Electroforming and resistive reversible switching effect in polycrystalline fullerene $C_{60}$ films

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Abstract. It has been found that the conductivity of a polycrystalline fullerene $C_{60}$ thin film increases by several orders of magnitude after lengthy exposure to an electric field of $\sim 10^6$ V/cm. This effect is called electroforming. After electroforming, the current–voltage characteristic shows high current stability and reproducibility of results. An increase in capacitance and a decrease in resistance by 4 orders is observed in a narrow voltage range of 0.1-1 V, which is the effect of reversible resistive switching. In fields with a strength of $10^5$-$10^6$ V/cm, the I–V characteristic of molded films is determined by the current with a limited space charge. Trap concentrations are defined as $N_{t,1} \approx 2.3 \cdot 10^{21}$ m$^{-3}$ and $N_{t,2} \approx 5.8 \cdot 10^{20}$ m$^{-3}$ and their depth $E_t \approx 0.17$ eV for polycrystalline $C_{60}$ films with thicknesses of 250 and 500 nm, respectively.

1. Introduction
The $C_{60}$ films belong to the class of organic semiconductors with the electronic conductivity type [1]. They have a fairly high resistivity. At room temperature, this parameter reaches values of the order of $10^8$ $\Omega \cdot$cm and significantly depends on the degree of crystallinity of the film and the degree of oxygen saturation in the material. The conductivity of the crystalline material is higher than for amorphous materials. Upon contact with oxygen, the electrical conductivity of $C_{60}$ films decreases by 3-6 orders within a few minutes [1]. $C_{60}$ films have hopping conductivity. At room temperatures, jumps to the nearest neighbors and thermally activated jumps to more distant molecules prevail [1-3].

The fullerene thin films that are used in various electronic devices can be exposed to strong electric fields [4, 5]. Indeed, at operating voltages of 10 V, the average value of the field strength in a film with a thickness of 100 nm reaches values of $\sim 10^6$ V/cm. The electric field of this intensity leads to the injection of charge carriers from the electrodes into the film and the formation of a space charge in the film, which significantly affects its electrophysical properties. At the same time, the effects of a strong electric field in fullerene films have not been sufficiently studied, which makes it difficult to solve some practical problems. Therefore, the purpose of this work was to study the influence of a strong electric field on the electrical and dielectric properties of fullerene $C_{60}$ thin films.

2. Sample structure and measurement technique
$C_{60}$ polycrystalline films with a thickness of 250 - 500 nm were obtained by vacuum evaporation of fullerene molecules on a cold p-type silicon substrate. The $C_{60}$ films had a polycrystalline structure with a crystallite size of $\sim 200$ nm. While forming the film, the crystallites were randomly arranged in several layers on the surface of a silicon substrate.
In electrical measurements, the silicon substrate was used as the lower electrode (cathode), and the upper electrode (anode) was a needle probe made of an indium-gallium eutectic. This probe, due to the interaction of the surface tension force and gravitational force, ensured a reliable electrical contact with a C$_{60}$ thin film without mechanical damage [6]. The diameter of the contact spot varied in the range from 100 to 300 $\mu$m, depending on the pressure force of the needle to the C$_{60}$ film. All measurements were performed at room temperature in air.

3. **Current–voltage characteristic of a fullerene C$_{60}$ polycrystalline film**

Figure 1 shows the current-voltage characteristic (I-V) obtained on the C$_{60}$ film with a thickness $L = (250\pm30)$ nm and a contact area $S \approx 0.03$ mm$^2$. Curve 1 corresponds to the situation when a stepwise increasing voltage is applied to the film. In this case, the sample has not previously been subjected to an electrical load. A remarkable feature of this I-V curve at the first electrical load is its unstable nature.

After the voltage applied to the sample reached ~ 10 V ($F = 0.4$ MV/cm), it began to gradually decrease (curve 2). The current recorded at a voltage decrease is greater than the current at the first electrical load. When the voltage was increased again (curve 3), even higher values of current were recorded, but curve 3 of the current-voltage characteristic appeared to be smooth since current surges no longer occurred. Curve 4 was obtained at a subsequent decrease in the voltage. One can see that curves 3 and 4 almost coincide. With further repetition of the cycles of increasing and decreasing the
voltage, the experiment demonstrated high current stability and reproducibility of the current-voltage characteristics.

An increase in the conductivity of the C_{60} film by several orders of magnitude after prolonged exposure to a strong electric field can be viewed as electroforming the structure under study. This effect has long been known in metal-insulator-metal sandwich structures with amorphous oxides [6-9] but was first established in this work for polycrystalline C_{60} thin films.

The nonlinear nature of the I-V characteristic recorded after electroforming in the studied films indicates that the current is limited by space charge, i.e. \( I \sim U^n \), where \( n \) defines the slope of the I-V characteristic in logarithmic coordinates. In curves 3 and 4, three characteristic regions with different values of \( n \) can be distinguished. Such a character of the I-V curves indicates a transition from the mode of trap-filled limit in region I to the trap quadratic law in region III [10].

Figure 2 shows the current-voltage characteristic obtained on a C_{60} film with a thickness \( L = (500\pm50) \) nm with a contact area \( S \approx 0.1 \) mm\(^2\). The measurement technique did not differ from that described above.

![Figure 2. Current–voltage characteristic of polycrystalline C_{60} film with a thickness of 500 nm before electroforming (curves 1 and 2) and after electroforming (curves 3 and 4).](image)

Increasing the thickness of the polycrystalline C_{60} film layer to 500 nm did not drastically change the I-V characteristic. Curve 1 also demonstrates non-reproducible character and unstable current. Curves 3 and 4 are also reproducible when repeating the cycles of increasing and decreasing the voltage. The change of the inclination angles of the curve \( n \) is not significant. One can see 3 sections with different angles of inclination of the curve. When analyzing the graphs in figures 1 and 2, we can...
conclude that a two-fold change in the thickness of the polycrystalline film of fullerene C_{60} does not have a strong effect on the I-V curve.

It is known that the trap-filled-limit voltage $U_{TFL}$ is determined by the expression [10]

$$U_{TFL} = \frac{eL^2N_t}{\varepsilon \varepsilon_0},$$

(1)

where $e$ is the electron charge, $N_t$ is the total concentration of traps, $\varepsilon$ is the permittivity of C_{60} film, $\varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$. The value $U_{TFL} \approx 1 \text{ V}$ was determined from figures 1-2 (curve 3). Having accepted, according to [11], for fullerene C_{60} polycrystalline films $\varepsilon = 2.6$, from relation (1) we obtain $N_t^{-1} \approx 2.3 \times 10^{21} \text{ m}^{-3}$ for a 250 nm film. For a 500 nm film, $N_t^{-2} \approx 5.8 \times 10^{20} \text{ m}^{-3}$.

The current density $j$ in the field of realization of the trap quadratic law (at a voltage $U > U_{TFL}$) is determined by the relation [10]

$$j = \frac{9}{8} \varepsilon \varepsilon_0 \mu U^2 \frac{L^2}{L^2},$$

(2)

where $j = \frac{I}{S}$ is the current density, $\mu$ is the effective electron mobility at $U > U_{TFL}$. Since $I = 3 \times 10^{-4} \text{ A}$ when $U = 1 \text{ V}$ (see figure 1 curve 3), using relation (2), we obtain $\mu_1 \approx (5.6 \pm 1.1) \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for a 250 nm film. For a film thickness of 500 nm, $I = 8 \times 10^{-5} \text{ A}$ at $U = 1 \text{ V}$ with $\mu_2 \approx (3.6 \pm 0.7) \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

Note that these $N_t$ values are about 1-2 orders of magnitude higher depending on the thickness, and the $\mu$ value is less than the values of the corresponding parameters in single crystal C_{60} [12].

To estimate the trap depth $E_t$, we used an analytical approximation of the current–voltage characteristic of an insulator with the Gaussian trap energy distribution in the form

$$j = \frac{e\mu U (\varepsilon \varepsilon_0 U)^{\alpha} N_e \exp(-E_t/kT)}{(eL^2N_t - \varepsilon \varepsilon_0 U)^{\alpha}},$$

(3)

where $N_e$ is the density of states at the conductivity level, $\alpha = \sqrt{2\pi \sigma^2/16k^2T^2} + 1$, and $\sigma$ is the Gaussian dispersion. Relation (3) can be used to approximate experimental data in a limited region of voltage variation $0.5U_{TFL} < U < U_{TFL}$ and at values $n > 3$ [10].

Using the method of least squares, we determined the values of $E_t$, $N_e$, and $\sigma$, which give the best agreement between the calculated curve (using formula (3)) and experimental I-V curve. For both thicknesses, the data coincide within the error. It was estimated that $E_t = (0.17 \pm 0.02) \text{ eV}$, $N_e = (3 \pm 0.4) \times 10^{21} \text{ m}^{-3}$, and $\sigma = (0.01 \pm 0.001) \text{ eV}$.

4. Capacitive and resistive characteristics of a C_{60} film at different voltages

Figure 3 shows the resistance and capacitance dependences of voltage for a polycrystalline fullerene C_{60} film 250-nm thick at a frequency of 1 kHz after electroforming. Curve 1 in this figure, which characterizes the resistance, rapidly decreases in the voltage range of $0.1-1 \text{ V}$. This corresponds to an electric field strength in the range of 4–40 kV/cm. At lower and higher voltage values, the curve shows a steady character. Such a change in resistance in a narrow voltage range is called the resistive switching effect. It should be noted that this effect is not observed in polycrystalline films of fullerene C_{60} before electroforming. Thus, electroforming, which occurs at electric fields of about $\sim 10^8 \text{ V/cm}$, is a prerequisite for observing the effect of reversible resistive switching.

Capacity, which is characterized by curve 2, increases by almost 4 orders of magnitude in the same range of electric field strength of 4–40 kV/cm. When the experiment was repeated many times, two switching states were stably observed up to 0.1 V and after 1 V.
Figure 3. Dependences of the resistance (curve 1) and capacitance (curve 2) on the voltage at a frequency of 1 kHz for a 250-nm thick polycrystalline C\textsubscript{60} film after electroforming.

It is important to note that the capacity in an E7-20 immittance meter is calculated using a parallel equivalent circuit. The capacity thus obtained does not represent the actual characteristic of the C\textsubscript{60} film in terms of its ability to accumulate a charge.

5. Conclusion
The presented results show that the long-term effect of a constant electric field with a strength of \(\sim 10^6\) V/cm (electroforming) on the polycrystalline C\textsubscript{60} film leads to an increase in its conductivity by several orders of magnitude and stabilization of the electrical properties. The current-voltage characteristics of the film after electroforming in the region of a strong electric field (\(F > 10^6\) V/cm) correspond to the trap quadratic law mode. In this case, the concentration of traps in the gap of forbidden energies and the density of states at the conductivity level turn out to be \(\sim 100\) times greater than in C\textsubscript{60} single crystal.

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