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Current filamentation and negative differential resistance in C_{60} diodes

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Current-Voltage (*IV*) measurements of C_{60} thin film diodes in the temperature range of 300–4.2 K are presented. The fullerene diodes exhibit space charge limited currents as well as reversible voltage instabilities (S-shape *IV* characteristics) at temperatures below 200 K and at high current densities. The instabilities are similar to certain charge transport effects in amorphous inorganic semiconductors, which are explained by injection of holes and electrons at the same time and charge trapping near the electrodes. Beyond certain current densities conductive filaments in the fullerene bulk phase are formed.

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1 Introduction C_{60} and its derivatives are dominantly used as acceptor molecules in conducting polymer matrices for solar cells. The investigation of the transport properties of these materials are therefore of high importance. Here we concentrate on the properties of C_{60} films processed by thermal evaporation in sandwich type diodes [1]. The high purity and reproducibility in thin films grown by evaporation allow the study of both, the transport properties as well as the morphology of these materials. The nature of charge transport in fullerenes and in amorphous or polycrystalline inorganic semiconductors is similar. In both cases charge injection follows the space charge limited current (SCLC) theory. With C_{60}, a reversible voltage instability is observed at low temperatures corresponding to similar effects in non-ordered inorganics [2, 3]. The voltage breakdown is originated by injection of holes and electrons and charge trapping, followed by the formation of conductive filaments in the bulk C_{60} layer.

2 Experimental Sandwich-type diodes were fabricated using 70 nm thick poly(3,4-ethylenedioxythiophene/poly(styrene-sulfonate) (PEDOT:PSS) spin coated film on ITO glass as hole injection electrode. 300 nm C_{60} films were grown on top by thermal evaporation. The substrate temperature was kept constant at 140 °C during the deposition process. The morphology studies were performed by transmission electron microscopy (TEM). For the transport measurements we used 50 nm Chromium layers as top electrode. All electrical characterizations were performed in a Helium flow cryostat (Oxford Industries) in a temperature range between 300 K to 4.2 K. The voltage drop between the PEDOT:PSS and the Chromium electrode was measured by applying a certain current density to the diode.

3 Results The device structure and the energy levels of the fullerene diode are shown in Fig. 1. The estimated built-in voltage between the Fermi level of the Chromium (-4.5 eV) and the Fermi level of PEDOT:PSS (-5.2 eV) is about 0.7 V. The energy levels of the C_{60} result in an theoretical barrier of 0.4 eV for both the hole and electron injection.

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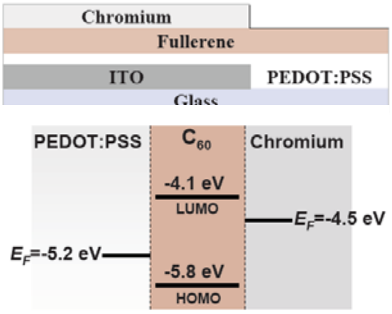

Figure 1 Diode structure and band diagram for the C_{60} diode.

The electrical characterization was performed in the high injecton regime. For gaining the effective voltage drop the built-in potential ($U_{eff} = U_{measured} - U_{BI}$) is subtracted from the measured voltage at the ITO/PEDOT:PSS anode in the device. In Fig. 2 the *IV* characteristics at three temperatures are shown.

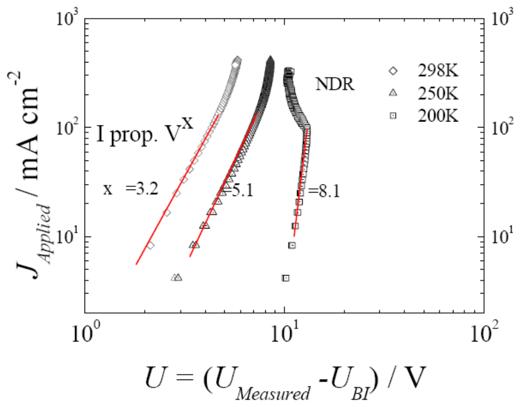

Figure 2 Double logarithmic *IV* characteristics at 300 K, 250 K and 200 K.

The *IV* behaviour is described with a formation of a space charge upon the dominant electron-injection (space charge limited currents, SCLC). The current density follows a power law dependence, described with the modified Mott-Gurney formula [7]

$$J = \frac{9}{8} \cdot \varepsilon \cdot \Theta \mu \cdot \frac{V^2}{L^3} \qquad \Theta = \frac{n_{free}}{n_{injected}}$$

where μ is the mobility, L the thickness of the diode and Θ the ratio of free to injected charge carriers. Ideally the ratio is close to 1 and the exponent is 2. The injection process into the disordered semiconductor is influenced by the presence of traps. Experimentally an exponent greater than 2 (Fig. 2) is observed, since Θ is voltage-dependent. In organic systems as well as in evaporated C_{60} defects influence the transport. Here, the cross section TEM studies verify crystalline and amorphous phases in the C_{60} diode. The crystallites along the growth direction seen in Fig. 3 have the same orientation domains. The defects are introduced at the crystallite grain boundaries and in the amorphous phases respectively [4, 5].

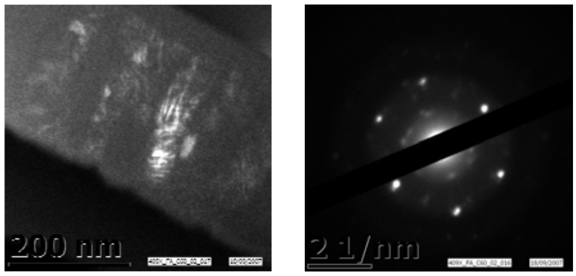

Figure 3 (Right) Dark-field analysis of diode cross section shows similar orientation domains in growth direction. (Left) Diffraction pattern of C_{60} crystallite exhibits fcc hexagonal structure.

The power law dependency is fulfilled when operating with current densities around 100 mAcm^{-2}. The exponent increases by decreasing the temperature, as expected. At temperatures below 200 K and current densities above 100 mAcm^{-2} deviations from the SCLC behaviour are observed. By applying a higher current density the measured voltage decreases showing a negative-differential resistance (NDR) seen in Fig. 4.

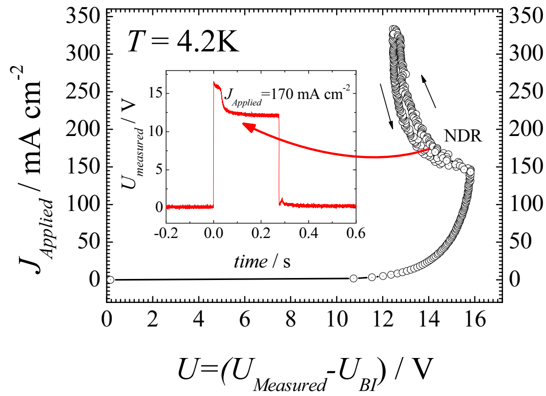

Figure 4 Negative differential resistance regime at 4.2 K showing a reversible voltage breakdown. Inset: Voltage drop measured time-resolved in negative differential regime.

The *IV* scan exhibits a well pronounced negative differential resistance regime at 4.2 K above 150 mAcm^{-2}. We exclude thermal effects as origin for the voltage breakdown, since the forward and back curves in the negative differential resistance regime are strictly reversible, seen in the plot in Fig. 4. The inset plot shows the measured voltage drop time resolved. In the first 20 ms of the current pulse the voltage remains at the value corresponding to a SCLC behaviour, then the voltage drops to a constant level until the end of the 250 ms current pulse.

4 Discussion

Two aspects can be pointed out from the results presented above. First, the electrical transport in C_{60} is following the space charge limited current theory with the presence of traps. A power law dependency in the

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injection region and a rising exponent at decreasing temperature is observed. The presence of traps and defects respectively correlated with the morphology studies presented in Fig. 3 by TEM. The investigated system consists of amorphous and crystalline phases. The dark field analysis show several crystallite domains along the growth direction with similar orientations. The second aspect is the observation of a negative differential resistance in the higher injection regime at lower temperatures (Fig. 4). In comparison to voltage instabilities in disordered inorganic semiconductors [3], we propose a similar mechanism in C_{60}. By a simultanous overcoming of the respecitve injection barriers to the HOMO (for holes) and LUMO (for electrons) of the C_{60} the voltage breakdown is initiated. The injection of holes and electrons over a non-uniform injection area leads to a filamented current flow. Interestingly, from the time resolved plot in Fig. 4, the filaments are formed after a delay of about 20 ms. The high conductivity at low temperatures indicates a band transport model and an existance of a mobility edge in undoped C_{60} as well as an operation in the trap filled regime [6].

5 Conclusions In this work space charge limited currents in C_{60} diodes as well as negative differential resistances in the current voltage characteristics have been demonstrated. The electrical transport studies correlate with the complex structure of the semiconductor consisting of amorphous and crystalline domains. The voltage instabilities at high current densities causing the negative differential resistance regime at lower temperatures are explained by an operation in a trap filled regime. Such filamented currents are observed and discussed in a series of amorphous inorganic semiconductors. We propose a similar mechanism in case of C_{60}.

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