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Influence of Axial Mechanical Stress on the Conductivity of Fullerite Powder

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Abstract

The possibility to use powder consisting of fullerite microcrystallines as a device sensitive to the external axial mechanical load is considered. We suppose that the change of conductivity of fullerite microcrystalline powder as a function of external mechanical stress will be useful for the creation of nanoscale devices of sensor electronics. This new effect based on changing of intermolecular distance between fullerene molecules due to the action of external mechanical force, which can change the distance between fullerene molecules because of weak van der Waals interaction exists. The founded effect is quite linear and sensitive to external mechanical stress is better then in well-known pressure transducers is based on silicon technology.

Key Words : fullerite, powder, conductivity, pressure, temperature

1. Introduction

Sensor electronics is one of the rapidly developed 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 measuring and technological parameters. The possibilities arise both to study electro-physical properties of the materials and to obtain new sensors with better characteristics. Recently discovered fullerenes is novel material whose sensor properties have not been investigated yet. It is interesting to study the sensor properties of fullerenes because new effects useful for electronics can be discovered.

Sensor electronics belongs to the areas in which new nano-structural materials can be used to construct sensors with unique properties for physical and chemical factors. In spite of the fact that fullerenes were discovered[1] in 1985, and industrial technology of their production was developed[2] in 1990, 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 summarized as follows: spherical shape and large size of fullerene molecule provide a substantial volume of empty intermolecular space in a face-centered 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 to superconducting as a result of intercalation[3,4]. 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 fullerite film deposited onto a dielectric substrate. A resistor of which the resistance depends on definite external actions can be proposed as a device based on the fullerite film. Such resistive sensor was described[5,6], where have been shown that fullerite films are sensitive in environmental pressure and humidity. Fullerene can be incorporated in etched ion tracks of polymer foil that allows create small-size temperature sensors[7]. Since the size of fullerene molecule is less

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then 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. It is the way for creation of high-sensitive humidity or gas sensors. As to pressure dependence of fullerene films conductivity, the resistance of oxidized fullerene films is strongly dependent on the pressure maintained by the evacuation system in the chamber where the sample is placed[6].

It is not well known the reasons for pressure dependence of fullerite films. One can suggest a few explanations of sensitivity of fullerite film to pressure. One of them is the loss of water from the film at reduced pressure, another 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[8].

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 200 – 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 isotropic pressure. It is typical that the dependence of resistance on pressure is observed also at pressures above the atmospheric pressure.

The main goal of the present study was to search in action of axial external force in conductivity of powder consisting of fullerite microcrystallines. If the action of external mechanical load will be quite effective it means the opening direction for new type of pressure sensors, which would be constructed in absolutely other way then traditional solid-state silicon pressure sensors.

2. Experimental

The cross section of experimental set up for measurement of resistance of fullerite powder as function of axial external mechanical load is shown in Fig. 1. Two types of glass pipe were used: glass capillary with a length of 5 mm, inner diameter (d_{inn1}) of 0.76 mm, the other is glass pipe: with a length of 50 mm and inner diameter (d_{inn2}) of 1.76 mm.

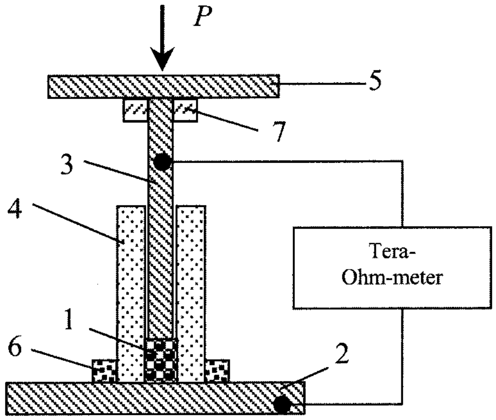

Fig. 1. Set up for measurement of electrical resistance of fullerite powder as function of external pressure (P): 1-fullerite powder, 2-bottom plane contact (silver), 3-upper-rod contact (copper), 4-glass pipe, 5-load area, 6-epoxy adhesive, and 7-reinforcing ring.

Repeatedly sublimated mixture of C_{60}/C_{70} fullerenes contained 84% C_{60} and 16% C_{70} was poured into bottom end of glass capillary. Diameter of conducting rod in glass capillary (d_{c1}) is 0.75 mm, the height of mixed fullerite-powder rod is about 2 mm, and diameter of contact rod for glass pipe (d_{c2}) is 1.5 mm. Mixture of C_{60}/C_{70} was poured into bottom end of big glass pipe. The height of C_{60}/C_{70} fullerene-powder rod is about 5 mm. A few droplets of toluene was added in pristine C_{60}/C_{70} powder to get deposition technology of fullerene quite closed to the same technology of fullerene deposition in etched ion tracks, which has been described in Ref.[5]. For both glass pipes were measured the dependencies of electrical resistance as function of external mechanical load and temperature dependencies of electrical resistance for different mechanical loads in temperature range 20 – 100°C.

3. Result and Discussion

The dependence of C_{60}/C_{70} powder electrical resistance on mass of external load was shown in inset of Fig.

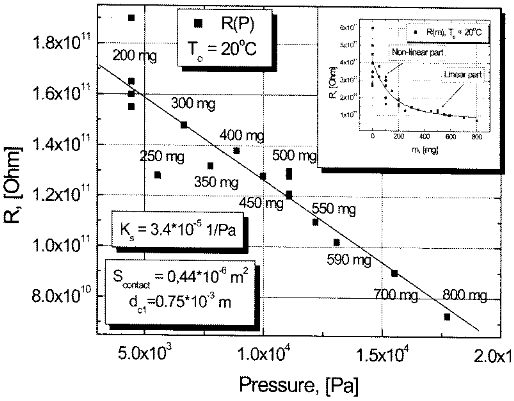

Fig. 2. Electrical resistance (*R*) of C_{60}/C_{70} powder as a function of external axial pressure (*P*) for glass capillary in linear part of *R*(*P*) function. In the inset: Electrical resistance (*R*) of C_{60}/C_{70} powder as a function of mass of external load in a range of *m* = 0 ~ 800 mg.

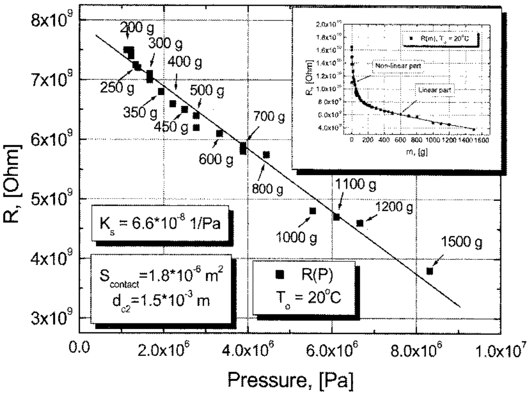

Fig. 3. Electrical resistance of C_{60}/C_{70} powder with few droplets of toluene in glass pipe in linear part of *R*(*P*) dependence. In the inset: Electrical resistance (*R*) of C_{60}/C_{70} powder as a function of mass of external load *m* = 0 ~ 1500 g.

2. One can see clearly the two parts of curve: non-linear part from 0 to 200 mg and quasi-linear part from 200 mg to 800 mg. There is a significant dispersion of electrical resistance values at m = 0 mg, which decreases for increasing values of mass (m = 100, 200, 500 mg). We suppose that non-linear part of *R*(*m*) is concerned with processes in contact system conducting rod-C_{60}/C_{70} powder and decreasing of distance between grains of C_{60}/C_{70} powder at the action of external force. The large dispersion of *R*(*m*) dependence for small values of mass could be concerned with small contact area of conducting rod and small length (~3 mm) of conducting rod inside of glass pipe. Linear part of *R*(*m*) dependence as function of electrical resistance on pressure is shown in Fig. 2.

The sensitivity factor in Fig. 2 was calculated by formula[9]: $K_S = \frac{R(P_1)-R(P_1)}{R(P_0)\cdot(P_1-P_0)}$, where P_0, P_1 are pressure correspond to masses m_0 = 200 mg and m_1 = 800 mg, respectively. It has to be emphasize that, in this case, the sensitivity factor is of much larger than that of traditional silicon or polysilicon pressure sensors, where $K_s = 10^{-8} - 10^{-9}$ Pa^{-1}.

The dependence of C_{60}/C_{70} powder electrical resistance on mass of external load for glass pipe is shown in inset of Fig. 3. One can see again two parts of dependence of *R*(*m*). The point with mass of m_0 = 200 g divides clearly *R*(*m*) dependence in two parts: non-linear and linear. This experiment much more stable from the point of results dispersion, because of the length of the pipe was long enough. Also the diameter of conducting rod is two times longer that of the first experiment. Due to enough length and contact area of conducting rod we could apply higher values of external load mass, see Fig. 3. Linear part of *R*(*m*) dependence as function of electrical resistance on pressure for glass pipe is shown in Fig. 3.

In this case, the low value of sensitivity factor K_S = 6.6 × 10^{-8} Pa^{-1} is supposed to be with crystallization of solved fullerenes after toluene drying. We expect that K_s will be greater in fullerite powder with small grain size then with large grain sizes which have been formed after recrystallisation in toluene drying process. The first situation was realized in experiment with glass capillary, where fullerite powder was used as working material of pressure sensor, and the second case was realized in experiment with glass pipe. One can see the difference in 515 times in K_s values for both experiments, but sensitivity factor for long-length glass pipe looks as the same for pressure sensor based on monocrystalline silicon resistors.

The non-linear dependence of resistance as function of pressure for both experiments could be concerned with change of space between fullerite microcrystallines owing to action of external force.

Temperature dependencies of electrical resistance of C_{60}/C_{70} with glass pipe are shown in Fig. 4. All curves

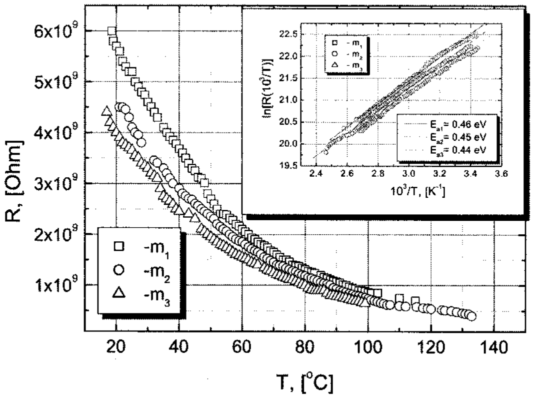

Fig. 4. Temperature dependencies of electrical resistance for different masses of external load. In the inset: Arrhenius plot of $R(T)$ for different masses ($m_1 = 200$ g, $m_2 = 500$ g, and $m_3 = 1000$ g).

follow semiconductor type of conductivity behavior. This is typical for fullerite, but the activation energy of the conductivity appears much smaller than that of pristine fullerite, C_{60}. The dependencies $R(T)$ were approximated by the Arrhenius equation: $R(T) = R_0 \cdot \exp\left(\frac{E_a}{2kT}\right)$. The values of activation energy, $E_a = 0.46\text{~}0.44$ eV, for different masses of external load are shown in inset of Fig. 4. The smaller values of E_a in compared to pristine and oxidized fullerite C_{60} films[6] ($E_a = 1.7 - 1.9$ eV) concerned with non-controlled self-intercalation of C_{60}/C_{70} powder by silver or copper atoms which was originated from electrodes or with organic chains which were remained between fullerene molecules after toluene evaporation. One can see from Fig. 4, that pressure sensitive effect of fullerite powder conductivity depends on temperature as well. The interval between curves at $T_0 = 20$°C looks bigger then for $T_1 = 80$°C and $T_2 = 100$°C.

We estimated the temperature coefficient of pressure sensitivity factor, TCK$_s$, which was shown in Fig. 5. The value of TCK$_s$ was estimated by the formula[9]:

$$TCK_S = \left| \frac{K_S(T_2) - K_S(T_1)}{K_S(T_1) \cdot T_2(T_1)} \cdot 100\% \right|.$$

The value of TCK_s is comparable with the value for silicon monocrystalline piezoresistors, where $TCK_s \approx 0.2 - 0.3\%/°C$ for different levels of concentration.

The pressure sensitive effect in fullerite powder and films allows design the new types of pressure sensors, which would have much smaller size and the other principle of operation then traditional silicon pressure sensors and devices.

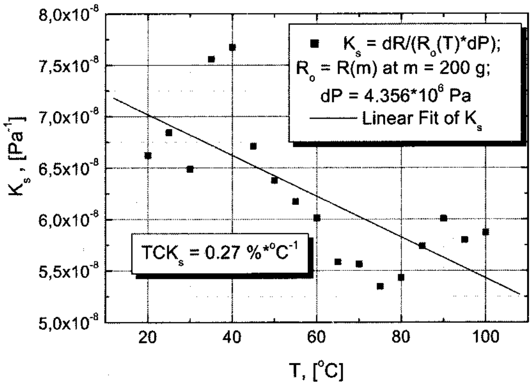

Fig. 5. Temperature dependence of sensitivity factor, K_s for experiment with fullerite powder in glass pipe.

4. Conclusion

The evidence of strong action of axial pressure in conductance of fullerite microcrystallines has been observed, which appears as microscale fullerite powder. The effect is quite linear and that is attractive for application. One of the explanation of this effect based on changing of intermolecular distance between fullerene molecules due to action of external mechanical force, which could change the interval between fullerene molecules because of weak van der Waals interaction exists. The other explanation of effect could be concerned with change of space between fullerite microcrystallines owing to action of external force. What is the main reason from both explanation model of pressure-conduction effect in fullerite microcrystallines, which were pointed above, is remained for future discussion.

The pressure sensitive parameters as factor of sensitivity, K_s, is much more or comparable with pressure sensors based on monocrystalline silicon piezoresistors. This fact depends on preparing technology of fullerite microcrystalline powder. Temperature coefficient of factor of pressure sensitivity is comparable with value for silicon pressure sensors. The usage of fullerite nano- and microcrystallines as functional material for pressure sensors is represented expedient in submicron etched ion tracks in polymer foils as polyethylene-thereftalate (PET) or polyimide (PI), which allow design pressure sensors with small size and thickness.

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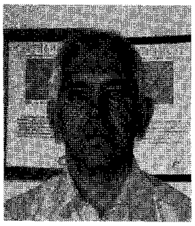

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- J. of Korean Sensors Society
- Vol. 6, No. 1 p. 34