# Conductivity and photoconductivity peculiarities observed in $C_{60}$ layers

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**Abstract.** Thin layers of various thickness prepared from $C_{60}$ with traces of $C_{70}$ were studied. They were deposited by thermal evaporation on quartz, glass, *p*-Si or *n*-Si substrates. An apparatus fixing current values every 3 ms was used to measure and register the kinetics of layer conductivity and photoconductivity. Series of peculiarities were observed in the kinetics of the current when an electrical field was applied to illuminated or darkened samples. For example, when voltage is applied to the sample the current immediately rises to a certain value and then falls to a different quasi-stationary value. These peculiarities depend on the particular state of the samples. After analyzing the phenomena, a scheme explaining these peculiarities was proposed which relates mainly to intrinsic polarization. The influence, which these processes might exert on the photoconductivity and data accuracy, was discussed. A substantial influence of ambient humidity was determined. Our study of the observed changes showed that humidity did not substantially affect the generation-recombination processes in the bulk material, but predominantly the carrier transport mechanism.

## 1. Introduction

Upon determination of the energetic characteristics of the electronic shell of the $C_{60}$ molecule [1, 2], it is acceptable to use the forbidden band of $C_{60}$ deposited as pure or as a hybrid compound with polymers [3-6] for the purposes of photoelectrical conversion of solar energy [7-10] and for the creation of photoelectrical sensors. The overwhelming part of the following studies was about pure fullerene material ($C_{60}$ or $C_{70}$), deposited alone or in combination with other materials as a thin film. It was necessary to gather knowledge both of problems concerning the generation-recombination processes in the fullerene molecule itself and the mechanisms, by which the generated carriers could be separated and transported inside the bulk of the layer. The present study concerns certain peculiarities of the conductivity and photoconductivity in thin layers of the fullerene material ($C_{60}$ with traces of $C_{70}$), obtained by direct sublimation from the fullerene containing soot.

## 2. Experimental details

Thin films were obtained by direct sublimation of soot heated to a certain temperature favors $C_{60}$ vacuum evaporation. The method for soot production is the classical one [11] – arc discharge in an inert atmosphere between carbon electrodes. The inert gas was Ar, the working pressure – $8 \cdot 10^4$ Pa, and the current of the AC discharge – 75 A. More details about the method used and the experimental set-up could be found elsewhere [12]. The soot was not treated for enrichment or separation of the various fullerene or cluster fractions, contained. This was the simplest possible method for the production of this type of thin films. The substrate material was glass, quartz, *p*-Si and *n*-Si. No additional heating of the substrate has performed. The layer thickness varied from 0.06 to 0.6 μm.

The conductivity measurement set-up is a routine technique. The measurements were performed using a vibrating-capacitor electrometer (VA-J-51) connected to

analog-digital converter to allow for computer control of the measurement. The electrometer has an input resistance of $10^8$ Ohm and input capacitance of 25 pF. The time constant of the measurement set-up was thus approximately 3 ms, while the observed current peaks were of the order of seconds. The measurement set-up and its time response was additionally fixed using commercial resistors with the resistance within the range of that of the $C_{60}$ layers. The same measurement set-up has been used in comparable investigations performed previously by us on a-Si:H, CdS and other thin layer samples [13], but no peaks have been observed in the photocurrent kinetics behavior.

## 3. Results and discussion

The obtained layers are uniform and have very good adhesion to the substrate. A grainy, morphology of the layers is seen under lower SEM power (Fig. 1). Diffractograms from various regions show the presence of microcrystals of different lattice types.

When using magnification of under higher SEM power (Fig. 2) the crystals are seen to be dispersed in an amorphous phase. The microcrystals are surrounded by the amorphous phase, and it can be assumed at this point that the both phases participate in the transport of the charge carriers.

For studying the electrical behavior of the layers, aluminum strip contacts were deposited on the surface of the layers at the distance 0.8 mm. We have also established the excellence of the ohmic behavior of those contacts. The current values and respective kinetics were registered by the apparatus fixing these values with the frequency 330 s$^{-1}$. Upon applying the voltage, the current increases until reached a maximum value and then slowly diminishes, converging towards an equilibrium value. Apart from the applied voltage, the appearance of the mentioned above peculiarities also depends strongly upon the starting state of the material, *i.e.* upon the previous treatment (*e.g.*, light, electric pulses, variations in the humidity of the ambient air). If the samples were kept without voltage, in the dark, and humidity 30-45 % before each experiment, the observed peculiarities always remain the same. All the results below have obtained, using this standard initial state of the sample.

Fig. 3 shows the dependence $I = I(t)$ recorded at the field 100 V/cm applied to the sample, kept in dark or after illumination with the excitatory light. The shorter time between measuring lowers the peaks of current measured (Fig. 4). The decrease was observed in the maximum value of the current peaks as well as in the interval of returning to a quasi-stationary state.

For both illuminated and non-illuminated samples (at 45% humidity of the ambient air) (see Fig. 3) the shape of the curve $I = I(t)$ is preserved, but in the illuminated samples the curve is shifted towards the higher values of current.

According to our previous investigations, it turns out that the fullerene layers tend to actively absorb and desorb large quantities of water molecules and other chemical compounds [14, 15], which also strongly changes the fullerene layer electrical conductivity.

Fig. 5 illustrates the dependence between the amount of absorbed water molecules as measured by a quartz microbalance and the percentage of ambient humidity. The frequency variation $\Delta f$ at 95 % humidity corresponds to $0.35 \times 10^{-6}$ g/cm$^2$ of water molecules absorbed in the sample.

For 80 % humidity a considerable change of the dependence $I = I(t)$ takes place (Fig. 6), both in the dark and upon illumination. The current increases more than one order of magnitude. An interesting conclusion is that, with the increase in amount of the absorbed water molecules, the photocurrent (i.e. the photosensitivity of the samples) rises steeply.

Taking into account the peculiarities of the layer morphology as well as our other studies, a scheme of the
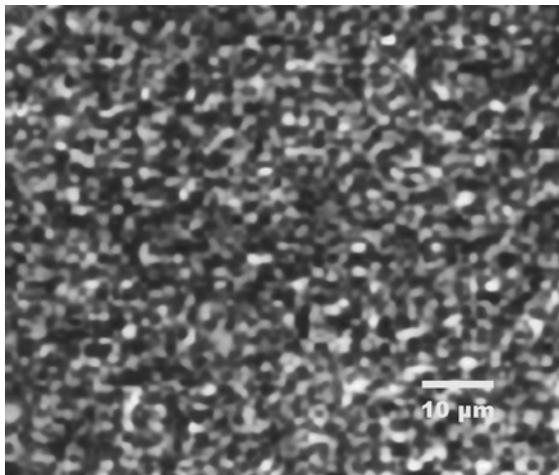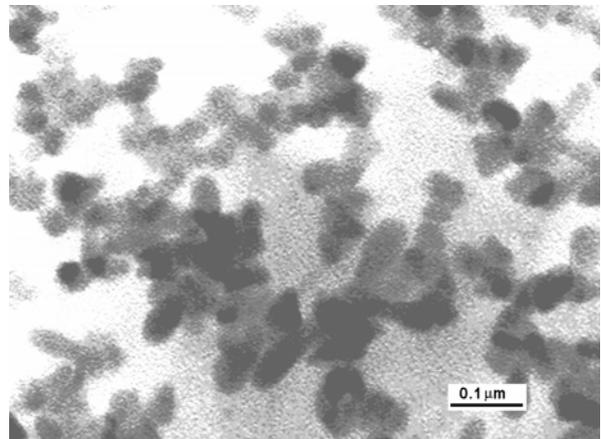


**Fig. 1**. Fullerene layer morphology.



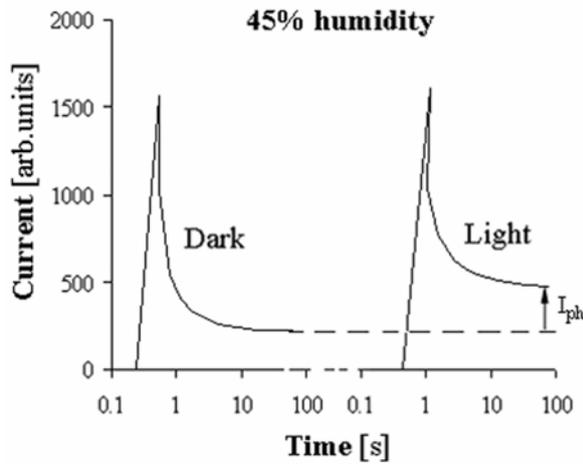**Fig. 2.** SEM - photo illustrating the presence of amorphous and microcrystal phases in the fullerene layer.

**Fig. 3.** Current kinetics when the voltage applying in the dark and on illumination.
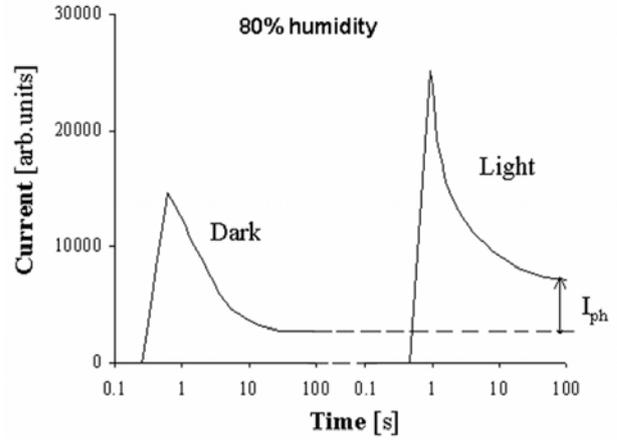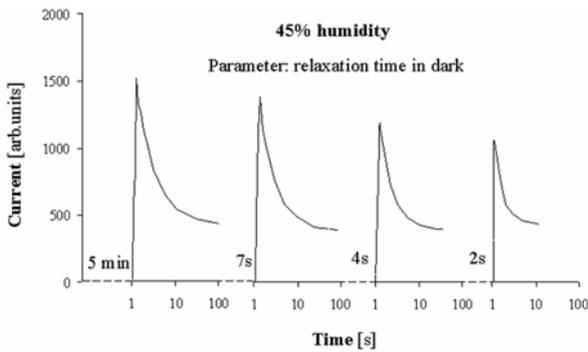


**Fig. 4.** Current kinetics $I = I(t)$ after a different time of relaxation (the voltage to the specimen is switched off).
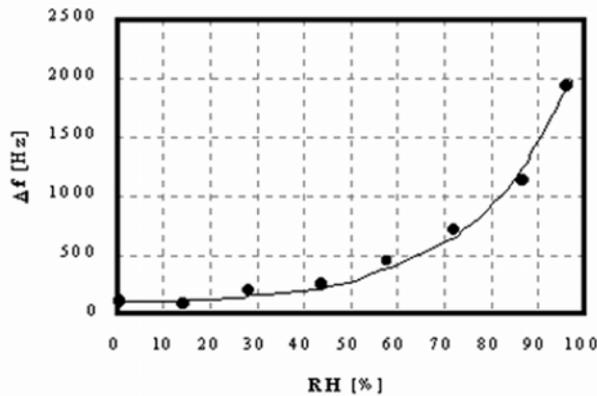


**Fig. 5.** Dependence between the frequency of a quartz resonator with a fullerene layer and the relative air humidity at the temperature 30 °C.



**Fig. 6**. Current kinetics at 80 % humidity.

processes explaining the dependences described above can be proposed. The thin fullerene layer is a heterogeneous system consisting of two phases. As concluded above, one of the phases is microcrystalline or made of other monolithic formations and is dispersed almost uniformly, the second phase is amorphous fullerene structure. Most probable a barrier type mechanism of current flow exists. The amorphous phase is low conducting, less photosensitive and of greater absorbing ability for water molecules. The basic photoelectrical processes (photogeneration and recombination) take place in the micrograins. Upon applying the constant voltage to the layer, fast polarization takes place, most probably connected with the interphase barriers. The obtained current describes with time a characteristic peak, the height of which depends on the depolarization time as well as on the amount of electric charge carriers, created by light or the absorbed water molecules at high humidity (for example 80 % – Fig. 6). At low humidity (for example 45 % – Fig. 3), the maximal peak value of the current remains almost equal both in the dark and under illumination. Consequently, the barriers and the corresponding polarization under illumination do not substantially influence on the stationary measured photocurrent. The increase of the photocurrent at higher levels of humidity is explained by the corresponding enhanced dark conductivity of the amorphous phase. This improves the transport between the electrodes of photocarriers generated mainly in the crystals.

On the base of the results presented here and the scheme for their explanation, a more accurate picture of the processes of photoexcitation and charge carrier transport can be drawn, if the spectral curve characteristics would be determined at its equilibrium value and low humidity.

## 4. Conclusion

The investigations of the conductivity and photoconductivity of thin fullerene layers, prepared by

vacuum sublimation of fullerene containing soot, show that the measured values are strongly dependent on the preliminaries and the ambient conditions (illumination, humidity, electrostatic field *etc.*). The accuracy of the investigations requires the knowledge of the exact point in time when each value of the conductivity and photoconductivity has measured. In the investigated processing peculiarities of the current kinetics occur in illuminated and non-illuminated samples. If those peculiarities are not taken into account and no steps are made to suppress their effect, the obtained results of electrical and photoelectrical measurements of this type of layer may differ from the real ones. Using the proposed scheme, we can explain the observed phenomena being based on the polarizing processes that occur under the influence of an external voltage. The experimental results enable optimization of the measuring methods.

**Acknowledgements**

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