RESEARCH ON INFRARED ABSORPTION AND CONDUCTIVE PROPERTIES OF FULLERENE-IODINE COMPOUND FILMS

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Introduction

The synthesis and research of intercalated fullerene are greatly significant in understanding for this new molecular modification of carbon. A number of reports are devoted to investigate fullerene/iodine interactions [1;2]. Here we report the results of infrared absorption and conductive properties of fullerene-iodine compound films.

Experimental

The synthesis of fullerene iodine-intercalated compound films was made by gas-phase deposition. For the synthesis of iodine intercalated fullerene film chromatographic pure fullerene C_{60} was used as a source of fullerene. The fullerene was re-sublimated at the temperature of 700 °C and pressure of 10^{-5} Pa. By laser mass – spectrometry, the stoichiometry of synthesised film was analysed, and the relative concentrations of atoms of carbon and iodine were determined. Fullerene was evaporated from source at the temperature of 600 °C from a stainless steel cell. Through the fullerene source, carrier gas hydrogen with the maximum flow-rate of 15 ml/min was passed. Molecular iodine evaporated at the temperature of 60 °C was transported from a source into the reactor with flow-rate of dry hydrogen 4 ml/min. Into the reaction chamber heated up to temperature 500 °C the mixed gas of fullerene and iodine with carrier gas was flown. The intercalated fullerene film deposited on sapphire substrate with temperature 250 °C has stoichiometry of C_{60}: $I_{1.6}$ under the pressure of 200 Pa in the reactor and for the reaction time of 30 min.

The thickness of iodine-intercalated fullerene film analysed by spectrophotometer was 2.08 microns. Density of iodine intercalated fullerene films is of (1.78 ± 0.06) g/cm^3 by weighing sapphire substrates before and after film deposition. To obtain IR-spectra the fullerene films were deposited on a chromium mirror with thickness of 0.5 microns deposited on a single-crystalline (100) sapphire substrate. By spectrometer with the resolution 2 cm^{-1} in all spectral range, the IR-spectra were obtained by the reflection from a chromium mirror at room temperature and pressure of 10^3 Pa. The spectra of pure fullerene C_{60} and compound of C_{60}: I_2 are shown together to compare them on Fig.1. Considering the thickness of the 4 microns of iodine intercalated fullerene film and 2 microns of pure fullerene film, intensity dropped half is natural. However, the intensity of IR-spectrum curves was decreased in middle range of frequency by iodine intercalation and some different peaks appeared and showed iodine states in the fullerene polycrystalline in the low frequency range.

We have investigated the resistance of fullerene-iodine compound films. The samples for resistance measurement are prepared as following procedure.
1. The chromium layer was deposited on a round sapphire substrate of 60 mm diameter; 2. To make configuration of chromium stripes, a photolithography process was used;
3. The substrate was cut for samples of the rectangular form by the size of 15 x 12 mm; 4. The fullerene-iodine film was deposited. The film covers the whole surface of a sample excluding of contact pads. The external contacts to a sample were made from beryllium bronze and hardly nestled on chromium contact pads.

The chromium contact was formed in interdigited configuration with 0.1 mm interval stripes 0.1 mm. The number of stripes is N = 45. Total width of resistor is increased up to about 353 mm to reduce the value of resistance. The temperature dependence of resistance for iodine intercalated fullerene films was measured between -58 °C and 127 °C range of temperature. The specific resistivity dependence on temperature is shown on Fig.2.

Results and discussion

At present research we have found out that during deposition of film, the interaction between fullerene and iodine causes the deposited film to differ essentially from pure fullerene film. The microphotograph of C_{60}: $I_{1.6}$ film obtained by scanning electron microscope has shown various texture on surface different from that of pure C_{60} film. The iodine intercalated fullerene film consists of polycrystalline form with length 0.7 micron and diameter 0.2 micron. X-ray diffractometer indicates the distinct fullerene structure and iodine-fullerene crystalline lattice as well.

The absorption optical spectrum of compound C_{60}: I_2 in IR range is shown similar to that of pure fullerene and the intensities of peaks are similar as well. There is no absorption corresponding to the oscillation of the C - I chain. this confirms existence of I_2 as intercalated molecules. Some of peaks related with iodine are observed in the area of deformational oscillations in long-wave part (below 500 cm^{-1}). This testifies to some reduction of structural symmetry of compound C_{60}: I_2 in comparison with pure C_{60}. It happens the small widening of peak at wave vector 526 cm^{-1}, which corresponds to oscillation of pentagons in C_{60} molecule. The appearance of broad bands at 1051 cm^{-1}, 871 cm^{-1} and 626 cm^{-1} can be stipulated by polymerisation of fullerene during the interaction of C_{60} with iodine. These three bands rather well coincide with bands of IR-spectra polymerised fullerene under pressure [3]. It is necessary to remark that, in fullerene spectra, the film may be polymerised owing to act of light (photo-irradiation). There is no broad peak in range 1000 cm^{-1} - 1150 cm^{-1}, which is usual for polymers obtained under the pressure. The photo-polymerised fullerene consists of mainly dimer and trimer which have other character of IR-spectra.

The measurement of electrical resistance of C_{60}: I_2 film has shown a resistance essentially distinguished from that of a pure C_{60} film not only in an absolute value but also on temperature dependence. The temperature dependence of film resistance was measured in temperature range of −196 °C ÷ 200 °C. At higher than 75 °C, as the iodine molecules are sublimated from the specimen, the resistance increases again as shown on Fig.2 and, at higher than 127 °C, iodine may be sublimated completely. It was shown that due to the intercalation of iodine the resistance of specimens became much less than the resistance of pure fullerene film, and come down to about 10^8 -10^9 Ohm at room temperature from order of ~10^{13} -10^{14} Ohm for pure C_{60} film. The resistance may be approximated by Arrhenius equation as R $R_0 \exp(E_a/2kT)$ with activation energy 1.95 eV and 2.04 eV in the temperature range -53 °C ÷ -23 °C, but in temperature range from -23 °C to 27 °C with activation energy 1.35 eV and 1.3 eV. From 27 °C to 75 °C is of weak dependence on temperature. If the temperature higher than 75 °C the resistance increases again due to iodine sublimation from film and shows a local peak of resistance at -23 °C due to the phase transition of fullerene molecule. At temperatures above 147 °C the resistance of films equals to that of pure fullerene film because of complete sublimation of iodine. During cooling the resistance of iodine intercalated film is similar to that of pure fullerene film.

Conclusion

The iodine intercalated fullerene films have a complex temperature dependence of resistance and the resistance of film decreases down to the value applicable for practice. The iodine intercalated fullerene film shows a peak in R(T) function about -23 °C due to a phase transition of fullerene molecule. At higher than 75 °C the resistance increases again due to the sublimation of iodine and at temperatures above 147 °C the resistance of film equals to that of pure fullerene film.

References

[1] Nakashima S, Norimoto M, Hamanaka Y. Raman scattering of iodine intercalated C_{60} crystals. Chem Phys Lett 1997; 268: 359-364.
[2] Zenner Th. Zabel H. Synthesis, characterization, stability of $C_{60}I_2$. J Phys Chem 1993; 97:8690-8691.
[3] Rao A.M, Eklund PC, Hodeu J-I. Infrared and Raman studies of pressure-polymerised C_{60}. Phys Rev B 1997;55(7):4766-4773.

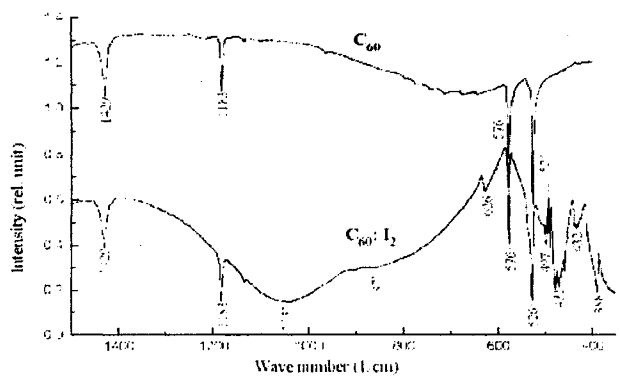

Fig.1. IR spectra of pure fullerene and iodine intercalated fullerene film.

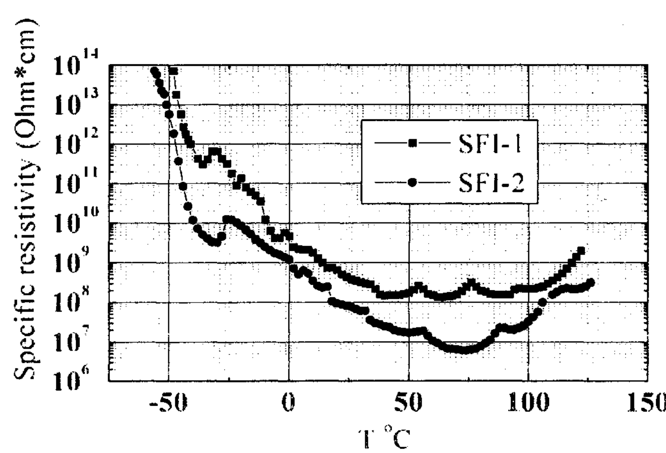

Fig. 2. The temperature functions of specific resistivity.