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Sensor Properties of Fullerene Films and Fullerene Compounds with Iodine

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Abstract

The possibility to use fullerene films and fullerene compounds with iodine in sensor electronics is considered. The technology of fullerene film preparation by means of gas-phase deposition is described in brief. The structure and preparation technology of resistive sensor based on fullerene films are described. Experimental results presented embrace the studies of the dependence of the sensor resistance on humidity, ambient temperature and pressure created by the evacuation system. It is demonstrated that fullerene films are very sensitive to pressure at room temperature. Temperature dependencies of the films of fullerene compound with iodine are presented. It is shown that fullerene intercalation with iodine leads to the increase of sample conductivity which is of semiconductor type. A local peak at −23 °C is discovered in the dependence of resistance on temperature. It is connected with the phase transition of the first type.

INTRODUCTION

Sensor electronics is one of rapidly developing areas of science and technology. The most widespread material for sensors is silicon, so the development of sensor electronics takes place in the direction of design and manufacture of silicon sensors. However, the search for new materials with novel properties is important for the creation of sensors with improved technological parameters. The possibilities arise both to study electrophysical properties of the materials and to obtain new sensors with better characteristics. Recently discovered fullerenes and carbon nanotubes are novel materials whose sensor properties have not been investigated yet. It is also interesting to study the properties of films composed of fullerene compounds with halogens and metals because new effects useful for electronics can be discovered. Sensor electronics belongs to the areas in which new nanostructural materials can be used to make sensors with unique properties for physical and chemical factors.

In spite of the fact that after fullerenes were discovered (1985) and industrial technology of their production was developed (1991), rather large number of fundamental works aimed at the investigation of their structure and properties has been carried out but fullerene-based electron devices have not been designed by present. The reasons why fullerenes and their films are attractive for the creation of devices can be formulated as follows: spherical shape and large size of fullerene molecule provide a substantial volume of empty intermolecular space in a face-centred cubic lattice of solid fullerite. As a consequence, this material is easily intercalated by different impurities changing its properties. Pure fullerene is a dielectric but it can change its properties from dielectric to superconducting as a result of intercalation [1, 2]. Besides, fullerene in solid fullerite under definite action, for example high pressure, UV irradiation and chemical interaction with intercalating substances, can form structures with linear, flat or voluminous polymerization.

The simplest subject of investigation can be fullerene film deposited onto a dielectric substrate. A resistor with the resistance depending on definite external actions can be proposed as a device based on the fullerene film. Since the size of fullerene molecule is about 1 nm, one can expect that the film structure will contain pores with the size of about several or tens nanometres. In this case, the film will be very active from the point of view of adsorption/desorption cycle of different substances.

The goal of the present study was to develop a resistive sensor based on fullerene film, as well as to elaborate the technology of fullerene film deposition onto the sapphire substrate. Besides, the work was aimed at the study of conducting properties of fullerene films, as well as the effect of humidity, temperature and pressure on the resistance of films. Conducting properties of the films composed of fullerene compound with iodine are studied in a wide temperature range.

EXPERIMENTAL

In order to synthesize the films, we used a mixture of C_{60}/C_{70} fullerenes or chromatographically pure C_{60} fullerene repeatedly sublimated in high vacuum. The synthesis, isolation and purification of fullerenes were carried out according to the standard technology with graphite evaporation in an electric arc [3, 4]. Fullerene quality was estimated according to the data of mass spectrometry and IR spectroscopy. Repeatedly sublimated mixture of C_{60}/C_{70} fullerenes contained 84 % C_{60} and 16 % C_{70} while repeatedly sublimated C_{60} fullerene contained not less than 99.95 % C_{60} [5].

A flow three-channel set-up was used to obtain fullerene films. Evaporation channels and the reaction chamber were made of quartz and supplied with independent heaters [6]. The films were deposited in the flow of inert gas under reduced pressure onto a cooled substrate placed inside the reaction chamber of the set-up. This set-up allows one to obtain the films of pure fullerenes and to synthesize the films from fullerene compounds and doped fullerenes.

A weighed portion of fullerene was placed in a stainless-steel cell and evaporated in the evaporation channel at a temperature of about 600–680 °C. Carrier gas was dry argon at the flow rate of 5–15 ml/min. Argon pressure in the reaction chamber was 670–1340 Pa. Substrates were placed into the reaction chamber at a temperature of 510 °C and cooled to about 250 °C. Weighed portion of fullerene loaded into the chamber was 20–40 mg. The thickness of thus deposited films was 2–4 μm. Gas-phase deposition of fullerene resulted in polycrystal films with characteristic crystallite size of about 300–500 nm which distinguishes these films substantially from those obtained by high-vacuum deposition. The latter are composed of much smaller crystallites. According to the data of X-ray diffraction patterns and transmission electron microscopy, crystallite structure is rather perfect packing mainly of hexagonal type with an admixture of face-centred cubic packing.

In order to synthesize the films of fullerene compound with iodine, a weighed portion of iodine (20 mg) was placed in a separate evaporation channel with argon flow rate of 6 ml/min. Iodine was evaporated at 60 °C. The flows of gaseous fullerene and iodine in argon were mixed in the reaction chamber at 510 °C. The resulting compound was deposited onto the cooled substrate. Thus synthesized films of fullerene compound with iodine $C_{60}I_{0.7}$ contained less iodine than the fullerite samples intercalated with iodine that were described in [7, 8]. The thickness of films was about 2 μm.

Single crystal polished sapphire plates (100) with metal electrodes prepared preliminarily were used as substrates. The preparation of electrodes included the deposition of metal mirror onto sapphire by means of high-vacuum deposition with the help of the VUP-5 set-up. Chromium was selected as a material for the electrodes due to the absence of its chemical interaction with fullerene under the experimental conditions. The chromium contacts were configured by means of photolithography. Sapphire plate was cut into rectangular samples, their dimensions being 15 × 12 mm. The film of fullerene or its compounds was deposited onto the contact regions. External tapings to chro-

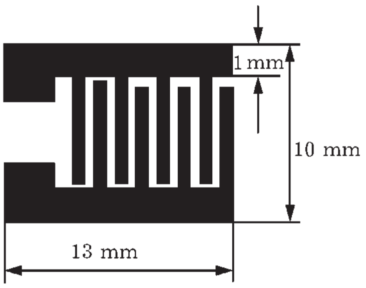

Fig. 1. Topology of chromium contacts to fullerene film.

mium contact areas were made by thermal compression of a thin aluminium wire or by means of clamping contacts made of beryllium bronze. At first the shape of chromium contacts was rectangular, 10 mm wide, the distance between the contacts being 0.3 mm. The resistance of fullerene film between the contacts was too large (about $10^{13}-10^{14}$) Ω which is very inconvenient for measurements in practice. So, chromium contacts were shaped as a comb (Fig. 1). The width of comb bands (dark strips) was 0.1 mm, the distance between the bands was 0.1 mm, and the number of bands was $N = 45$. The overall width of the resistor increased up to 353 mm which allowed us to decrease its resistance for pure fullerene film down to $10^{11}-10^{12}$ Ω.

Pure fullerene films were oxidized by the oxygen of air for 30 min in a tube furnace within a temperature range of 300–400 °C [9]. We measured the dependence of the resistance of pure fullerene films, as well as of oxidized fullerene ones, on humidity, temperature and pressure created by the evacuation system. Besides, we measured temperature dependence of the resistance of films composed of fullerene with iodine.

RESULTS AND DISCUSSION

We studied the samples prepared at different fullerene evaporation temperatures: T_{E1} = 600–640 °C, T_{E2} = 610–650 °C, T_{E3} = 620–660 °C. Temperature is listed as ranges within which it changes because temperature was increased during the evaporation from the initial to final point at a rate of 1 °C/min. This provided more uniform rate of film deposition. Evaporation time was 40 min for temperatures mentioned. These temperature ranges allow us to obtain the films of different appearance and porosity. Lower-temperature films deposited at the fullerene evaporation point T_{E1} were glossy while higher-temperature films (at T_{E2} and T_{E3}) were more tarnished and, respectively, more porous. Measurements showed that temperature dependencies $R(T)$ for the films obtained at T_{E1} and T_{E2}, T_{E3} are substantially different. Figure 2 shows $R(T)$ dependencies for the films deposited at T_{E3}.

The dependencies $R(T)$ are characterized by extremum and the resistance decreases with the increase of oxidation temperature. We suppose that the presence of maximum is connected with the fact that tarnished films are highly porous and absorb water. The film loses water till temperatures about 80 °C, and the resistance increases; then, in the region where resistance drops down, semiconductor character of the conductivity is exhibited. At temperatures above 80 °C, with increasing oxidation temperature, the activation energy of the process decreases from 1.7 eV (non-oxidized sample) till 0.9 eV (T_{ox} = 390 °C). The oxidation of fullerene film is a complicated process that proceeds *via* a series

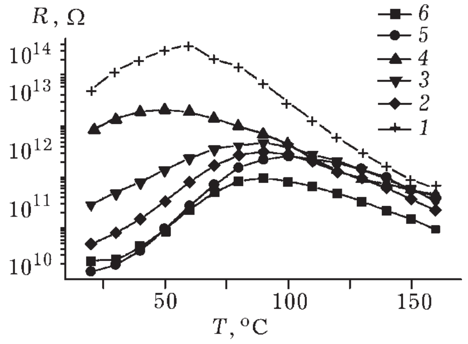

Fig. 2. The dependencies $R(T)$ for porous films treated in air at different temperatures: *1* – initial film; treatment temperature, °C: 330 (*2*), 345 (*3*), 360 (*4*), 375 (*5*), 390 (*6*).

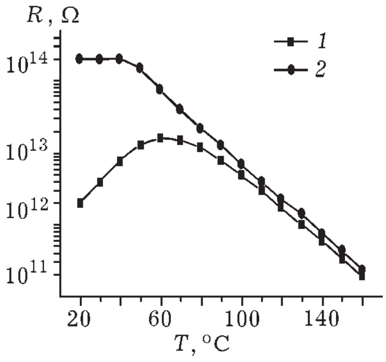

Fig. 3. $R(T)$ dependencies for porous film treated in air at 390 °C: *1* – heating, *2* – cooling.

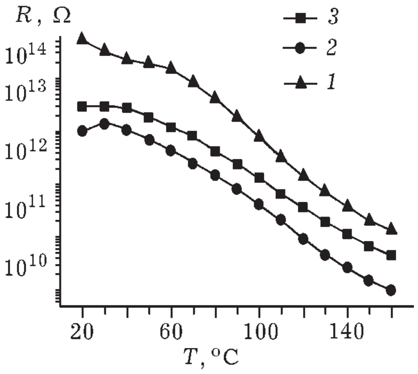

Fig. 4. $R(T)$ dependencies for dense films treated in air at different temperatures: *1* – initial film; treatment temperature, °C: 370 (*2*), 390 (*3*).

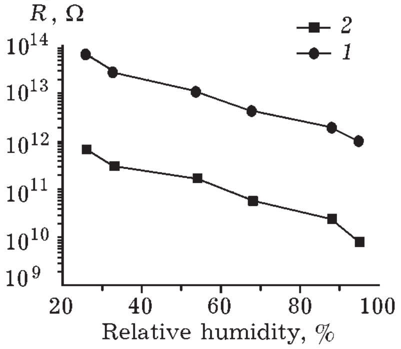

Fig. 5. The dependencies of the resistance of porous films on relative humidity: *1* – initial film, *2* – the film treated in air at 390 °C.

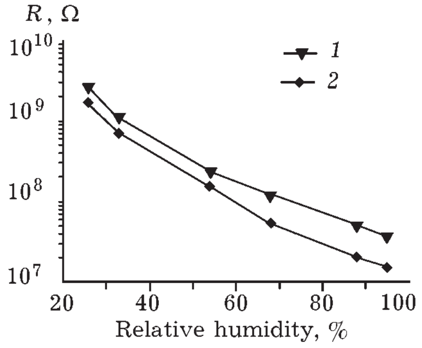

Fig. 6. The dependencies of sensor resistance on relative humidity: *1* – untreated film, *2* – the film treated in air at 300 °C.

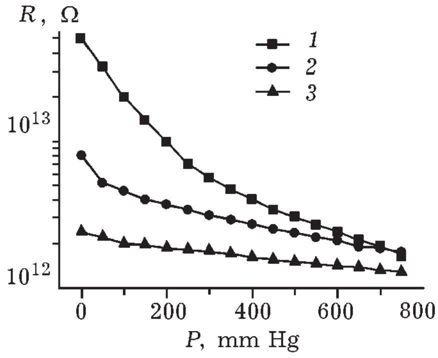

Fig. 7. Pressure dependencies of the resistance of porous film treated in air at 390 °C. Temperature, °C: 20 (*1*), 50 (*2*), 70 (*3*).

of intermediate stages at which the formation of oxidation products and fullerene polymerization take place. A complete destruction of the film occurs after heating in air for 30 min at temperatures above 390 °C. The oxidation leads to the decrease of the width of forbidden gap which is also confirmed by the data on the change of absorption band edge observed in the spectra in visible and near IR regions [9]. The presence of water in the film is confirmed by experimental results (Fig. 3). A typical hysteresis of the temperature dependence of resistance is observed. Its reason is the loss of water during the heating of the film. The behaviour of $R(T)$ dependence during cooling is substantially different from that during heating. The measurements of the temperature dependence of the resistance of oxidized films in vacuum and in dry argon [10] show that the extremum in the temperature dependence of conductivity is absent in the case of vacuum or neutral atmosphere. Thus, in our opinion, the presence of the resistance maximum in the $R(T)$ dependence is connected with the porous structure of film and adsorption of water.

Temperature dependencies of the resistance of dense films obtained at T_{E1} are shown in Fig. 4. The monotonous character of the decrease of film resistance can lend information concerning the fact that dense fullerene films are less porous and absorb water to a less degree. However, these films are also sensitive to humidity. Figure 5 shows the dependence of film resistance on the relative humidity of the environment. These data allow us to conclude that it is possible to make a humidity sensor based on fullerene films. Oxidized films are better suitable for this purpose. The dependence of humidity sensor resistance on the relative humidity of the medium is shown in Fig. 6. One can see that oxidation leads to the increase of the sensitivity to humidity. The ratio of R_i to R_f (resistance at the initial and final points of the range) was as follows. Non-oxidized samples are characterized by $R_i/R_f = 81.2$; for the oxidized samples at $T_{ox} = 300$ °C, $R_i/R_f = 141.6$. The comparison of fullerene film-based sensor parameters with those of the known lithium chloride humidity sensors based on porous silicon suggests that the sensitivity of the former is higher (for the latter, $R_i/R_f = 2$).

TABLE 1
The sensitivity of fullerene films to pressure at different temperatures

T_E, °C	S, Pa^{-1}, at T, °C		
	20	50	70
610–650 (T_{E2})	$1.32\cdot10^{-3}$	$1.1\cdot10^{-4}$	$1.5\cdot10^{-5}$
620–660 (T_{E3})	$2.6\cdot10^{-4}$	$3.4\cdot10^{-5}$	$1\cdot10^{-5}$

The resistance of oxidized films is strongly dependent on the pressure maintained by the evacuation system in the chamber where the sample is placed. Figure 7 shows this dependence for the film obtained at T_{E3}. It is important to note that the dependencies $R(P)$ are not linear and are substantially temperature-dependent. The pressure sensitivity of the films obtained at T_{E2} and T_{E3} is shown in Table 1. The sensitivity of fullerene films to pressure is much higher than that of silicon or polysilicon pressure sensors for which $S(20\ °C) = 10^{-7}$–10^{-6} Pa. The sensitivity at different temperatures was determined according to the equation

$$S = (R(0) - R(P_{atm}))/(R(P_{atm})\Delta P),\ \mathrm{Pa}^{-1}$$

where $R(P_{atm})$ and $R(0)$ is the resistance of the sample at atmospheric pressure and in vacuum.

The oxidized fullerene films are very sensitive to pressure and exhibit a strong temperature dependence of the effect. Temperature coefficient of the sensitivity was 2 %/°C which is about an order of magnitude worse than the corresponding value for silicon sensors of pressure. However, it is interesting that the sensor based on fullerene film is able to determine pressure below 200 mm Hg, till low vacuum. The sensitivity of fullerene film to pressure can be due to several reasons. One of them is the loss of water from the film at reduced pressure, another one is connected with fullerene polymerization. Partial oxidation of fullerene in solid fullerite is accompanied by the polymerization of fullerene molecules which is confirmed by the appearance of broad bands in IR spectra in the range of stretching vibrations at 800 and 1000 cm^{-1} characteristic of fullerite polymerized at high pressures [9, 11]. Partial polymerization proceeds with the decrease of the distance between the polymerized fullerene molecules and thus with the increase of the distance between fullerene molecules bound by van der Waals interaction which causes the strain in crystallites, as well as between separate fullerite crystallites comprising the film (their size being about 300 nm). As a result of this process, the film becomes stressed and possesses a large number of defects in intermolecular bonds and in the interactions between the crystallites comprising the film. The number of conducting electrical chains and their conductivity in these films depends on the isostatic pressure. It is typical that the dependence of resistance on pressure is observed also at pressures above the atmospheric pressure.

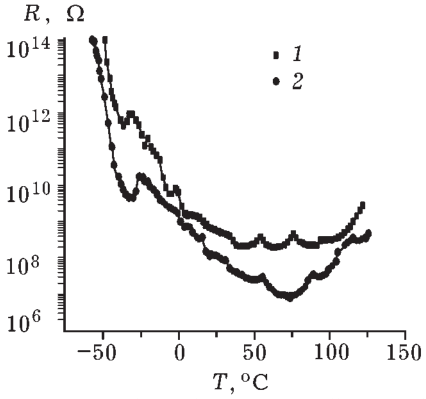

Fig. 8. $R(T)$ dependencies for fullerene films intercalated with iodine: *1* – sample 1, *2* – sample 2.

The measurements of the resistance of film composed of fullerene with iodine showed that the resistance and its temperature dependence are quite different from $R(T)$ for pure C_{60} fullerene film. The addition of iodine causes a sharp decrease of the film resistance down to 10^8–$10^9\,\Omega$ at room temperature. We measured temperature dependence of the film resistance within the temperature range of −196 °C ... +200°C. At temperatures above 80 °C iodine is sublimated off the sample and the resistance increases as one can see in Fig. 8. Above 120 °C sublimation is practically over and the resistance is close to that of the pure fullerene film. After heating, the resistance of the film is not recovered. The behaviour of temperature dependencies of film resistance after heating resembles the behaviour of similar dependencies for pure fullerene. The dependencies $R(T)$ for two samples were approximated by the Arrhenius equation: $R(T) = R_0\exp(E_a/2kT)$ with the activation energy of 1.95 and 2.04 eV within the temperature range of −53 ... −23 °C. Activation energy for the temperature range of −23 ... +20 °C was found to be 1.35 and 1.3 eV. We discovered a local peak of resistance at −23 °C conditioned by the phase transition of fullerene molecules. Films based on the compound of fullerene with iodine also exhibit the dependence of resistance on humidity.

CONCLUSION

The synthezis of films composed of fullerene and its compounds for use in electronics is demonstrated to be promising. Experiments confirm the possibility to use fullerene films in sensor electronics to produce humidity sensors. It is also possible to use the sensitivity of these films to isostatic pressure. Further search for new sensor materials based on the films of fullerene compounds is necessary.

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