution of deep trap states.

One final thing to note is that Eqs. (3) and (4) also predict a current that is dropping for temperatures approaching T_2 (see Fig. 1). For temperatures beyond T_2 (up to $2T_2$), the equations do not yield a real value for the current. Interesting in this respect is the lack of presented results in literature for measurements at the isokinetic temperature. In all cases the Meyer–Neldel point is found by extrapolation of the curves.

In a conclusion, we showed that the observation of the MNR is a direct result of traps. Therefore, the MNR is a sign of conduction governed by trap states and the isokinetic temperature T_{MN}, the temperature where the current or the mobility is independent of bias, is a parameter describing the distribution of these trap states. As such, the Meyer–Neldel temperature is a reliable and easily measured parameter to determine trap states. T_{MN} can be called a figure-of-merit as suggested by Pichon et al. [15]. The theory was applied to an FET of sexithiophene which shows to conform to this model, although, due to stressing, the parameters were difficult to extract.

As a final remark, we do not exclude the possibility that other systems or factors will result in the observation of the MNR. Moreover, even for trap-rich systems there might be various explanations for the MNR observation. Shur and Hack [8], Crandall [16] and Vissenberg and Matters [17] all use models of trap-rich systems resulting in similar temperature and gate-bias dependence. We can apply the same analysis to show that these models will thus predict the MNR observation. Vissenberg et al. do not include the band states and the conduction is solely through hopping from trap state to trap state. In a recent work we have shown the model of Shur and Hack to be most adequate for describing the α-T6 FETs [11]. In the current work we have shown how this then predicts a Meyer–Neldel rule.

We would like to acknowledge D.M. De Leeuw for valuable discussion. This work has been financed by Portuguese grant POCTI/FAT/47956/2002.

References

[1] W. Meyer, H. Neldel, Z. Tech. 18 (1937) 588.

[2] Y. Lubianiker, I. Balberg, J. Non-Cryst. Solids 227–230 (1998) 180.

[3] M. Kondo, Y. Chida, A. Matsuda, J. Non-Cryst. Solids 198–200 (1996) 178.

[4] S.K. Ram, S. Kumar, R. Vanderhaghen, P. Roca i Cabarrocas, J. Non-Cryst. Solids 299–302 (2002) 411.

[5] K.L. Ngai, Sol. Stat. Ionics 105 (1998) 231.

[6] K. Shimakawa, F. Abdel-Wahab, Appl. Phys. Lett. 70 (1997) 652.

[7] E.J. Meijer, M. Matters, P.T. Herwig, D.M. de Leeuw, T.M. Klapwijk, Appl. Phys. Lett. 76 (2000) 3433.

[8] M. Shur, M. Hack, J. Appl. Phys. 55 (1984) 3831.

[9] S.M. Sze, Physics of Semiconductor Devices, second ed., Wiley Interscience, 1981.

[10] See for example S.V. Rakhmanova, E.M. Conwell, Appl. Phys. Lett. 76 (2000) 3822, and other papers by the Conwell group.

[11] P. Stallinga, H.L. Gomes, F. Biscarini, M. Murgia, D.M. De Leeuw, J. Appl. Phys. 96 (2004) 5277.

[12] M. Shur, Physics of Semiconductor Devices, Prentice Hall, New Jersey, 1990.

[13] H.L. Gomes, P. Stallinga, F. Dinelli, M. Murgia, F. Biscarini, D.M. De Leeuw, T. Muck, J. Geurts, L.W. Molenkamp, V. Wagner, Appl. Phys. Lett. 84 (2004) 3184.

[14] M.J. Powell, IEEE Trans. Electr. Dev. 36 (1989) 2753.

[15] L. Pichon, A. Mercha, J.M. Routoure, R. Carin, O. Bonnaud, T. Mohammed-Brahim, Thin Solid Films 427 (2003) 350.

[16] R.S. Crandall, Phys. Rev. B 43 (1991) 4057.

[17] M.C.J.M. Vissenberg, M. Matters, Phys. Rev. B 57 (1998) 12964.