

**SYNTHESIS AND ELECTRICAL PROPERTIES OF THIN FILMS
OF FULLERITES ON THE VARIOUS SUBSTRATES****J. Vincenc Oboňa^{a,1}, Š. Chromík^a, D. Machajdík^a, I. Kostič^b, M. Kadlečková^c**^a*Institute of Electrical Engineering, SAS, Dúbravská cesta 9,
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In the process of intercalation, C₆₀ samples in the form of polycrystalline films prepared on various substrates are used. To obtain a homogeneous doping we test two geometrical set-ups of our apparatus, horizontal and vertical. In the present work we focus on the study of transport properties of the samples. We demonstrate the temperature dependence of the conductivity of doped C₆₀ films during the doping process. The time evolutions of the sample resistivity after its exposure to the atmosphere are studied. The structural properties of the samples are examined by X-ray diffraction technique in Bragg-Brentano geometry and Raman Spectroscopy. Scanning Electron Microscopy is used to compare the surface morphology of the undoped and doped C₆₀ films.

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1 Introduction

The discovery of the conductivity and the superconductivity [1, 2] in the K_xC₆₀ system opened a question of a potential application of these interesting materials for cryoelectronics. Many authors have focused on the preparation and study of superconducting and transport properties of the K_xC₆₀ system in the ultra-high vacuum at the level of 10⁻⁷ Pa in situ [1–3], however the physical properties of the sample investigated after breaking the vacuum are not sufficiently known [4].

The K_xC₆₀ reacts very fast on the air. This fact seems to be a serious restriction for the application of the K_xC₆₀. Because a detailed information about the preparation of the K_xC₆₀ films in the literature is missing or is unclear, our effort was to prepare the K_xC₆₀ films exhibiting a low resistivity. The K (potassium) was intercalated to the C₆₀ film in two different procedures.

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We present the resistivity measurements of the K_xC_{60} as a function of doping and temperature. Some of the prepared films were in situ covered with insulating layers, then exposed to the atmosphere, and the time evolution of the resistivity was studied. We present a possible model of this reaction which explain the changes of the resistivity of the samples.

2 Experimental

The undoped C_{60} films with a thickness of 70–500 nm were grown by a sublimation of a commercially produced C_{60} of 98 % purity in the vacuum. The amount of the deposited material was monitored with a quartz monitor. Ni-Cr pads were evaporated at the corners of the mica (00 ℓ) and Si (111) substrates of the $0.8 \times 1.0 \text{ cm}^2$ size. Subsequently, Cu contact wires were attached to the pads with In and covered with silver epoxy. The substrate temperature was measured by Cu-Constantan thermocouple.

To obtain a homogeneous doping we test two geometrical set-ups of our apparatus. In the first case the sample and the source of K are put into a horizontal pyrex tube. Two horizontal ovens ensure the temperature gradient. The C_{60} film located in the pyrex tube is held at about 200°C and the source of the K is cycled between the room temperature and 150–200°C. To achieve a homogeneous doping (minimum of the resistivity) the films are kept at 200°C for 5–7 hours after each cycle. We used diffblock AV 63 to hold vacuum at the level of 10^{-3} Pa.

In the second case the source of the K and the sample are in the vertical arrangement. The substrates are fixed on the heater and mounted by the contact wire on vacuum feedthrough. The fullerene is evaporated from a Ta boat, the K from a Mo boat, respectively. The distance between the boats and the heater is approximately 10 cm. For the vertical doping the vacuum in the chamber is in the range of 10^{-4} Pa. The substrate with the C_{60} thin film is heated up to about 150°C and subsequently the K is evaporated on it. This step we repeat several times. When the minimum of the resistivity is achieved, in some cases the insulating layer $Na_3AlF_6+C_{60}$ is evaporated on the sample.

The structural properties of the samples are examined by X-ray diffraction technique in Bragg-Brentano geometry and Raman Spectroscopy. Scanning Electron Microscopy is used to compare the surface morphology of the undoped and doped C_{60} films.

3 Results and discussion

The fullerene thin film with a thickness of 70–500 nm were evaporated on mica (00 ℓ) and Si (111) substrates. In the process of the sample preparation several parameters, such as the thickness of the C_{60} layer, the rate of the deposition and the temperature of the substrates were varied. In all cases the prepared films exhibited a polycrystalline nature.

In the solid state the C_{60} molecules have a face-centered cubic (fcc) structure and the K is doped into the octahedral or tetrahedral sites [5]. X-ray diffraction patterns show a polycrystalline character of the C_{60} thin films grown on the mica (00 ℓ) and Si (111) substrates with the preferred (111) and (600) orientation perpendicular to the substrate surface (Fig. 1).

Figure 2 shows SEM images of the mica (00 ℓ) surface (Fig. 2a), undoped C_{60} film (Fig. 2b) and doped C_{60} film (Fig. 2c) on the mica substrate. The layered structure of the mica surface can

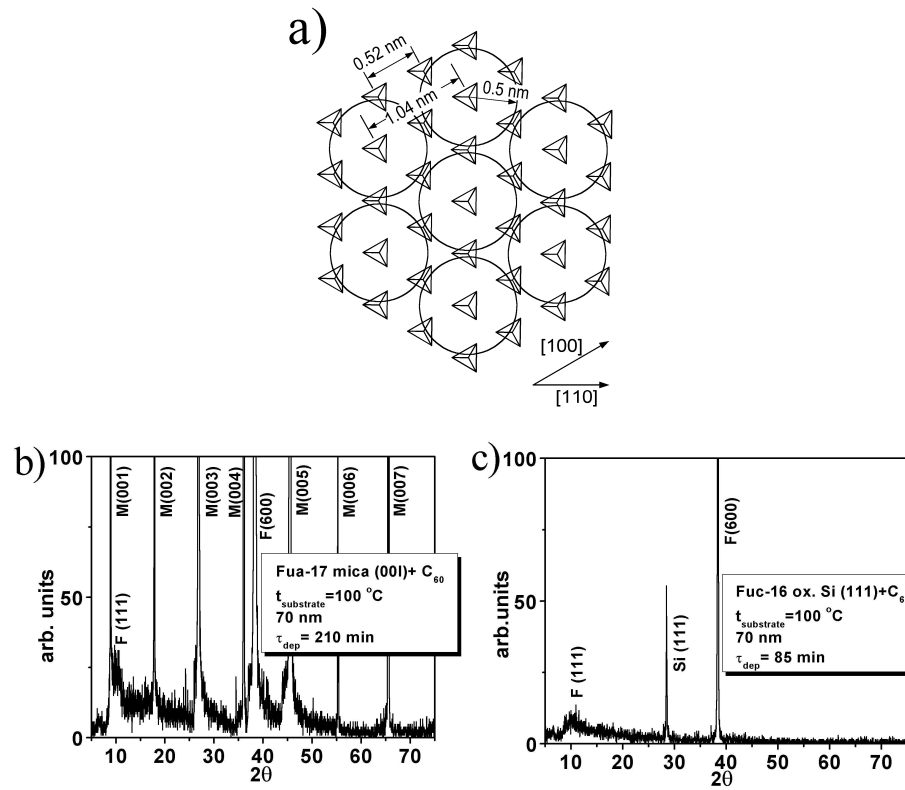


Fig. 1. Schematic view of a mica layer, which consists of a hexagonal array of SiO_4 tetrahedra, upon which a C_{60} monolayer is then deposited (a) [6]. X-ray diffraction patterns of the 70 nm thick C_{60} film grown on the mica (00 ℓ) (b) and on the oxidized Si (111) substrates (c).

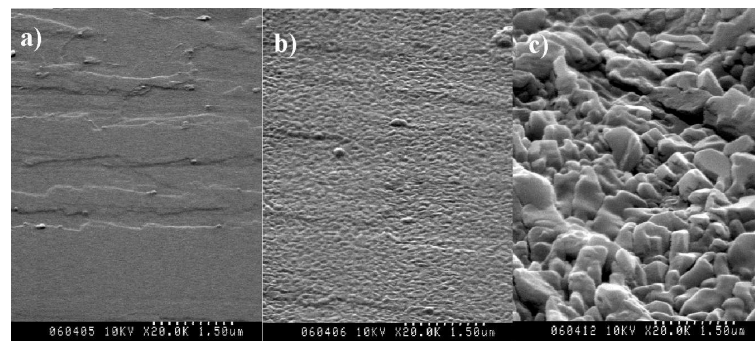


Fig. 2. Scanning Electron Microscopy image of the surface of the mica (00 ℓ) substrate (a), the mica (00 ℓ)+70 nm C_{60} (b) and the mica (00 ℓ)+110 nm C_{60} +intercalation (c).

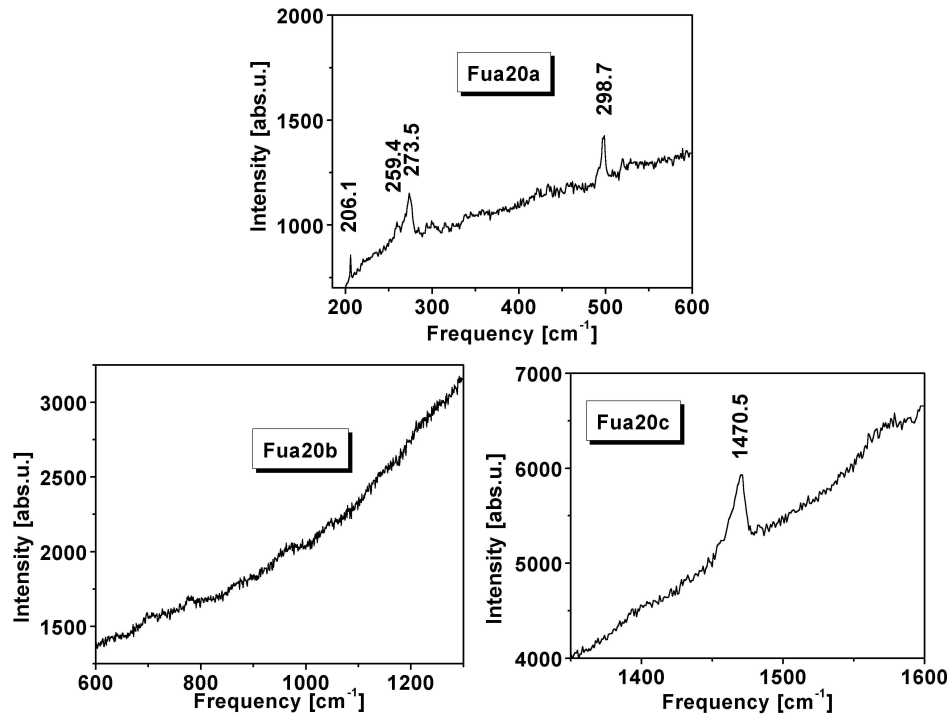


Fig. 3. Raman spectra of the 500 nm thick C_{60} film on the mica (00 ℓ) substrate for three different frequency ranges. Hg (1) mode at 273.5 cm^{-1} and Ag (2) mode at 1470.5 cm^{-1} for C_{60} was appeared.

be clearly seen. The polycrystalline C_{60} film grown on the mica substrate consists of grains with a mean size of approximately 100 nm. After doping the grain coalescence is becoming (Fig. 2c).

We used Raman spectroscopy (Fig. 3) to confirm the existence and to characterise the C_{60} films. When the film thickness increased up to 500 nm two strong vibrational modes were appeared at 273.5 cm^{-1} Hg (1) and at 1470.5 cm^{-1} Ag (2) and it is in a good agreement with the value from the literature [7].

In our experiments the pressure was essentially higher at the level of 10^{-3} – 10^{-4} Pa comparing to other groups [1–3]. Although we used vacuum background about 5 orders worst, we prepared the samples with the comparable resistance.

We measured the resistivity as a function of exposure time by the two-probe geometry during the doping process. The minimum of the ρ (exposure time) corresponds to the K_3C_{60} system [8]. It could be appeared the metallic resistivity either in this point or close to this point.

Our samples in the minimum of the resistivity ($3.23 \times 10^{-3}\ \Omega\text{cm}$) for the vertical arrangement of the experiment have a semiconductor-like temperature dependence because K_3C_{60} cores of the grains are surrounded by insulating K_4C_{60} and K_6C_{60} grain boundaries [8] (Fig. 4). The arrows denote the changes for a fixed temperature increment. The value of the ρ (exposure time)

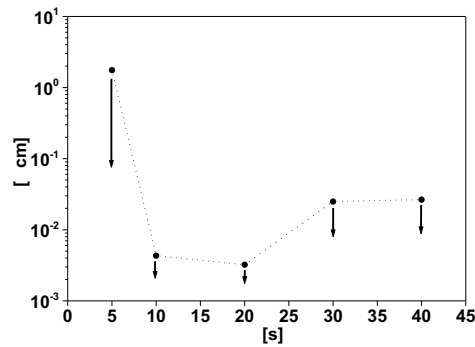


Fig. 4. Exposure time dependence of the resistivity of the K_xC_{60} film during the evaporation of the K at ambient temperature near 25 °C. The $\rho(0)$ was higher than 320 Ωcm . The arrows show changes in the resistivity of the sample as it was heated from room temperature to 50 °C.

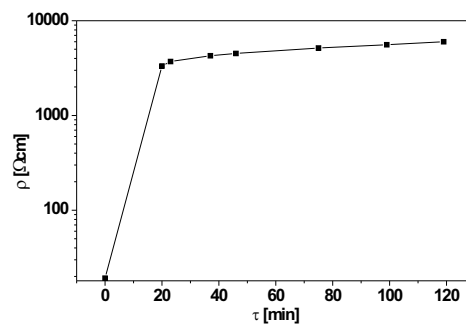


Fig. 5. The time dependence of the resistivity of the sample after breaking the vacuum.

dependence obtained by four-probe geometry can be different due to contact resistance.

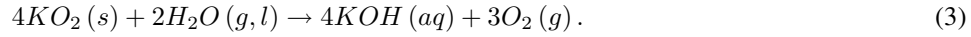
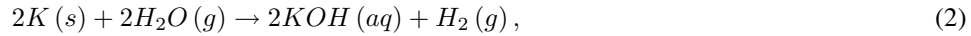
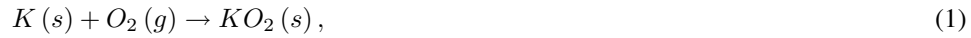
In the case of the horizontal arrangement of the experiment we obtained the lowest resistivity value of $5.8 \times 10^{-2} \Omega\text{cm}$.

After doping process, at which the minimum of the sample resistivity was achieved, we covered the K_xC_{60} film (in some cases) with C_{60} layer (200 nm) and subsequently with Na_3AlF_6 (500 nm) to limit degradation in atmosphere. The 200 nm thick evaporated C_{60} layer slowly decreased the sample resistivity due to diffusion of non-stoichiometric potassium from the interstitial sites of the K_xC_{60} . It seems that this effect can be used for the optimisation of the minimum resistivity value in the future.

In spite of the surface passivation after breaking the vacuum and exposure the sample to the ambient atmosphere the rapid reaction and consecutive changes of the resistivity in the K_xC_{60} system was detected. We do not see any difference between the passivated and not passivated film concerning of the evolution of the resistivity. It can be due to leakiness of the upper film (pinholes, imperfections). Figure 5 shows the typical resistivity changes as the sample is exposed

to atmosphere.

The left side of the curve in the diagram (Fig. 5) represents the interaction (1) of the K_xC_{60} with O_2 which is characterised by a sharp increase of the resistivity. However, when potassium attracts from air enough humidity, the reaction of the K_xC_{60} (K in the interstitial sites of fcc C_{60}) with gaseous H_2O from air is supposed to be dominant (2, 3):



Then, the conductivity of KOH (aq) shunts the interaction of the K_xC_{60} with O_2 (right side).

4 Conclusion

We prepared C_{60} films on mica (00 ℓ) and oxidized Si (111) substrates. X-ray patterns confirm polycrystalline nature of the films. We applied an intercalation of potassium into the fullerene films. We attained the minimum of the resistivity of the samples comparable with the literature in spite of the fact that our experiment were made at standard vacuum conditions ($\sim 10^{-4}$ Pa). The time dependence of the sample resistivity after breaking the vacuum as well as the possible model of the reaction are added. In the future we will be focused on appropriate methods for the preparation of a stable K_xC_{60} system on ambient air.

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