Dependence of Meyer–Neldel energy on energetic disorder in organic field effect transistors

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(Received 12 March 2010; accepted 17 April 2010; published online 28 May 2010)

Meyer–Neldel rule for charge carrier mobility was studied in C_{60}-based organic field effect transistors (OFETs) fabricated at different growth conditions which changed the degree of disorder in the films. The energetic disorder in the films was found to correlate with a shift in the Meyer–Neldel energy, which is in excellent agreement with the predictions of a hopping-transport model for the temperature dependent OFET mobility in organic semiconductors with a Gaussian density-of-states (DOS). Using this model the width of the DOS was evaluated and it was found to decrease from 88 meV for the films grown at room temperature to 54 meV for films grown at 250 °C. © *2010 American Institute of Physics*. [doi:10.1063/1.3435477]

In disordered organic semiconductors the electronic states are localized and energetically distributed, so that transport occurs via incoherent thermally assisted hopping[1–3] in the density-of-states (DOS) distribution most often described by the Gaussian disorder model.[3] Recently it was recognized that charge carrier mobility in actual organic electronic devices, as organic field effect transistors (OFETs), depends essentially on carrier concentration which was theoretically rationalized within Extended Gaussian Disorder model.[4–6] In the latter case a sizeable fraction of the DOS distribution is occupied by charge carriers, so carrier jumps from the Fermi level dominate charge transport giving rise to an Arrhenius-type $\ln(\mu) \propto T^{-1}$ temperature dependence of the mobility[6,7] with virtually constant (yet dependent on carrier concentration) activation energy reflecting the temperature independent position of the Fermi level position with respect to the center of the DOS. This is in contrast of the case of low carrier concentration, characterized by the non-Arrhenius type temperature dependence $\ln(\mu) \propto T^{-2}$ since in such a case charge transport is dominated by hopping from the equilibrium occupational DOS distribution which is temperature dependent.[1,3]

In a number of studies[8,9] it has been well documented that mobility obeys Arrhenius-type $\mu(T)$ dependences. Measured at different gate voltages (V_G) and, concomitantly, at different charge carrier densities, these Arrhenius plots intersect at a given finite temperature T_0, suggesting that the Meyer–Neldel rule (MNR) (Ref. 10) is obeyed. The MNR is an empirical relation, originally derived from chemical kinetics.[10] More generally, it states that in a thermally activated rate process an increase in the activation energy E_a is partially compensated by an increase in the prefactor so that thermally activated charge carrier mobility in semiconductors is given by,

$$\mu = \mu_{p0} \exp\left[- E_a \left(\frac{1}{k_B T} - \frac{1}{E_{\mathrm{MN}}} \right) \right], \tag{1}$$

where $E_{\mathrm{MN}} = k_B T_0$ is called the "Meyer–Neldel energy" and μ_{p0} is a constant prefactor. E_a is the activation energy being affected, for instance, by the gate voltage in OFETs. Justification of the MNR effect for the charge carrier mobility and the physical meaning of E_{MN} is still heavily under debate and several theoretical attempts based on polaron concept have been suggested to justify the MNR in different systems.[11]

Most recently, Fishchuk *et al.*[6,12] have formulated an analytical theory based on the effective medium approximation (EMA) to describe the MNR for the OFET mobility of charge carriers irrespective of their polaronic character by employing the conventional hopping transport concept for a disordered system with a Gaussian DOS distribution of width σ and Miller–Abrahams jump rates. It was shown that the results of the EMA calculations can be parametrized in terms of an approximate analytical equation[12] for the charge carrier mobility μ_e as a function of $\sigma/k_B T$, the ratio of densities of occupied and total transport states n/N, and the ratio a/b of the intersite distance (a) and the localization radius (b) of the charged site. At moderately high temperatures and commonly accepted value $a/b = 10$ (Refs. 4 and 5) for organic semiconductors, the approximate relation for the temperature dependent OFET mobility reduces to,

$$\frac{\mu_e}{\mu_0} \propto \exp\left[- E_a \left(\frac{1}{k_B T} - \frac{1}{k_B T_0} \right) \right], \tag{2}$$

where

$$E_a = \left[0.75 - 0.67 \log_{10}\left(\frac{n}{N} \right) \right] \sigma \quad \text{and finally}$$

$$T_0 = \frac{2}{5} \frac{\sigma}{k_B}. \tag{3}$$

Equation (2) is nothing else than the conventional MNR re-

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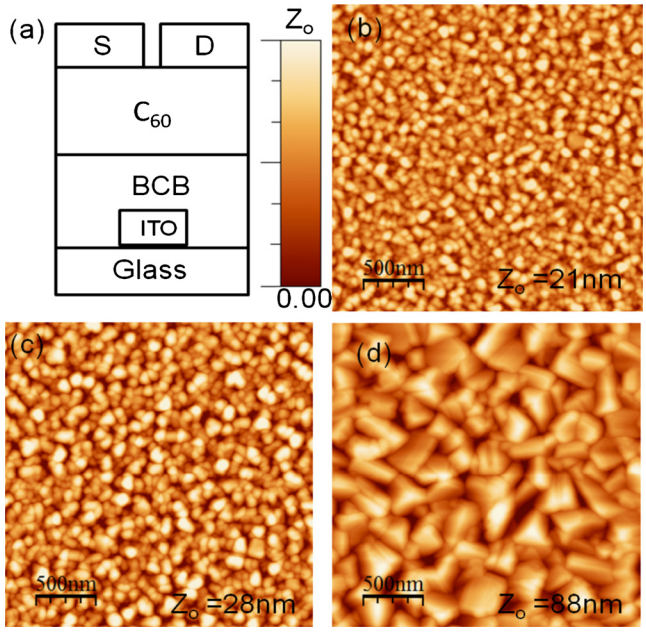

FIG. 1. (Color online) Schematic cross-section of OFET structures (a). AFM images of C_{60} films grown by flush evaporation at room temperature (b) and by HWE at a substrate temperature of 130 °C (c) and 250 °C (d).

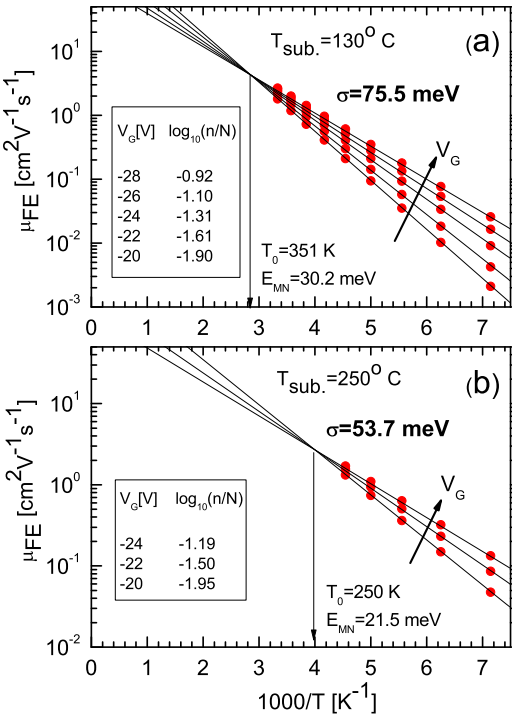

FIG. 2. (Color online) Temperature dependence of the OFET mobility measured at different V_G in C_{60} films grown by HWE at T_{sub}=130 °C (a) and 250 °C (b) (symbols) and results of their fitting with Eq. (2) (solid lines). The isokinetic temperature T_0 is indicated by an arrow.

lation [cf. Eq. (1)]. E_a depends on the relative carrier concentration n/N and σ, so it can be influenced by both parameters. An important prediction of the suggested theory is that the MNR energy E_{MN} in organic semiconductors is directly related to the width of the Gaussian DOS, σ, providing thus a method for evaluation of the amount of the energetic disorder in the material. Another prediction of the theory is that the MNR effect for the temperature dependences of the charge carrier mobility arises upon varying the carrier concentration, but not regarding varying the width of the DOS, σ.[12] In the present work, we performed a systematic experimental study of the interrelation between the energetic disorder and the MNR energy as derived from the temperature dependent OFET mobilities in C_{60} films grown at different conditions resulting in different film morphologies.

The top-contact bottom-gate OFET devices, as schematically shown in Fig. 1(a) were fabricated on ITO covered glass substrates using divinyltetramethyldisiloxane-bis(benzocyclobutane) (BCB) as gate-insulating layer. The thin C_{60} films were deposited at different substrate temperatures using standard flush evaporation or hot-wall epitaxy (HWE) technique.[13] As one can see from Figs. 1(b)–1(d) the film morphology depends quite considerably on the growth conditions, increasing the substrate temperature (T_{sub}) results in larger grain size of the C_{60} films. The smallest grains were obtained in films grown by conventional thermal evaporation without substrate heating [Fig. 1(b)], and the largest ones in films grown by HWE technique at T_{sub}=250 °C. Finally LiF/Al top contacts were evaporated in high vacuum. The completed devices were loaded for electrical characterization in an Oxford cryostat inside the glove box. The field-effect mobility μ_{FE} of the C_{60}-based OFET has been determined in the linear regime of the I_D-V_G characteristics (at low source-drain voltage V_D=2 V).

Figures 2(a) and 2(b) (symbols) show the μ_{FE} as a function of inverse temperature at different gate voltages V_G obtained for C_{60} films grown by HWE at substrate temperature T_{sub}=130 °C and 250 °C, respectively. It is evident that the extrapolation of these graphs intersect at the isokinetic temperature T_0=351 K and 250 K for the films grown at 130 °C and 250 °C, respectively, thus clearly demonstrating a MNR-type behavior. This yields to corresponding MNR energies of E_{MN}=30.2 and 21.5 meV. The MNR effect has been reported recently by our team for the flush evaporated C_{60} film which was deposited at room temperature[12] [Fig. 1(a)], which featured also a clear MNR-type behavior resulting in E_{MN}=34 meV for this highly disordered film. Using Eq. (3) for each T_0, determined from experiment, the corresponding width of the DOS, σ=88 meV, 75.5 meV and 54 meV can be obtained for films grown at room temperature, 130 °C and 250 °C, respectively.

Figure 3(a) shows temperature dependence of the mobility for the two samples with two different morphologies as described above, but for the same gate voltage, V_G, which means for the same effective carrier concentration. Due to the different degree of disorder the activation energies are different. But most striking is the fact, that extrapolation of the data do not intersect at a finite temperature and consequently show no MNR effect. This experimental finding can be well fitted by the EMA theory[12] [Fig. 3(a), bold curves] using the same σ-parameters as derived from Figs. 1(a) and 1(b). This provides an additional cross-check for the validity of the suggested theoretical model. As predicted by the theory, extrapolations of these temperature-dependences [thin solid lines in Fig. 3(a)] intersect at infinite temperature in accordance with Eqs. (2) and (3). Figure 3(b) summarizes the mobility data at room temperature, together with the width σ of the Gaussian DOS as the function of the grain size of the C_{60} layers, deduced from AFM pictures. It can be clearly seen, that with increasing grain size the degree of disorder decreases and the mobility increases. The reduced

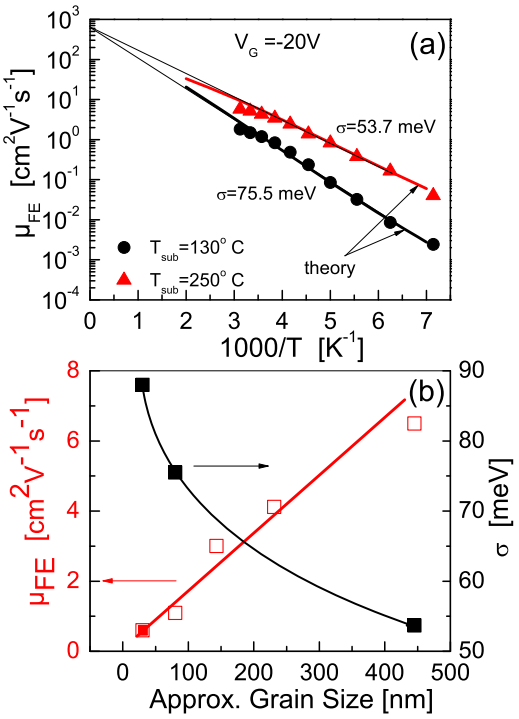

FIG. 3. (Color online) (a) Temperature dependence of the OFET mobility measured at constant V_G=−20 V in C_{60} films grown by HWE at T_{sub} =130 °C and 250 °C (symbols) and results of calculated temperature dependences by the EMA theory (Ref. 12) (bold curves). Fitting experimental data with Eq. (2) is shown by thin solid lines. (b) Average OFET mobility in C_{60} films and width of the Gaussian DOS as a function of grain size in C_{60} films.

E_a for the C_{60} film grown at higher substrate temperature is a direct evidence for the reduced energetic disorder in this film.

It is worth noting that E_{MN}=21.5 meV observed for the C_{60} film grown by HWE at 250 °C is probably the smallest reported so far for OFET mobility in organic transistors and is reflected also by a very reduced energetic disorder of σ =53.7 meV. Normally, σ-values determined for the OFET mobility are somewhat larger than that for the time-of-flight mobilities measured in the same bulk material due to the interface effects in OFETs (surface traps, surface dipoles, etc.).[14] In the present study an organic BCB nonpolar gate isolator was used, so the interface effects are expected to be very weak compared to SiO_2. This circumstance combined with the optimized structure of C_{60} films grown by HWE technique can explain the significantly reduced energetic disorder in the C_{60} films.

In conclusion, MNR behavior of the temperature dependent FET mobility has been studied in C_{60} films grown at different growth conditions and the experimental observations are found to be in excellent agreement with the predictions of the recently suggested theoretical model[12] for organic semiconductors with a Gaussian DOS distribution. The apparent MNR effect was observed at variable activation energy of the mobility due to changing the gate voltage and not due to changing the energetic disorder, exactly as predicted by the theory described above. An amazing strong shift of the Meyer–Neldel (isokinetic) temperature T_0 (from T_0 =408 K→351 K→250 K), was found in C_{60} films upon increasing the substrate temperature during film growth from room temperature to T_{sub}=130 °C and T_{sub}=250 °C, respectively, and this correlates with the change of the film morphology and, consequently, a change of the energetic disorder. An unusually small MNR energy of 21.5 meV was found for the C_{60} films grown at T_{sub}=250 °C which correlates to a significantly reduced energetic disorder of σ=53.7 meV and, consequently, a very high charge carrier mobility of 6.5 $cm^2\ V^{-1}\ s^{-1}$ in these films. Finally, we should note that the Meyer–Neldel energy could be used as sensitive testing parameter characterizing quality of active organic semiconductor layers in OFETs.

The research was implemented within the bilateral ÖAD under Project No. UA-10/2009 and supported by the project M/125-2009 and the Austrian Science Foundation (NFN Project Nos. S9706 and S9711). The authors would like to thank Heinz Bässler and Jan Genoe for helpful discussions.

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