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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to be present close 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. 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. This corresponds to a physical regime whose relevance has not been sufficiently appreciated in the past. In particular, the effect of trapped surface charge on the electrostatic profile throughout the entire bulk of the sample has never been analyzed theoretically.

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 analysis of this case is carried out by solving numerically Eqs. 1 and 2, 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. 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 in 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

![Fig. 1](image)

**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; the open symbols correspond to the case of holes injected from the top (evaporated) contact. The device configuration is shown in the inset.
not have any considerable influence on the results) are the hole mobility, which only contributes as an overall scale factor (we take $\mu = 1 \text{ cm}^2/\text{Vs}$), the density of dopants and their energy depth $\left[11\right]$.

The calculations show that in the range between 1 and 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.

Fig. 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.

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. Fig. 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). 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 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 ago 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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