Advanced Materials '93, I / B: Magnetic, Fullerene, Dielectric, Ferroelectric,
Diamond and Related Materials, edited by M. Homma et al.
Trans. Mat. Res. Soc. Jpn., Volume 14B

ELECTRICAL CONDUCTIVITY OF PLASMA-POLYMERIZED C_{60}/C_{70} MIXTURE FILMS

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The electrical conductivity of plasma-polymerized C_{60}/C_{70} mixture has been investigated. The dark current conductivity was determined to be 10^{-9} S/cm in the atmosphereThis value is 4 orders of magnitude higher than that determined under vacuum or for sublimed C_{60}/C_{70} films measured in the atmosphere or under vacuum. In the higher temperature domain, a semiconductor-type temperature dependence was observed and the band gap energy was estimated to be 2.1eV. We suppose that the electric conductivity is enhanced by the existence of water molecules on the film, the surface of which is characterized by a high hydrophilicity.

INTRODUCTION

The discovery of the metallic conductivity [1] and superconductivity [2] in potassium-doped C_{60} fullerenes has led to much interest in their electric and structural properties [3]. Although, there are very few studies on polymerized C_{60} films [4]. Thus, in this work, we report on the synthesis of polyfullerene in plasma, along with the temperature dependence of its electrical conductivity, temperature dependence.

EXPERIMENTAL

We used a C_{60}/C_{70} mixture prepared in our laboratory. The electric arc in the reactor was generated by the contact-arc method [3e]. The electric current was set to 100 A, with a voltage in the range of 20-30 V. The C_{60}/C_{70} mixture obtained was extracted with toluene, and the content of C_{70} was estimated to be 10% by HPLC measurements. From now on, we will refer to this C_{60}/C_{70} mixture simply as C_{60}.

The plasma reactor used to polymerize C_{60} consists of SAMCO BP-10 capacitance-coupled outer electrodes operating at 13.56 MHz. The inter-electrode distance is fixed at 3.5cm. The sample films were deposited by subliming C_{60} powder under an argon plasma at a pressure of 1.3Pa (0.01torr) from a molybdenum boat. The films were up to 100nm in thickness with an sublimation rate of 0.1~0.2 nm/sec. Samples were synthesized at 25, 50 and 100W. We also prepared simply sublimed films under a pressure of 6.7×10^{-3} Pa (5×10^{-5} torr). The distance between the molybdenum boat and the substrates was set to 6.7 cm.

The films were deposited on comb-shaped gold electrodes, prepared by electron beam sublimation on glass substrates through an appropriate mask. The conductivity measurements were carried out in a Faraday-cage-type cell using a computer controlled Keithley 617 digital multimeter both in the atmosphere (~60%RH) and in a vacuum of approximately 7 Pa (0.05 torr) at 25°C.

The molecular weight was measured using an LDI-1700 Time-of-Flight mass spectrometer equipped with a N_2 laser in order to ablate and ionize the sample.

RESULTS AND DISCUSSION

1/ Molecular weight, and wetting properties

We tried to measure the molecular weight using a time-of-flight mass spectrometer (TOF-mass). The plasma-polymerized samples were dissolved in N, N-dimethyl-formamide (DMF) and then mounted on the sample stage without any matrix compound. The spectrum obtained is shown in figure 1. As sequence bands following the C_{60} monomer band at an m/z value of 720, bands corresponding to $(C_{60})_2$, $(C_{60})_3$, ...were observed in the spectrum. Although the band structure becomes vague as the m/z value increases, the intensity never fell to zero within the range of this measurement. This clearly shows the existence of highly

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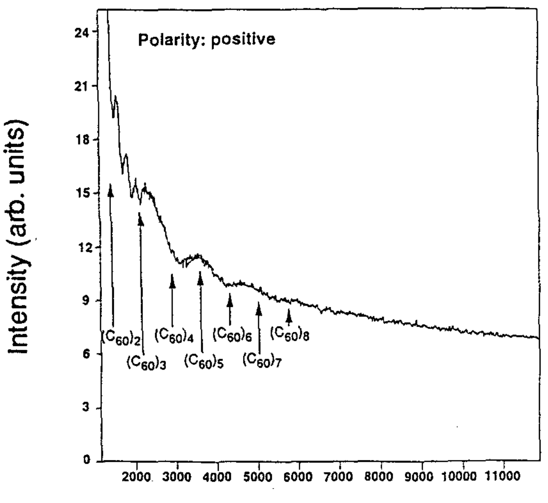

Figure 1 Time-of-Flight mass spectrum of C_{60} samples polymerized under plasma of 100W.

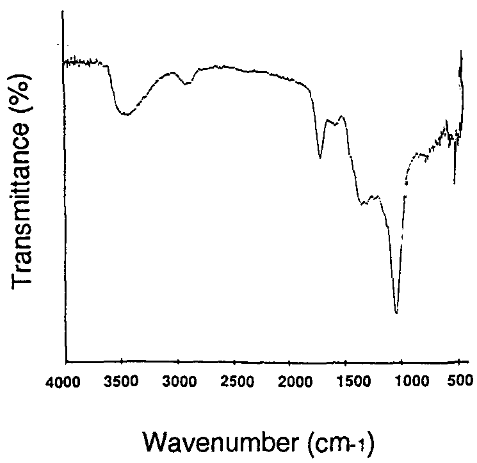

Figure 2 FTIR spectrum of C_{60} film polymerized under plasma power of 100W.

Table I Surface energies and hysteresis of C_{60} sublimed and plasma-polymerized films.

Surface Parameters	Sublimed	100W-Plasma
$\cos\theta_a$ (H_2O)	0.133	0.744
$\cos\theta_a$ (solv.) [a]	0.368 (FA)	0.944 (MI)
γ_{SV}^d (mJ/m^2)	23.0	36.3
γ_{SV}^p (mJ/m^2)	3.35	21.7
γ_{SV}^{total} (mJ/m^2)	26.4	58.0
H (mJ/m^2)	3.18	25.0

[a] FA represents Formamide ($HCONH_2$) and MI methylene iodide (CH_2I_2)

polymerized samples of more than $(C_{60})_{10}$. The reason for the diffuse spectrum in the higher m/z region may be attributed to the existence of C_{70} molecules, the partial oxidation of the sample and/or the imperfect dissolution of the sample in DMF.

The surface energy of the samples was obtained by using a Fowkes-Kaelble's two liquids method [5]. The results are shown in table 1. The polar and dispersive components of the surface, represented respectively by γ_{SV}^p and γ_{SV}^d are both greater for the plasma-polymerized sample than for the sublimed one, showing that the plasma-polymerized films have a more hydrophilic surface.

The wetting hysteresis H which represents a heterogeneity of the surface [6,7] is defined by $H=\gamma_{LV}(\cos\theta_r-\cos\theta_a)$, where θ_r represents the receding angle, and θ_a the advanced angle. As θ_a was also larger for the plasma-polymerized sample, we can conclude that the morphological roughness and chemical heterogeneity were greater.

The hydrophilicity was also indicated by an FTIR spectrum measured for a 100W-plasma-polymerized sample (figure 2). A large and intense absorption near 3500cm^{-1} shows the existence of -OH groups in the film.

We conclude that the plama-polymerized C60 was highly polymerized and its surface was highly hydrophilic and heterogeneous.

3/ I-V and aging characteristics

The I-V characteristics of the 100W-plasma-polymerized sample were obtained and we observed that the current varied linearly with the applied voltage (figure 3), which substantiated the ohmic behavior in the +25V to -25V voltage range under investigation. In vacuum, plasma polymerized and sublimed films possessed similarly low conductivities (~10^{-12}-10^{-13} S/cm). In the atmosphere, the conductivity was about 4 orders of magnitude higher for plasma polymerized films than for sublimed ones. The sublimed films did not exhibit the increase in conductivity compared with

Table II Electrical conductivity of fresh C_{60} films under different conditions

Samples	Sublimed	Sublimed	RF Plasma	RF Plasma
Environment	atmosphere	vacuum	atmosphere	vacuum
Conductivity (S/cm)	$\sim 10^{-12}$	$\sim 10^{-12}$-10^{-13}	$\sim 10^{-9}$	$\sim 10^{-12}$-10^{-13}

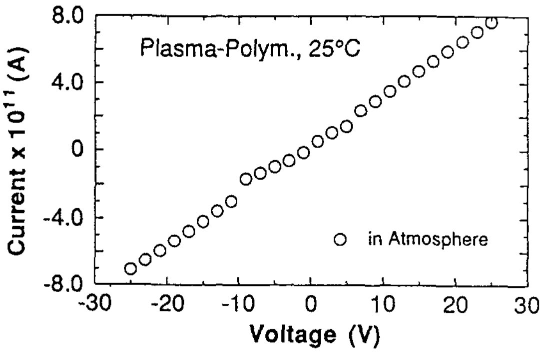

Figure 3 Current versus voltage curves for plasma-polymerized C_{60} samples measured in atmosphere.

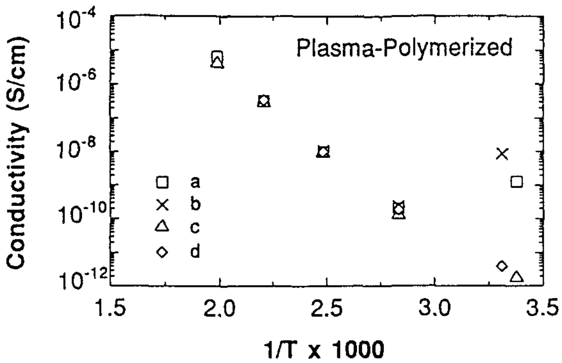

Figure 5 Conductivity versus 1/T for polymerized C_{60} samples measured in atmosphere (a and b) or vacuum (c and d) in increasing (a and c) or decreasing (b and d) temperature.

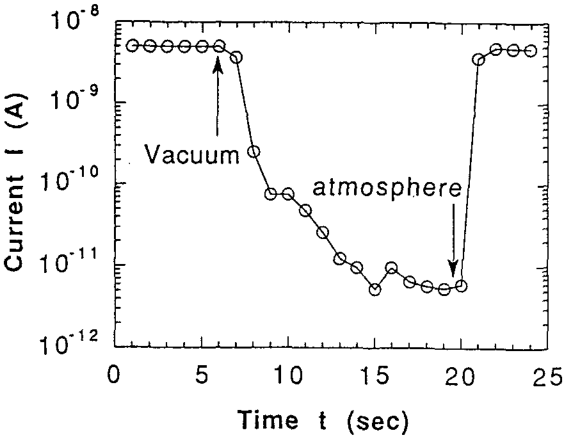

Figure 4. Switching diagram of a plasma-polymerized C60 film between vacuum and the atmosphere.

the measurements under vacuum. The conductivity values of the deposited films are shown in table 2. The change in conductivity between these two atmospheric conditions took place in no more than one second (from vacuum to ambient) and is shown in figure 4. This rapid process strongly suggests the absorption of water molecules on the sample surface.

The power of the plasma did not significantly influence the conductivity of the films we obtained, at least in the 25-100 W range under investigation.

4/ Temperature dependence of the conductivity

Figure 5 shows the Arrhenius plot of plasma polymerized C_{60} films in the atmosphere and in vacuum. We observed in both case that between 80°C and 230°C the conductivity increased exponentially with temperature. This exponential behavior is similar to that of a semiconductor in this temperature range. The polymerized film manifested the same behavior as the sublimed one[3f] in vacuum except for temperatures below 80°C where the conductivity increases with decreasing temperature. The obtained 'V-shaped' curve in the atmosphere strongly suggests that two different phenomena are at the origin of the conductivity, one predominating at higher temperatures while the other one is more significant at ambient temperatures:
The first, only significant at higher temperatures, is common to sublimed and plasma polymerized C_{60}

and seems to be governed by semiconductor-like properties. In the high temperature region, the conductivity behavior may be considered to be of the Arrhenius type and can therefore be described by the Arrhenius equation:

$$\sigma = \sigma_0 \exp(-\Delta E_f / k_B T) \quad (1)$$

where σ is the conductivity, σ_0 a constant, E_f the Fermi energy, k_B Boltzmann constant and T the absolute temperature. If we assume that this is an intrinsic semiconductor, can estimate the Fermi energy from the slope of figure 5. We then obtain 1.06 eV which leads to a band gap of about 2.1eV, similar to that found in the reference for sublimed films (1.9eV) [3f].

In the latter phenomenon, a higher conductivity at ambient temperatures is generated if the sample is plasma polymerized and if it is surrounded by the atmosphere but not by oxygen, nitrogen or hydrogen. This phenomenon seems to be due to the existence of water molecules in the film as described in the previous section.

CONCLUSIONS

The deposited C_{60} films under RF-plasma of 25, 50 and 100W were found to be polymerized. The surface was highly hydrophilic, polar and heterogeneous.

The electric conductivity of plasma polymerized C_{60} is approximately 10^{-9} S/cm in the atmosphere. It does not depend on the applied voltage in the range -50V to 50V and is about 10^4 times greater than that that measured in sublimed film of C_{60}. A semiconductor-type temperature dependence of conductivity in the higher temperature domain was observed and the band gap energy was estimated to be 2.1eV. This is comparable to a previously reported value for sublimed films. The conductivity increases with increasing temperature from 25°C to 230°C in vacuum, whereas in the atmosphere, the conductivity increases upon decreasing the temperature below 80°C. In the temperature domain below 80°C the electrical conductivity may be enhanced by the existence of water molecules on the film which are attracted, onto the surface at least, from the atmosphere and should increase the intermolecular conductivity of the synthesized film in the atmosphere.

ACKNOWLEDGEMENTS

The authors wish to acknowledge Messrs. K. Nojima, K. Tanaka and A. Kusai of *JEOL* Ltd., for their facilities of TOF-mass observations and Dr. A. Hudson of Sony Corporation for his useful discussions.

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