Dark injection transient spectroscopy and density of states in amorphous organics

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ABSTRACT

We simulate the process of a dark-injection transient spectroscopy (DITS) measurement on an amorphous organic thin film, by modeling the charge transport on a 'microscopic' level, with carriers hopping through a three-dimensional network of energetically disordered sites. Our aim is to see what restrictions have to be placed on the form of the energetic disorder to obtain the kind of a DITS response observed in many polymer films, which features significant current attenuation following a distinguishable transient current maximum. We find that the popular models of energetic disorder, with a Gaussian density of states (DOS), cannot account for the observed DITS response, no matter the strength of disorder. A modified DOS, which is sometimes suggested, possessing a Gaussian 'body' and an exponential 'tail', can explain the transient response. Attenuation of the current in systems with such DOS is of a power-law type, a quality that we connect with relaxation of carriers into deeper states in the exponential tail. We note that such a response, with timescale-free attenuation, should be interpreted with care when extracting the carrier mobility, as the standard procedure significantly underestimates the transit time at low applied voltages. Further, the efficiency of the injecting electrode in this case cannot be unambiguously evaluated from the response.

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1. Introduction

Dark injection transient spectroscopy (DITS) is a commonly used method for characterization of organic thin films. It consists of recording the transient current in a thin film device upon application of a rectangular voltage pulse [1]. The method is principally used to measure the mobility of charge carriers in organic thin films, but is also applied to estimate the injection efficiency of the electrodes. These are evaluated from the time and the magnitude of a characteristic maximum of the transient current, which is connected with the exit of firstly-injected carriers from a device.

Recently a question was raised about the correct reading of mobility from the transient response in a polymer film that displays noticeable trapping and memory related effects [2,3]. There is also disagreement among experimental groups about the proper way to interpret data when checking the ohmicity of an injecting electrode [4].

The DITS response in the above-mentioned confounding cases shares some common features, which can be seen in other polymer films [2,4–6], but also in some molecular materials [6–8]. The transient current slowly attenuates from its peak value, over timescales long compared to the charge passage time, to a significantly lower (by one or two orders of magnitude) final, steady-state, value. The characteristic current peak, related to the carriers passage time, generally remains clearly distinguishable. The above features are in part visible in the pictured transients, and in part inferable from the related I–V characteristics. There has been no detailed investigation of this attenuating

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response, however, and the temporal evolution of the current at long timescales was generally not recorded.

It was demonstrated in early applications of the method, on inorganic films of crystal iodine [9–11] and of an amorphous alloy [12], that this record can provide information about the density of deep trapping states. The attenuation of the current in those films had a characteristic timescale, connected to a singular deep trapping level below the conduction band. By conducting an analogue investigation, we might gain new knowledge about the depths of DOS in the amorphous organics.

One possibility is that the attenuation of current is caused by existence of a deep trapping level in the DOS, that is clearly separated from the shallower states involved in conduction. Such addition to the DOS would likely appear if impurities are present in the material. If the arrest of carriers in these deep states is the dominant cause behind the attenuation of the current, the later will exponentially decrease with time [10–12]. This may serve as a recognizable feature of the attenuation due to *extrinsic* impurities. However, the *intrinsic* DOS of a pure organic material will also provide opportunities for carrier entrapment and may be behind the observed attenuation of the DITS response. We focus on this possibility of an intrinsic cause, and examine in this paper whether the commonly assumed and used models of organic DOS can be responsible for the attenuation of the current, and, if so, what distinguishing qualities will mark the transient response.

Charge transport in the amorphous organic materials is markedly different from their inorganic counterparts in that *all* states participating in transport are localized, and hence can be considered 'traps' [13]. The model most successful in describing the transport, in particular in replicating the Pool–Frenkel dependence of mobility, assumes a Gaussian-shaped DOS, where energies of localized states are spatially correlated [14–17]. Such correlated DOS can be induced by randomly oriented molecular dipoles [14,17,18] or quadrupoles [17], or by twisting a chain of aromatic monomers [19]. A non-correlated Gaussian DOS can also, to a certain extent, replicate the transport characteristics [20,21].

There are also some attempts to explain transport features by a trap-and-release model assuming an exponential DOS below some mobility edge [22–25]. We are not aware of any theoretical justification for such DOS in organics. Kelvin probe measurements on an α-NPD thin-film transistor suggest a mixture of the two above possibilities: a dominantly Gaussian-shaped DOS, with an exponential dependence on energy in the tails of DOS [26]. A Kelvin probe in such geometry might be measuring surface states instead of the intrinsic DOS of the film, but the same mixed DOS was recently invoked to explain *I–V* characteristics of another polymer [27], and small-molecule [28], materials in a sandwich-type device. This widening of the tails of DOS was attributed to several possible causes: chemical imperfections of the material, presence of impurities, or contamination with water and oxygen [27]. We point, however, to other microscopic mechanisms of a more 'intrinsic' origin, which can cause such distortion of the DOS. Randomly oriented electric dipoles will create such wide-tail DOS, if their concentration is low compared to that of the transport sites (ratio

of 0.1 or less) [18]. We may expect likewise pattern also to appear in case of randomly oriented rare quadrupoles [17]. One of these scenarios could be realized in copolymer materials in which different constituents have widely different multipole strengths [18]. A wide-tail bell-shaped DOS can also be a product of nanoscopic inhomogeneities in the material [29,30]. Partial crystallization of the material can produce regions where orientations of the molecular dipoles are strongly anti-correlated [30]. Such ordered regions will dominate the 'belly' of the DOS, while the more disordered remainder will be reflected in its wider tails. The question of the exact shape of electronic DOS in the amorphous organics thus still remains open.

In this paper we answer part of the question. We investigate how the two forms of DOS, the purely Gaussian and the mixed Gaussian-exponential, are reflected in the DITS response. For this we need to properly model the hopping transport on a 'microscopic' level. We have developed a three-dimensional simulation that does this on the scale of an entire device, recording its temporal evolution. Our results show the Gaussian DOS cannot cause the observed attenuating response, while the mixed form is in accord with the experimental evidence. We raise caveats regarding the reading of transient mobility at low fields, and find that the mixed DOS causes a response which can easily be mistaken for a result of sub-Ohmic injection.

The content of this paper is structured as follows. In Section 2 we describe our device model and simulation procedure, and also our way to construct a mixed Gaussian-exponential energetic disorder. In Section 3 we investigate the DITS response in a film with a Gaussian DOS, with and without spatial correlations among site energies. In Section 4 we study the transient response in a system with a mixed DOS and look at the issues of its proper interpretation. The concluding Section 5 discusses avenues that look promising for further research.

2. Method

Our focus is on the proper simulation of hopping transport within an organic material, so we deliberately assume idealized conditions of the rest of the experimental setup. Specifically, in accord with prerequisite assumptions of the original analytic derivation of Many and Rakavy [1], we treat the injecting electrode as perfectly Ohmic, provide no resistance to the external circuit, and apply a perfect rectangular-shaped voltage pulse to the device, which is initially void of charges. Also, we assume the transport is monopolar, i.e. only one type of carrier is injected and present within the organic material.

2.1. Device model

We simulate temporal evolution of the spatial distribution of carriers in a cut-out part of an infinitely wide and broad thin film device, see Fig. 1. The organic medium is represented, in a common manner [20,21,31], as a rectangular grid of sites that carriers can hop among. The sites correspond to the individual conjugated segments of a polymer material, each characterized by its LUMO/HOMO energy, E_i, and a time-dependent probability of carrier