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Gas-Phase Technology and Microstructure of Fullerite Films

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Abstract

The technology of C_{60} fullerite films preparation by means of gas-phase deposition and structure of fullerite films are described. A three-channel flow plant was used to obtain fullerite films. The films were deposited in the flow of inert gas under reduced pressure onto a cooled silicon or sapphire substrate placed inside the reaction chamber of the plant. The plant allows one to obtain the films of pure fullerenes and to synthesise the films from fullerene compounds and doped fullerenes. The structure of two types of films were investigated by FE-SEM and SEM techniques: pure fullerite films onto silicon and sapphire substrates as well as compound films were studied by FE-SEM technique. All samples have shown columnar structure with high level of porosity. The synthesis of films composed of fullerene and its compounds for use in electronics is demonstrated to be promising. For example, experiments confirm the possibility to use fullerite films in sensor electronics to produce humidity and thermal sensors. It is also possible to use the sensitivity of these films to isotropic pressure. The experiments with C_{60}-Cu-J films have shown quite strong dependence of their resistance on pressure of different sort of medium-gas that could be used in gas-sensitive sensors. The structure and preparation technology of resistive sensor based on fullerite films are described.

Keywords : Gas-phase deposition, C_{60} films, C_{60}-Cu-J films

1. INTRODUCTION

The search for new materials with novel properties is important for the creation of novel electronic devices with improved parameters. Recently discovered fullerenes and carbon nano-tubes are novel materials whose electronic properties are not well established yet. It is also interesting to study the structure and properties of films composed of fullerene compounds with halogens and metals because new effects useful for electronics can be discovered. The films based on new nano-structural materials can be used to make devices with unique properties for physical and chemical factors. In spite of the fact that after fullerenes were discovered in 1985[1)] and industrial technology of their production was developed in 1991[2,3)], 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 fullerene, named 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 super-conductive as a result of intercalation[4-6)]. Besides, fullerene in fullerite under definite action, for example high pressure, UV irradiation and chemical interaction with intercalating substances, can form structures with linear, flat or voluminous polymerisation.

The simplest subject of investigation can be fullerite 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

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fullerite 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 nanometers. 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 fullerite film, as well as to elaborate the technology of fullerite film deposition onto the sapphire substrate and silicon substrates. 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 copper-iodine are studied in a wide temperature range.

2. EXPERIMENTAL

To synthesise the films a mixture of C_{60}/C_{70} fullerenes or chromatographically pure C_{60} fullerene repeatedly sublimated in high vacuum were used. The synthesis, isolation and purification of fullerenes were carried out according to the standard technology with graphite evaporation in an electric arc[7].

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}. FE-SEM image of repeatedly sublimated C_{60} powder, which is ready for film deposition is shown in Fig. 1. The crystal size is of 30-40 μm in diameter.

A three-channel flow plant was used to obtain fullerene films as shown in Fig. 2. Evaporation channels and the reaction chamber were made of quartz and

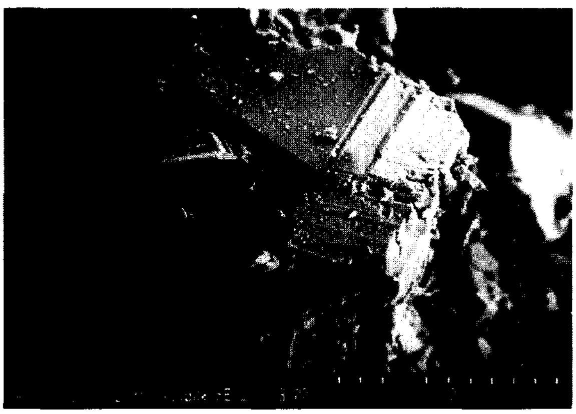

Fig. 1. FE-SEM image of high vacuum sublimated C_{60} micro-crystal.

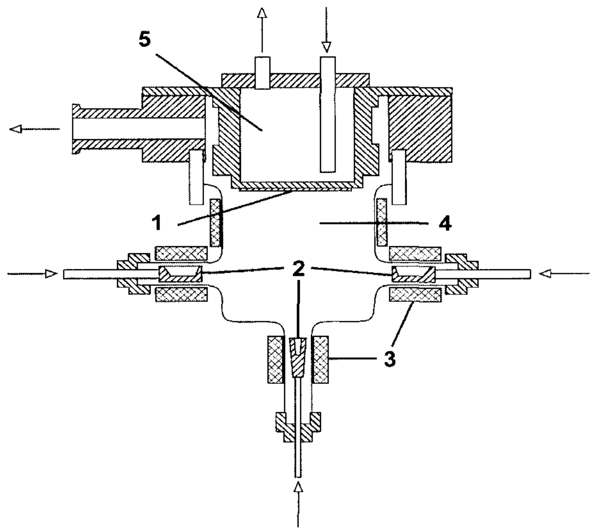

Fig. 2. The plant for gas-phase deposition of fullerene films. 1-substrate holder; 2-crucibles with initial substances; 3-heater; 4-chamber; 5-cooler.

supplied with independent heaters. The films were deposited in the flow of inert gas under reduced pressure onto a cooled substrate placed inside the reaction chamber of the plant. This plant allows one to obtain the films of pure fullerenes and to synthesise 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 600-620°C. Carrier gas were dry argon or hydrogen at the flow rate of 5-15 *ml/min*. Carrier gas 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 time of deposition is 20 min. In order to synthesise fullerene-copper-iodine compound films an initial weighed portion of fullerene was placed in a stainless steel crucible and fine-dyspersated copper powder heated at 400°C in the other channel. Portion of iodine (c. 20 mg) was heated at 60-80°C so as molecular iodine has been transported above copper powder by gas-carrier. The synthesis of copper mono-iodide occurs in this channel. It's being noted that to synthesise fullerene-iodine film a weighed portion of iodine was placed in a separate evaporation channel with hydrogen flow rate of 6 m*l*/min. The flows of gaseous fullerene and copper-iodine or iodine in gas-carrier were mixed in the reaction chamber at 510°C. The resulting compound was deposited onto the cooled substrate.

The two materials were used as substrates: silicon (100) and sapphire (100).

3. RESULTS AND DISCUSSION

The FE-SEM images of pure fullerene film on silicon substrate are shown in Figs. 3 and 4. It can be observed that the film has polycrystalline columnar structure with high level of porosity. The thickness of the deposited films was of 4.3 μm (Fig. 4). The end of columns have spherical or oval surface with the size of 100-250 nm (Fig. 3). The FE-SEM images of the pure fullerite films deposited on sapphire substrate are shown in Figs. 5 and 6.

Also the film has polycrystalline columnar structure with high level of porosity. The thickness of the deposited films was of 1.0 μm (Fig. 6). The ends of columns look like grains with the size of 100-250 nm (Fig. 5). The film on sapphire looks denser then one on the silicon substrate. The clear columnar structure appears at quite thick films compared to the silicon substrate. One can assume that film grows as dense polycrystalline structure at initial stage of growth, then distinct columnar structure grows at the second stage. Gas-phase deposition of fullerene resulted in polycrystalline films with characteristic crystallite size of about 100-250 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.

The structure of two samples with C_{60}-Cu-J composition was investigated by SEM techniques. Top view of sample №15 is shown in Fig. 7. Substrate temperature for this sample is of 100°C. One can see the absence of well-ordered structure as in pure fullerite films. The cross-sectional view for sample №15 is shown in Fig. 8.

The thickness of the film is of 44 μm. The main point is the preservation of initial columnar structure.

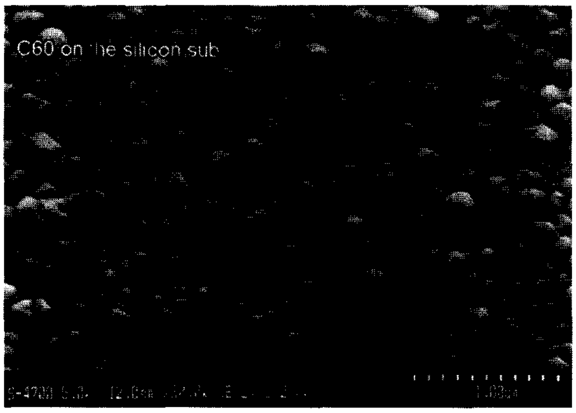

Fig. 3. FE-SEM top view of pure fullerite film on silicon substrate.

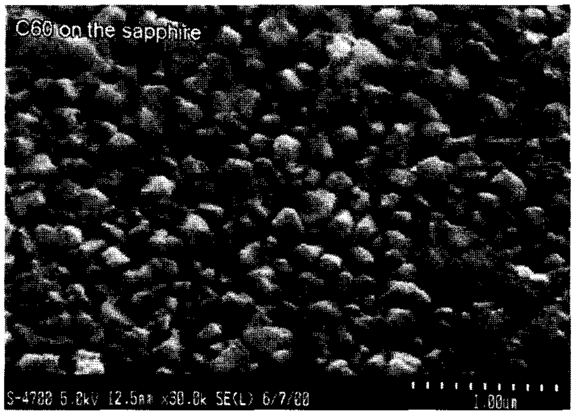

Fig. 5. FE-SEM top view of pure fullerite film on sapphire substrate.

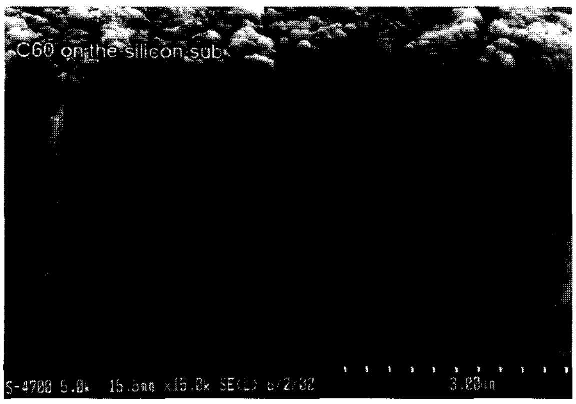

Fig. 4. FE-SEM image of fullerene film cross-section on silicon substrate.

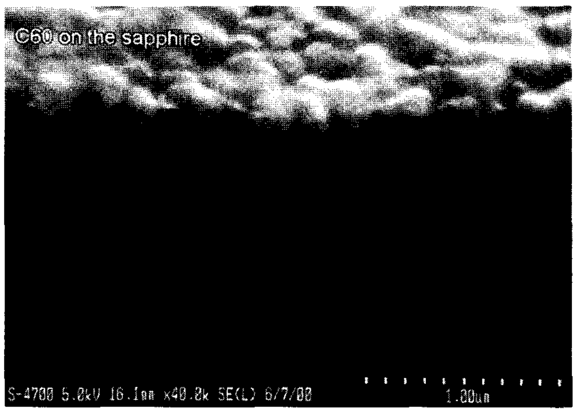

Fig. 6. FE-SEM image of fullerite film cross-section on sapphire substrate.

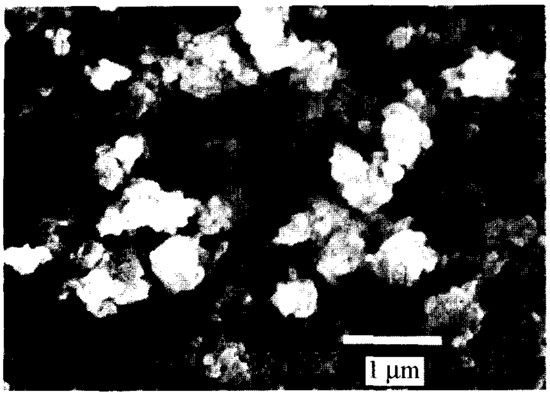

Fig. 7. SEM image of C_{60}-Cu-J sample. (№15). Top view, (X20000 magnification).

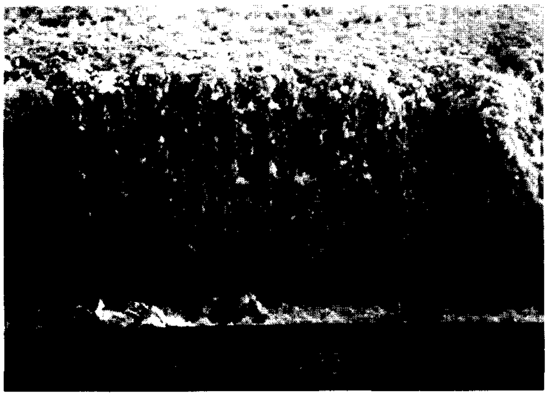

Fig. 8. SEM image of C_{60}-Cu-J sample. (№15). Cross-section, (X1000 magnification).

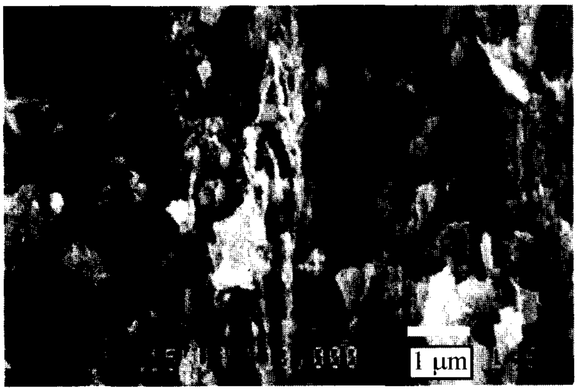

Fig. 9. Cross-section SEM image of C_{60}-Cu-J sample (№15).

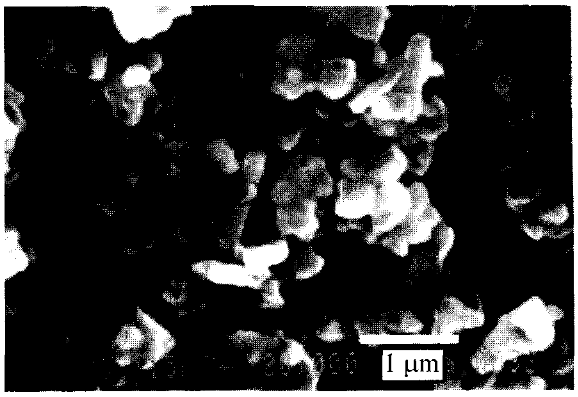

Fig. 10. SEM image of C_{60}-Cu-J sample (№16).

Fig. 11. Cross-section SEM image of C_{60}-Cu-J sample (№16).

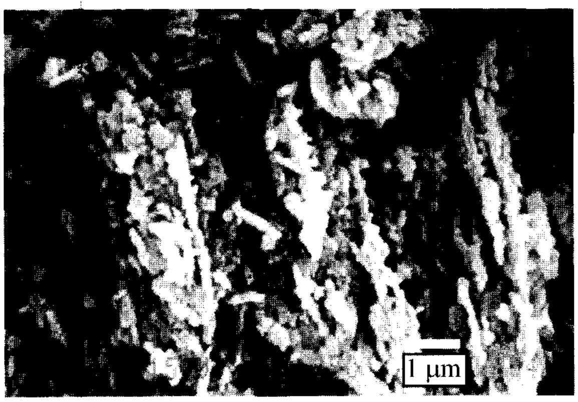

Fig.12. Cross-section SEM image of C_{60}-Cu-J sample (№16).

The film looks quite dense, but one can see the high level of porosity as well. Much more enlarged image of cross-sectional structure has shown by Fig. 9. One can say that quite ordered columnar structure have been transform in columnar-whiskered structure. It may be concerned with interaction of copper and iodine with fullerene and quite low substrate temperature. The intercalation of fullerite film by copper and iodine leads to dramatically decreasing of film resistance till the values of 100-200 Ohm at room temperature in comparison with 10^{11}-10^{13} Ohm for pure fullerite film[8,9]. Top view of sample №16 is shown in Fig. 10. Substrate temperature for this sample is of 250°C. The top view looks as quite disordered structure where grain sizes and voids are bigger then for sample №15. So the porosity for sample №16 is bigger then for sample №15.

One can see the thickness of C_{60}-Cu-J film for sample №16 in Fig. 11. The thickness is of 20 μm. Magnified image of cross-sectional structure is shown in Fig. 12, which looks more disordered then for sample №15. Higher level of porosity and smaller thickness may be concerned with higher substrate temperature. The resistance of sample N16 is of 5.8 kΩ at room temperature. X-ray-phase analysis (XRPA) has shown the low decreasing of Cu-J contains for the sample №16 in comparison with the sample №15. XRPA for both samples has shown that phases of C_{60} and Cu-J exist separately since there is no chemical interaction between these two phases.

The experiments with pure Cu-J (without C_{60}) have shown that copper mono-iodide can be deposited onto relatively cooled substrate (100°C). Deposition of Cu-J onto more hot substrate at 250-400°C occurs only at the presence of fullerene.

4. Conclusion

The synthesis of films composed of fullerene and its compounds for use in electronics is demonstrated to be promising. One can see from FE-SEM analysis that fullerite films have polycrystalline columnar structure with column cross-section size about 100-300 nm and clear boundaries between the columns. C_{60}-Cu-J films have high level of porosity and quite small resistances, which make them more convenient for an application. Experiments confirm the possibility to use fullerite films in sensor electronics to produce humidity sensors. It is also possible to use the sensitivity of these films to isotropic pressure. The experiments with C_{60}-Cu-J films have shown quite strong dependence of their resistance on pressure of different sort of medium-gas that could be used in gas-sensitive sensors.

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