Influence of surface traps on space-charge limited current

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We analyze the effect of surface traps on unipolar space charge limited current and find that they have a profound influence on the *I-V* curves. By performing calculations that account for the presence of these traps, we can reproduce experimental observations not captured by the conventional theory that only considers the presence of traps in the bulk of the material. Through the use of realistic material parameters, we show that the effects discussed have clear experimental relevance.

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Space charge limited transport occurs in undoped, widegap semiconductors in which the density of charge carriers at equilibrium is vanishingly small. In these materials, the current is carried by charge injected from the contacts, whose density is determined (limited) by electrostatics. Space charge limited current (SCLC) is relevant for the operation of electronic devices (e.g., organic light emitting diodes) and is routinely used in the characterization of semiconductors to estimate parameters such as the mobility of charge carriers, the density of trap states, and their energy depth.[1–5]

The description of SCLC relies on a simple phenomenological theory first developed in the 1950s and extended later to include model specific details.[6,7] These extensions have led to predictions of SCLC *I-V* characteristics that resemble rather closely what is actually measured. In practice, however, the comparison between space charge limited current (SCLC) measurements and theory is not very satisfactory in many cases, especially for experiments performed on high-quality materials with a low density of defects. First, an independent validation of specific assumptions adopted in the analysis of SCLC *I-V* curves is almost always impossible, which causes ambiguities in the interpretation of the experiments. Even when the theoretically predicted *I-V* characteristics exhibit a behavior close to that observed experimentally, a sufficiently detailed analysis often reveals inconsistencies.[8] Second, SCLC *I-V* curves measured on nominally identical samples often exhibit significant differences,[3] which makes it inappropriate to compare experimental data with theoretical predictions that are critically sensitive to the assumptions on which models rely. This current situation suggests that some important aspects of the physics of space charge limited transport are being overlooked.

In this context, and motivated by recent experimental work on high-quality organic single crystals, we investigate the effect of deep traps at the surface of the semiconducting material, underneath the electrical contacts used to inject charge carriers. We show that these surface traps are an essential ingredient for the proper understanding of SCLC *I-V* curves, which has been neglected until now. In particular, surface traps cause a large change in the electrostatic profile throughout the bulk of the material, profoundly affecting the behavior of SCLC. Calculations accounting for the presence of surface traps enable us to reproduce experimental observations that are not captured by the conventional theory, such as orders-of-magnitude asymmetries in the *I-V* curves. These calculations, which do not require any detailed, model-specific assumption, further illustrate how the combined effect of surface and bulk traps also results in features in the *I-V* curves that have been so far attributed to different physical mechanisms. In this way, our work provides the correct framework for the interpretation of SCLC measurements and may explain inconsistencies often found in the analysis of past experimental results.

To understand how the effect of surface traps is taken into account in our calculations, we first briefly review the main aspects of the conventional theory of unipolar SCLC.[6] The theory relies on the simultaneous solution of the Poisson and the continuity equation,

$$\frac{dE(x)}{dx} = \frac{en_s(x)}{\epsilon} \tag{1}$$

and

$$J(x) = en_f(x)\mu E(x) = \text{constant}, \tag{2}$$

that self-consistently relate the local electric field $E(x)$ and the current density $J(x)$ (x is the distance from the injecting electrode). Here $n_s(x)$ is the total space charge at position x and $n_f(x)$ is the part of space charge that is free to move, which is smaller than $n_s(x)$ if deep traps are present. Given the bulk density of traps N_t and their energy depth E_t, a relation between $n_f(x)$ and $n_s(x)$ can be found via the Fermi-Dirac distribution. This enables the solution of the equations above that gives the relation between $J(x)$ and $E(x)$, i.e., the *I-V* characteristics of the material.

The bulk density of deep traps N_t is usually assumed to be uniform throughout the material. In real materials, however, many more traps per unit volume are likely to be present close to the sample surface than in the bulk. These surface traps can have different physical origins. In inorganic covalently bonded materials, for instance, they may be due to dangling bonds resulting in the presence of surface states whose energy is deep inside the semiconducting gap. In organic systems, such as van der Waals bonded molecular single crystals, traps can originate from molecules at the surface that are damaged during the contact fabrication process.

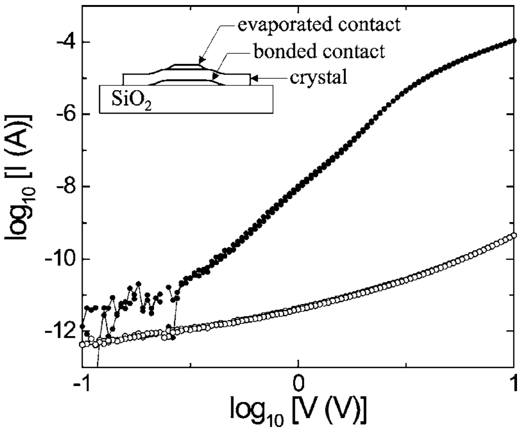

FIG. 1. *I-V* characteristics of a 1 μm thick tetracene single crystal, measured for opposite polarities of the bias voltage. The full symbols correspond to the current measured when holes are injected from the bottom (electrostatically bonded) contact (i.e., the bottom contact is at a positive bias V with respect to the top contact); the open symbols correspond to the case of holes injected from the top, evaporated contact (i.e., the top contact is at a positive bias V with respect to the bottom contact). The device configuration is shown in the inset.

For pure semiconducting materials in which the bulk density of traps is low, the total number of traps at the sample surface can be comparable or even larger than the total amount of bulk traps even for rather thick samples. The distinction between surface and bulk traps is conceptually very important. In particular, if SCLC transport is dominated by the presence of surface traps, SCLC *I-V* curves measured on nominally identical bulk samples (e.g., identically grown single crystals) can exhibit a large spread in their behavior, simply because the quality of the sample surface is different. This is indeed what is observed experimentally.[3]

As we now proceed to show, the main effect of charge trapped at the surface is to modify the electrostatic profile throughout the entire bulk of the sample. This effect has not been appreciated and analyzed theoretically before. In spite of its conceptual relevance, the modification of the conventional SCLC theory needed to take into account the electrostatic effects due to surface traps is minimal. It is sufficient to allow N_t to depend on position, so that its value in the region close to the contacts is much larger than the bulk value. The simplicity of this approach is important, because it permits to describe quantitatively the effect of surface traps without introducing any detailed—and experimentally not verifiable—microscopic assumption. This makes our conclusions robust and independent of specific aspects of a specific model.

The analysis of the effect of surface traps is carried out by solving numerically Eqs. (1) and (2) with an x-dependent N_t, from which we directly obtain the *I-V* characteristics. The most interesting case is that in which the density of surface traps present under one of the contacts is considerably larger than that present under the other contact. This is experimentally relevant because in general bottom and top contacts (see inset Fig. 1) are prepared in different ways, which results in different surface trap densities. Also for contacts prepared in a nominally identical way, the surface density of traps at the two contacts can differ considerably because the defects introduced at the surface depend on unknown parameters that are not under experimental control.[3,9] We compare the simplest possible situations in which surface traps are present only under one of the two contacts (bulk traps are also present). The case of traps present at both contacts with different densities can be analyzed in an identical way and does not add new physics.

Our considerations are valid for different classes of materials. Nevertheless, here we will mainly have in mind the case of organic molecular single crystals (such as tetracene, rubrene, the metal phthalocyanines, etc.), to which we have recently devoted considerable experimental effort. This enables us to insert in our calculations realistic values of the parameters and to prove that the effect of surface traps is relevant in actual experiments.

An illustrative example of SCLC through tetracene (a hole conductor) crystals is shown in Fig. 1. The data are measured on an approximately 1 μm thick single crystal contacted with two gold electrodes prepared in different ways. One of the contacts is fabricated by placing the thin crystal onto a metal film deposited on a substrate to which the thin, flexible crystal adheres spontaneously. This procedure is known to result in high-quality electrical contacts between the metal and the crystal.[10–12] The other contact is prepared by electron-beam evaporation of gold onto the crystal, which is known to cause “damage” to the crystal due to the exposure of the crystal surface to x-ray and high-energy electrons generated by the electron-beam, during the evaporation process. The most striking feature of the SCLC *I-V* curves is the large (five to six orders of magnitude) asymmetry: the measured current depends very strongly on the contact used to inject holes into the material. Order-of-magnitude asymmetries are regularly found for different contact fabrication techniques.

Figure 2 shows the *I-V* characteristics calculated for a sample with bulk traps and surface traps under only one of the two contacts. The separation between the contacts is taken to be 1 μm, corresponding to the case of the device whose data are shown in Fig. 1. The bulk density of traps is taken to be 1×10^{14} cm^{-3}. This is a conservative, realistic estimate[3] and lower values[5] would result in a more pronounced effect of the surface traps. The surface density of traps is set to correspond approximately to one trap per every 1000 molecules in the first few molecular layers of the crystal, which we model as a region of approximately 10 nm at the crystal surface, containing a density of traps of $\sim3\times10^{18}$ cm^{-3}. For both bulk and surface traps, the energy depth is taken to be the same (to avoid the insertion of unnecessary additional parameters) and equal to 0.7 eV, with the precise value of this parameter not being critical for our conclusions. Other parameters are required by the model, but do not have any considerable influence on the results. Apart from the hole mobility, which only contributes as an overall scale factor (we take $\mu=1$ cm^2/V s), there are density of dopants and their energy depth.[13] These parameters, which mainly affect the magnitude of the current in the linear regime, are treated identically to what is done in the conventional SCLC theory.[6,7]

The calculations show that in the range between 1 and

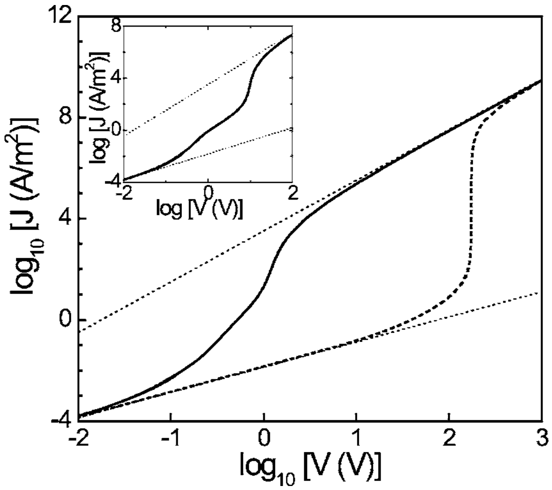

FIG. 2. Calculated SCLC *I-V* curve for two different polarities of the applied bias. The continuous (dashed) line represents the current flowing when holes are injected from the contact without (with) surface traps. Note the large asymmetry, which reproduces the experimentally observed behavior (see Fig. 1). The inset shows that, when the surface traps are located at the extracting contact, the amount of surface and bulk traps can be chosen so that the transition to the trap-filled limit exhibits multiple steps.

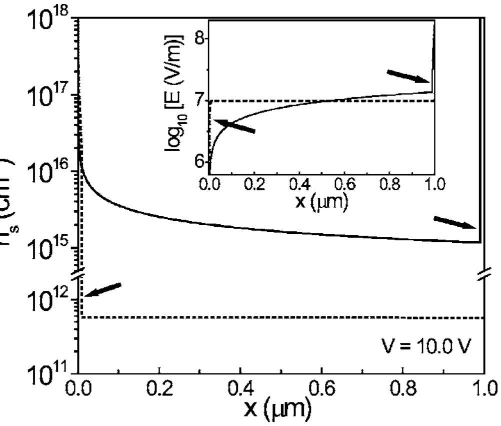

FIG. 3. Profile of the total (trapped plus free) density of charge in the sample whose *I-V* curves are shown in Fig. 1, for a 10 V applied bias. The injecting and extracting contacts are located at $x=0$ and $x=1$ μm, respectively. The continuous (dashed) line corresponds to the case where the surface traps (pointed to by the arrows) are at the extracting (injecting) contact. A large density of charge is injected into the bulk when the surface traps are located at the extracting contact, but not when the traps are located at the injecting contact. In the inset, the electric field profile is shown in the two cases.

100 V the current depends very strongly on the voltage polarity. This reproduces the huge asymmetry in the *I-V* characteristics observed experimentally. In agreement with the experiments, the current is large when the polarity is such that holes are injected from the contact free of surface traps. This result, which is robust and does not critically depend on the values of the parameters chosen above, clearly demonstrates the relevance of surface traps.

Microscopically, the asymmetry originates from a large difference in the electrostatic profile in the bulk of the samples, for the two bias polarities. This is illustrated in Fig. 3, where the density of charge is plotted as a function of position for the two polarities, with 10 V applied bias. When traps are located at the injecting contact, the bias is not sufficient to reach complete filling of the surface traps, so that no charge is injected in the bulk. The current is then carried only by thermally activated carriers and its magnitude is therefore small. On the contrary, the same bias is largely sufficient to fill the same amount of traps at the extracting contact. In this case the injected charge is present throughout the bulk of the sample, enabling a large current flow. We conclude that surface traps at the injecting contact suppress charge injection and the current flow much more drastically than trap at the extracting contact. As we will discuss at the end, this behavior can be easily understood qualitatively.

Figure 2 also shows that the shape of the *I-V* curve differs, depending on the contact used to inject the carriers. If the carriers are injected from the contacts where the surface traps are, the transition is very sharp and similar to that predicted by the conventional theory when only bulk traps at a discrete energy value are present. However, if the carriers are injected from the trap-free contact, the transition from the linear to the trap-filled regime (where $I \propto V^2$) is smooth and power-law like, with an exponent larger than 2. In this case, the precise shape of the transition is governed by the ratio between the density of surface traps at the extracting contact and the density of bulk traps. This is illustrated in the inset of Fig. 2, where this ratio has been changed to produce two apparent transitions in the *I-V* curve. We note that in the analysis of experimental SCLC curves based on the conventional theory of SCLC, similar features are attributed to a distribution of energies of the bulk traps. Specifically, a power-law-like ($I \propto V^n$ with $n > 2$) transition is invariably attributed to a continuous distribution of trap energies, whereas multiple discrete traps are invoked to account for multiple transitions. Our results show that such an interpretation is not unique and may explain inconsistencies found in the past.[8]

One more experimentally relevant finding regards the value of the voltage V_{TF} at which the transition to the trap-filled limit occurs. In the conventional theory $V_{TF} \propto N_t L^2$, which is often used to estimate the bulk density of deep traps. Figure 4 shows the behavior of SCLC curves when surface traps are present at the injecting contact. In this case, the qualitative shape of the SCLC curves is identical to that obtained with the conventional theory. However, the value of V_{TF} is different, and is found to scale linearly with L (see inset to Fig. 4). Thus, the experimental observation of such a linear scaling provides a direct way to demonstrate the relevance of surface traps.

The results discussed above can be understood in terms of the electrostatics of the system. In very simple terms, in a SCLC experiment a device can be thought of as a capacitor that is charged by the applied voltage. The spatial distribution of traps determines the capacitance of the device. Since in a parallel plate geometry the capacitance is inversely proportional to the distance between the charges, traps at the injecting contact have a low capacitance (the distance between the charges corresponds to the total thickness of the

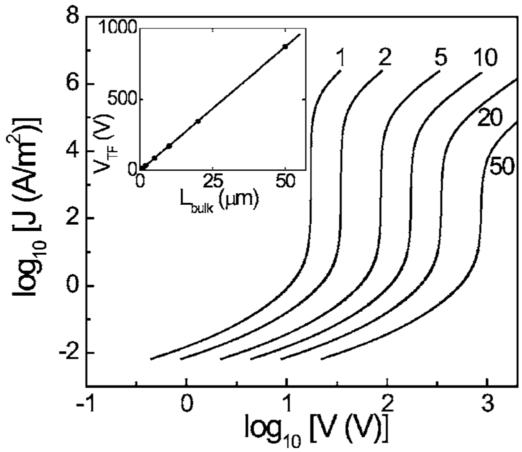

FIG. 4. SCLC *I-V* curves with surface traps at the injecting contact, for different contact separations L, ranging from 1 to 50 μm (as indicated in the figure). If the total number of surface traps is larger than the total number of bulk traps, the shape of the *I-V* curve is essentially identical to that predicted by the conventional SCLC theory. However, V_{TF} scales linearly with L, as shown in the inset.

crystal L), so that the application of a large voltage bias is needed to fill them. Since essentially no charges are injected in the bulk until a sufficiently large voltage is applied to fill all the surface traps, this results in a strong perturbation of the electrostatics throughout the bulk of the device, which is why surface traps at the injecting contact have such a large influence on the *I-V* curve. On the contrary, surface traps close to the extracting contact have a large capacitance, so that their filling occurs already at a very small voltage bias. On the voltage scale used in the measurements (and for sufficiently thick crystals) the perturbation to the electrostatics is only minor and does not prevent the injection of charges into the bulk. This difference directly accounts for the asymmetry of the *I-V* curves. It also accounts for the behavior of V_{TF} (see Fig. 4 inset), since the capacitance of traps located at the injecting contact scales linearly with L.

In conclusion, we have shown that the influence of surface traps is an essential ingredient for the proper understanding of SCLC experiments. The crucial point is that in high-purity samples, the total amount of surface traps can dominate over the total amount of bulk traps, even for sizable contact separations. Under these conditions, charge trapped at the surface strongly modifies the electrostatic profile inside the bulk, which in turn determines the amplitude of the measured current. Although SCLC measurements have been performed for over 50 years and their theoretical description is now textbook material, the large effect of surface traps on the electrostatics had never been recognized earlier.

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[13] In the regime that we are analyzing, the density of dopants is much smaller than the density of traps and their energy depth is shallower than for trap states. The conclusions of this work do not depend on the precise values. The density of states in the valence band is also needed in our calculations and it is taken to be one state per molecule (3.3×10^{21} cm^{-3}), as usually done in literature.