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Structure and Conductivity Characteristics of Sandwich Structures with Fullerite Films

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Abstract

We report on the technology of formation of sandwich structures based on fullerite films and on experimental results in research of optical and conductivity properties of these sandwich samples. Single crystals of sapphire (100) or silicon were used as substrates. The sandwich specimens were based on the structure $M/C_{60}/M$ (M=Cr, Pd, Ag, Al, Cu). The thickness of the fullerite films was about 0.2~1.0 μm. The area of the C_{60} film under the top contact was about 1 cm^2. The specimens have been investigated by infrared spectroscopy, spectra-photometry, ellipsometry and X-ray diffraction analysis. Measurements of the current/voltage characteristics and research on the temperature dependence of conductivity were performed as well. It was shown that metals such as Cr, Pd, Ag, Al, and Cu penetrate easily into the fullerite films. It appears that these specimens have a large conductivity. For silver/C_{60} and other sandwich structures the conductivities show a semiconductor-like behaviour.

Key Words : fullerite film, sandwich structure, conductivity

1. Introduction

The intense research on fullerene, C_{60}, during the last years has led to an accumulation of evidence for great experimental and theoretical results and has obviously illuminated the necessity to find out the ways for device applications of fullerenes and films of fullerite (i.e. solid fullerene). Fullerite films have a great potential application as material for light, pressure and chemical sensors. The electrical conductivity, σ, and its temperature dependence were measured from 400 to 160 K in 1.5 μm thick vapor-deposited films of C_{60}/C_{70}. At room temperature, σ is as large as 10^{-14} $(\Omega \cdot cm)^{-1}$[1]. Since the pure fullerite films have high values of resistivity[2], it was necessary to search for ways to decrease the later.

One way for solving this problem is the creation of fullerite films intercalated by different elements. The d.c. conductivity of C_{60} fullerite films treated by SbF_5 vapour is three order of magnitude higher than that of the C_{60} film and is seen to increase by further eight orders of magnitude upon heating up to 400 K[3]. Also the conductive properties of fullerene-iodine intercalated films had been measured. However, in spite of intercalation the specific resistivity of fullerene-iodine films persists still at high values of ρ, 10^7~10^8 $\Omega \cdot cm$, at room temperature[4]. The interaction of fullerene with such metals as tin, aluminium and palladium had been examined as well. Tin-doped C_{60} thin films with different Sn contents have been prepared by co-evaporation.

The room temperature conductivity for tin-doped C_{60} films was found to be in the range of σ, 10^{-3}~10^{-11} $(\Omega \cdot cm)^{-1}$ for different samples. The temperature dependence of the electrical resistivity of these Sn-doped films shows a semiconducting behaviour in the temperature range from 20 to 420 K. Hall effect measurements indicated that the conduction type of theses Sn-doped films is n-type[5].

The interaction of palladium and fullerene was studied more thoroughly. A new metal-fullerite structure $C_{60}Pd_3$ has been found recently[6]. A series of new organometallic polymers, Pd_nC_{60}, with varying Pd/C_{60} ratios was prepared and studied using the EXAFS spectroscopy. It was shown that the Pd atoms act as bridges

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between adjacent C_{60} molecules by coordination to the π-electrons of their double bonds. There exists another way to obtain technologically acceptable resistivity values. This way includes the use of sandwich structures with thin fullerite films[7]. Thin-film multilayer structures up to 20 repeated layers have been growth in a high vacuum chamber by sequential deposition of aluminium and fullerene on substrate at room temperature[8].

The result of this work demonstrates the charge transfer across planar metal-C_{60} interfaces. The resistivity of such multilayer structures has been reduced to values of about 100 Ohm. These results suggest that multilayers may become useful vehicles for forming fullerene interface compounds in two-dimensional structures. The results of tunneling spectroscopy of fullerene/Ge multilayer (~10 nm) systems have been shown[9] and first thin film layers and insulating barriers were made of that system. Each layer in the sandwich junction was thermally evaporated at room temperature. A typical base electrode was Cu (~35 nm), and the counter electrode was typically made of Ag (~200 nm).

There is not yet much information available about the interaction of fullerenes with different metals and about the properties of metal-doped fullerite films, but this field is still good for many surprises. For example, co-deposition of the Ni and C_{60} leads to the stripe self-organization phenomena of Ni appeared just after deposition, i.e. the sample was not annealed. The first information about this phenomena was presented[10]. When annealing a co-deposited Ni-C_{60} layer structure deposited onto a MgO (100) substrate, new types of large intercalates from 300 to 600 nm were formed, where cubic Ni crystallites are embedded within a shell of C_{60} molecules.

In this paper we report on the technology of formation of sandwich structures based on fullerite films and on experimental results in research of optical and conductivity properties of these sandwich samples. Electron microscopic and XRD investigations have revealed the polycrystalline nature of the deposited films. The microstructure of the crystallites comprises the disordered hetero-poly types of hexagonal and cubic forms of fullerite, with a preference of the later form. The size of the crystallites depends on the deposition conditions and is significantly decreased in the case of the high vacuum deposited films. Single crystals of sapphire (100) and silicon were used as substrates. Onto them, the sandwich structures containing a C_{60} film between different metallic contacts were deposited. The following sandwich structures were studied: Cr/C_{60}/Cr; Pd/C_{60}/Cr, Pd/C_{60}/Pd, Ag/C_{60}/Pd, Ag/C_{60}/Cr, Al/C_{60}/Cr and Cu/C_{60}/Cr.

2. Experimental

Fullerite C_{60} films were obtained by two methods: 1. The gas-phase-deposition method in a quartz reactor under low pressure of dry argon; and 2. The high vacuum deposition method. The typical thickness of the films was about 0.2~1.0 μm. There were prepared three types of specimens each, the first one for the purpose of infrared spectroscopy (IRS), the second one for spectra-photometry (SP), ellipsometry and X-ray diffraction (XRD) studies, and the third one for the measurement of the current/voltage (I-V) characteristics and the study of the temperature dependence of conductivity.

For preparing the IR-spectroscopy specimens, a silicon (100) substrate was taken upon which a chromium mirror was vapor-deposited for $t_d = 20$ min. Then followed a thin layer of C_{60} (between 250 nm and 750 nm thick), deposited by thermal evaporation at $T_e = 773$ K, $P = 10^{-3}$ Pa, and for $t_d = 60$~120 min. Finally a thin metallic layer (~40 nm of Cu, Pd, or Ag) was deposited by electron beam evaporation for $t_d = 15$ s. The gas-phase deposition of fullerite was used for preparation of the second type of samples, with silicon (100) or sapphire being the substrate.

For the fullerene evaporation, the temperature was raised for in total 100 min from 773 K with a constant rate of 0.5 K/min up to 823 K. This enabled us to get a constant mass-transfer of fullerene molecules during the evaporation, resulting in an uniform structure of the fullerite film. The optimum evaporation temperature for fullerene was found to be 808~883 K. The thickness of the fullerite film is then about 500 nm. The film has a dense structure with a mirror-like surface. The film structure as examined by SEM and TEM is polycrystalline, with the average size of the crystallites being around 200 to 300 nm. After that the thin metallic top contact layer was deposited by electron-beam evaporation ($P = 10^{-3}$ Pa, $t_d = 40$ s).

The third type of specimens was made by the follow technology. The bottom chromium contact was deposited onto a sapphire substrate, then the fullerite film (~1.5 μm) was deposited by the gas-phase technology, and after that a metal (Cu, Pd, Ag, Al, or Cr) was depos-

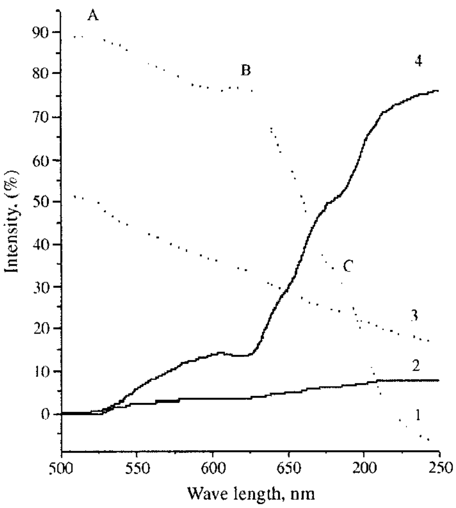

Fig. 1. Absorption edge in the visible spectrum; 1-absorption spectrum of C_{60} film in reflection, 2-transmission spectrum of Ag/C_{60} sandwich structure, 3-absorption spectrum of Ag/C_{60} structure in reflection, and 4-transmission spectrum of C_{60} film.

ited by electron-beam evaporation (t_d = 20 min) through the mask onto the fullerite film surface. The area of the top contact is about 1 cm^2.

3. Results and Discussion

The samples were investigated by IRS, ellipsometry, SP, and XRD, apart from measurements of the current/voltage characteristics and the temperature dependence of conductivity. The absorption and transmission spectra have been obtained by the spectra-photometer SP-18 (λ = 400~750 nm), Fig. 1. In this case, the fullerite film was deposited through a mask onto monocrystalline ZrO_2 (100) as a substrate. The thickness of the fullerite film was adjusted to be about 0.5 nm, so that the sample was still optically transparent. After that a silver film of around 63 nm thickness was deposited by electron-beam evaporation.

To compare the spectra of the pure fullerite film and of the Ag/C_{60} sandwich structure the sample was prepared so that part of the fullerite film on the ZrO_2 substrate remained uncovered. The forbidden gap of the pure fullerite film was determined to be 1.7 eV. This value is in a good agreement with results shown earlier[10]. The fundamental absorption edge for the Ag/C_{60} structure moves to longer wavelengths. As we supposed

Table 1. Ellipsometric measurements for different structures refractive index (n), absorption coefficient (k), and layer thickness (d)

Structure	N	K	d, nm
C_{60}	2.15	0.02	211.4
Ag	0.17	3.99	63.5
1st layer in Ag/C_{60} structure	0.59	2.15	54.5
2nd layer Ag/C_{60} structure	2.04	0.01	147.0

the great interaction of Ag and C_{60} lead to the formation of a new semiconductor, which has a smaller forbidden band gap.

Ellipsometric measurements were made to determine the refractive index (n), the absorption coefficient (k), and the thickness (d) of the silver and C_{60} layers, either as isolated films or in the Ag/C_{60} sandwich structure. For this purpose the silver film covered the fullerite layer only partially, and some part of the silver film covered the ZrO_2 substrate directly. A He-Ne laser (λ = 633 nm) was used as a light-source. The incidence angles (φ) were varied from 50° to 80° in 5° steps. By adjusting several polarizations at different angles ψ and Δ, the inverse problem was solved for both the one- and two-layer film models. This enabled us to determine the film parameters n, k, and d[12]. The results are shown in Table 1.

The results indicate that silver diffused into the bulk of the fullerite film without increasing the film thickness. Under the assumption of a homogeneous distribution of silver atoms within the Ag/C_{60} structure the approximate correlation of silver atoms and C_{60} molecules was calculated by using the ellipsometric data. It appears that the approximate composition of such a structure is $C_{60}Ag_x$, where x = 12.4. The measurement of the refraction angle of light in the double layer structure Ag/C_{60} reveals that the film is quite rough, i.e. that the silver is distributed irregularly within the film. The measurement of the specific resistivity in different types of samples has shown that irregularity of the silver distribution as well.

The XRD technique was applied for the examination of the Ag/C_{60} and Pd/C_{60} structures. Here, the thickness of the fullerite films deposited onto the silicon substrate by gas-phase deposition is about 1 μm, and the thickness of the metal layer deposited by electron-beam evaporation is about 1 μm as well. The XRD data are shown in Fig. 2. A decrease of the peak intensities in

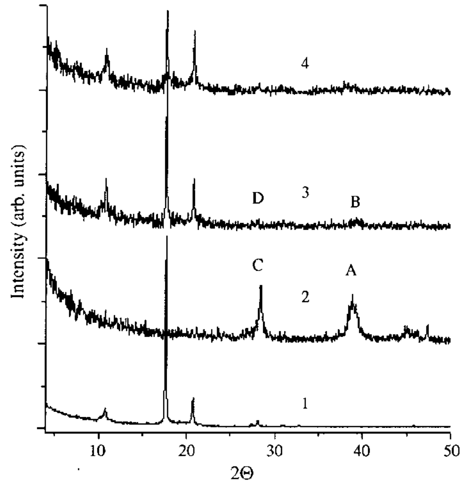

Fig. 2. XRD spectra of fullerite films with different deposited metals. 1-pure C_{60} film; 2-pure palladium film; 3-Pd/C_{60} compound; 4-Ag/C_{60} compound.

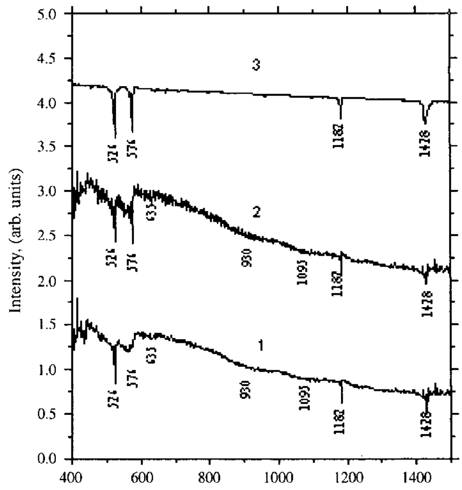

Fig. 3. IR-spectra of M/C_{60} structures (medium wave lengths); 1-Ag/C_{60}, 2-Cu/C_{60}, 3-pure C_{60}.

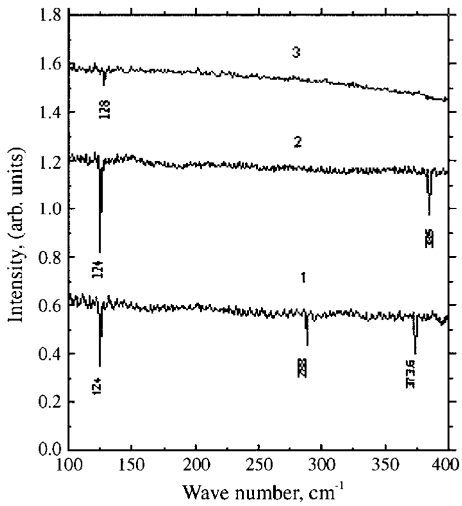

Fig. 4. IR-spectra of M/C_{60} structures (long wave lenghts); 2-1-Cu/C_{60}, 2-Ag/C_{60}, 3-pure C_{60}.

the bilayer structures in comparison with those of pure fullerite indicates the partial amorphisation of the metal/fullerite structure, i.e. the distances between the fullerene molecules become irregular. Since there is not observed any displacement of the peak positions of the metal/fullerite structure, hence there is no formation of any new crystal phase. The peak intensities b and d of C_{60} of the metal/fullerite structure decrease in comparison with those of pure palladium (peaks a and c), in the same way as the crystalline palladium fraction in the structure decreased, too.

The IR spectra for medium and long wavelengths are shown in Figs. 3 and 4, respectively. All the oscillation frequencies of the pure C_{60} remain in the absorption spectra of the M/C_{60} structures at medium wavelength. It appears that the peaks at 526 and 576 cm^{-1} broaden. These peaks correspond to oscillations related with the deformation of the fullerene molecules. One may explain them by a reduction of the symmetry of the fullerene molecules due to intercalation of alien atoms. There appears a small peak at 635 cm^{-1} which is distinctive for fullerenes polymerised under high-pressure conditions and for photo-induced polymers[13,14]. These results show that polymerisation of fullerene molecules appears to be one of the consequences of interaction of metal atoms and fullerene molecules.

For IR studies in the long wave length region specimens of a peculiar structure were made. The top metal layer was very thin (3~4 nm) so that IR spectra could be measured in reflection from the metallic mirror. Such a sample structure allowed us to obtain high resolution spectra. The peak at 385 cm^{-1} corresponds to the interaction of silver with fullerite, and the peaks at 288 cm^{-1} and 373.6 cm^{-1} correspond to the interaction of copper with fullerite. The peak at 124 cm^{-1} may correspond to the oscillation of the C_{60}-C_{60} bond. The shift of this peak from wave number of 128 cm^{-1} to 124 cm^{-1} is explained by the deformation of the C_{60}-C_{60} bond.

The optical characteristics of the fullerite films at medium and far infrared wave lengths were measured with the spectrometer. The IR spectrum of a fullerite film on a chromium electrode correlates well with the spectrum of pure solid fullerene. These results have shown that chromium interacts only weakly with the fullerite film. Hence chromium can be considered as the best contact material for pure fullerite films in a planar configuration of the resistor.

Two types of samples were used for the measurement of the temperature dependence of the specific resistivity and the I-V characteristics. The first one is a sandwich structure. In order to avoid here a short circuit between top and bottom contacts the area of the fullerite film was made larger than the area of the bottom contact. The second one is a planar structure with a ridged configuration of the chromium contact on a sapphire substrate[4].

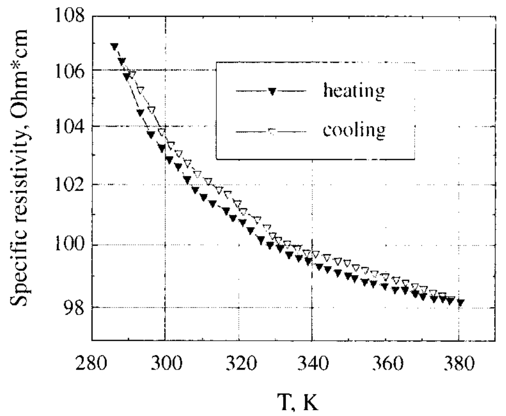

Fig. 5. Specific resistivity versus temperature for Ag/C_{60} sandwich structure.

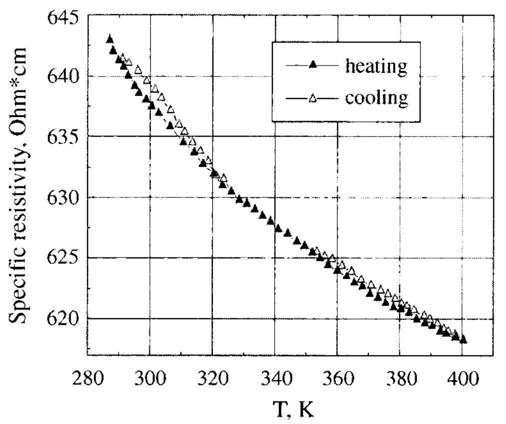

Fig. 6. Specific resistivity versus temperature for Ag/C_{60} planar structure.

The thickness of the fullerite films was about 1.5~2.0 μm for both sample types. The results of the specific resistivity versus the temperature are shown in Figs. 5 and 6. Both curves show a semiconductor-like behaviour of their conductivity. The greater value of the specific resistivity in case of the planar structure shows that the conductivity is anisotropic in both vertical and horizontal film directions. This is possibly a consequence of the non-uniform silver distribution in the film. The I-V characteristics at temperatures ranging from 293 to 373 K deviate only moderately from a linear correlation and do not depend much on the sign of the bias voltage. The resistivity of different sandwich structures versus the temperature for 293~463 K was in the range of 100~200 Ohm. All the structures show a decrease in resistivity with increasing temperature.

4. Conclusion

In the present study on metal/C_{60}/metal sandwich structures we have obtained the following results. Ellipsometry measurements show that the metal diffuses completely into the bulk of the C_{60} film, with the metal distribution being non-uniform. The interaction of silver and C_{60} leads to the appearance of a new compound with good conductivity. IR spectra show that there emerges chemical bonding between the metal and the fullerene molecules. The XRD study demonstrates the partial amorphisation of the C_{60} crystallites and a decrease in size of the metal crystallites. It was also shown that metals such as Cu, Ag, Al, Pd, and Cr penetrate easily into the fullerite film due to the large intermolecular distances between the C_{60} balls, due to the polycrystalline nature of the used films with an average crystal size of 200 nm, and probable also due to chemical interaction between the metal atoms and the fullerene molecules. The resistivity of such sandwich samples was decreased strongly down to typical values around 100~200 Ω. It depends only weakly on the temperature. Though Cr, Cu, Ag, Al and Pd could be considered as contact materials for planar C_{60} resistors, it is necessary to take into account that all of them except for Cr penetrate readily into the C_{60} layer. The sandwich structures based on fullerene films would be considered as thermo-sensitive resistor with negative temperature coefficient of resistance. Research in conductive properties of fullerite films is prospective for sensor electronics. The high sensitivity of fullerite to temperature, light, pressure, humidity and chemical ambient is useful for creation of small size sensors due to nanometric dimension of fullerene molecules by itself.

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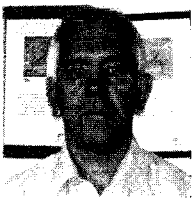

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