

Structural, morphological and optical properties of C₆₀ cluster thin films produced by thermal evaporation under argon gas

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 2883

(<http://iopscience.iop.org/0953-8984/13/13/303>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.226

The article was downloaded on 16/05/2010 at 11:44

Please note that [terms and conditions apply](#).

Structural, morphological and optical properties of C₆₀ cluster thin films produced by thermal evaporation under argon gas

Haiyan Zhang¹, Chunyan Wu¹, Lizheng Liang¹, Yiming Chen¹,
Yanyang He¹, Yanjuan Zhu¹, Ning Ke², J B Xu², S P Wong²,
Aixiang Wei³ and Shaoqi Peng³

¹ Department of Applied Physics, Guangdong University of Technology, Guangzhou 510090, People's Republic of China

² Department of Electronic Engineering, The Chinese University of Hong Kong, Hong Kong, People's Republic of China

³ Department of Physics, Zhongshan University, Guangzhou 510275, People's Republic of China

E-mail: hyzhang@gdut.edn.cn

Received 4 October 2000

Abstract

C₆₀ cluster thin films were obtained by thermal evaporation under argon atmosphere. The surface morphology, optical absorption characteristics and structure of these films have been investigated. The ultraviolet–visible optical absorption spectrum of this C₆₀ film is obviously different from that of the film obtained under vacuum conditions. The position and intensity of absorption peaks of the films grown in argon are modified compared with the film grown in vacuum. The bandgap energy changes from 2.02 eV to 2.24 eV. IR analyses show no evidence of chemical change. The x-ray diffraction pattern reveals the existence of a mixture of face-centred cubic and hexagonal close-packed phases. The collisions of C₆₀ molecules and buffer gas molecules are discussed. We also found the surface particles of these C₆₀ cluster films are larger and sharper than those of C₆₀ films prepared in vacuum by the observation of atomic force microscopy (AFM). This may be advantageous for using C₆₀ for electron field emission.

1. Introduction

Solid C₆₀ is the most abundant fullerene discovered by Kroto *et al* [1]. These highly symmetric cage molecules can be assembled in a close-packed solid structure to form a new class of molecular solids. C₆₀ solid thin films offer exciting possibilities for the science and technology of molecular films because of their high stability and relatively strong intramolecular interactions compared with conventional organic molecules. Indeed, studies have shown that solid C₆₀ has many unusual properties such as superconductivity, photopolymerization, and optical nonlinearity [2, 3]. Although the optical properties of

molecular C₆₀ and solid C₆₀ are well characterized [4–7], there remain a number of questions for the solid state C₆₀, such as the photochemical and photophysical characteristics of the structure variations of material. On the other hand, although C₆₀ powder can be produced in inert atmosphere in a large amount, C₆₀ solid thin films produced in inert atmosphere have hardly been investigated. In this paper, we focus on the growth of C₆₀ solid thin films in argon atmosphere. The surface morphology was observed by atomic force microscopy (AFM), and the structure of these thin films is determined by infrared spectra (IR) and x-ray diffraction (XRD). The remarkable change of the optical absorption of C₆₀ thin films grown in argon atmosphere compared with that grown in vacuum was studied by ultraviolet/visible optical absorption spectroscopy spectra.

2. Experiment

C₆₀ cluster thin films (thickness about 3000 Å) were prepared from a pure C₆₀ powder purified to 99.99%, by a thermal evaporation system using 400 °C evaporation temperature in argon (Ar) atmosphere at a pressure of 30 Torr. These C₆₀ cluster thin films grown in Ar atmosphere were deposited on quartz substrates for the purpose of UV/visible absorption spectrum and x-rays diffraction measurement, and silicon substrates for the purpose of infrared measurement, which were not heated during deposition. As comparison, pure C₆₀ thin films were prepared in a vacuum of about 10⁻⁵ Torr. The samples were measured by atomic force microscopy (AFM) using a standard Nanoscope AFM system with a resolution of 5 nm, infrared spectra (IR) using a Bruker Equinox55 FTIR spectrometer, UV/visible optical absorption spectroscopy with an UV-2501 PC Shimadzu UV-VIS recording spectrophotometer and x-ray diffraction (XRD) using a Y-4Q system with scan speed 0.1° s⁻¹, respectively. In order to protect the oxygen sensitive films from environmental influence, the films used for all measurements were kept under vacuum prior to measurements.

3. Results and discussion

3.1. AFM surface morphology

In figure 1 we show the three-dimensional AFM micrographs. The C₆₀ thin film grown in vacuum (figure 1(a)) presents a relatively flat surface in contrast to the film grown in Ar atmosphere (figure 1(b)), in which much higher and sharper protrusions formed in the surface were observed. The average size of surface particles of C₆₀ thin film prepared in Ar atmosphere is about 80 nm, while the average size of surface particles of C₆₀ thin film prepared in a vacuum atmosphere is about 30 nm.

The average growth rate of C₆₀ thin film (V) is determined by its thickness (d) and evaporation time (t)

$$V = d/t. \quad (1)$$

The thickness of C₆₀ thin film can be measured by interferometry of light. An interferometric microscope is employed to examine the thickness of thin film. When the evaporation time is 130 min in Ar atmosphere, the thickness of thin film measured is about 300 nm. So under Ar atmosphere the average growth rate of the thin film (V_{Ar}) is 2.3 nm min⁻¹, while under vacuum the thickness of thin film measured about 150 nm with evaporation time of 30 min. The average growth rate of the thin film (V_0) is 5 nm min⁻¹. Obviously, V_{Ar} is smaller than V_0 .

In Ar atmosphere, the decrease of growth rate is mainly due to collisions between evaporated C₆₀ molecules and Ar molecules in the gas phase. The collision frequency increases

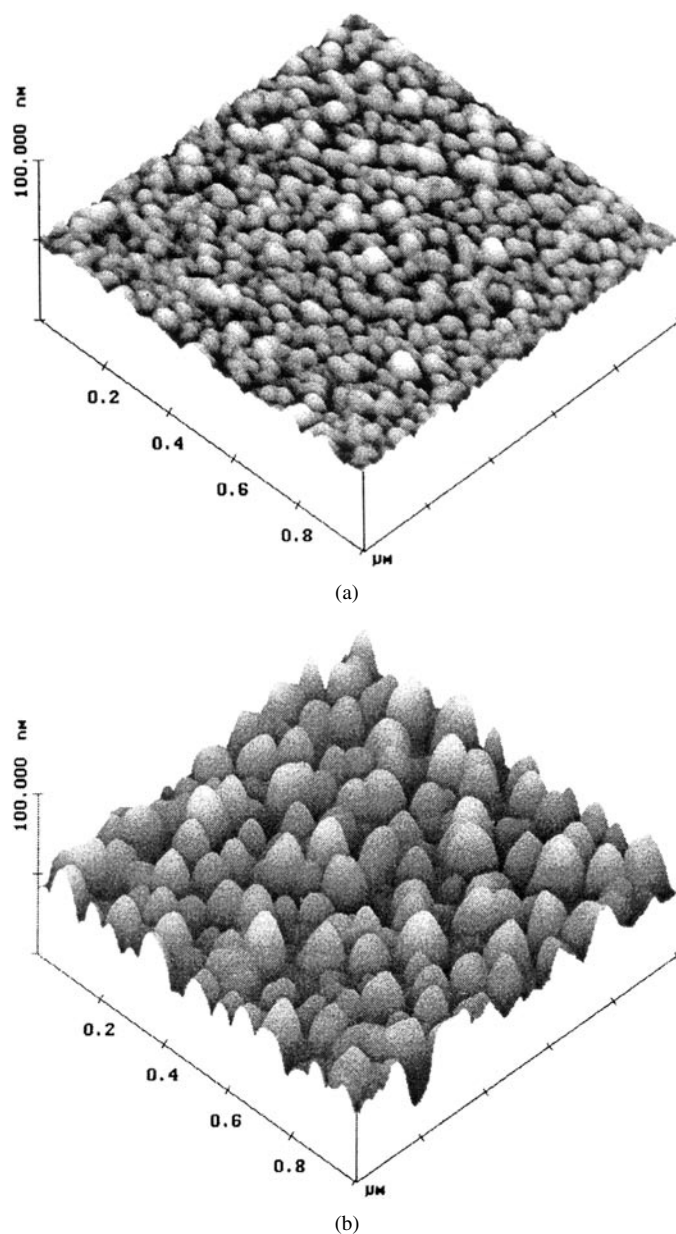


Figure 1. Three-dimensional AFM micrographs of C₆₀ thin film prepared in vacuum (a) and one prepared in Ar atmosphere (b). The x scale is $0.2 \mu\text{m div}^{-1}$ and the z scale is 50 nm div^{-1} in all two micrographs.

rapidly under a certain pressure (e.g. 30 Torr) in comparison with that under vacuum, so that the number of C₆₀ molecules entering the surface of the substrate reduces, which results in the decrease of growth rate of the thin film.

Under a certain pressure P and temperature T , the average collision frequency of evaporated C₆₀ molecules and Ar (or air) molecules in gas phase is determined by the following

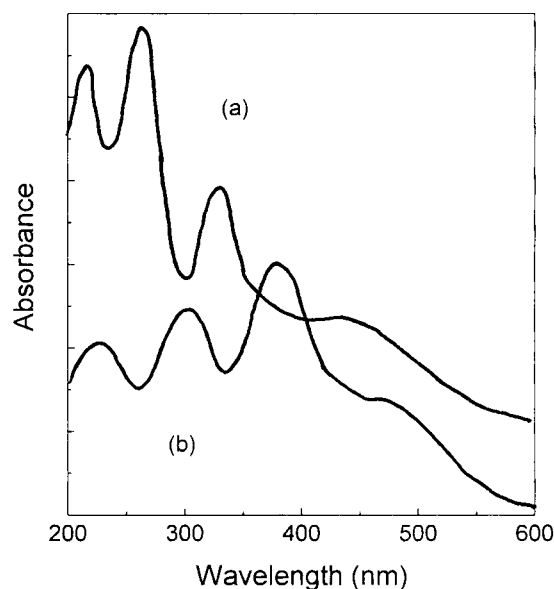


Figure 2. UV/visible absorption spectra of (a) vacuum C₆₀ film, (b) Ar gas C₆₀ film.

formula [8]:

$$Z_x = 1.4\pi d_x^2 v_x P / kT \quad x = \text{Ar (or air)} \quad (2)$$

where v_x is the average velocity of Ar molecules (or air) at temperature T , d_x is the effective diameter of Ar (or air) molecules, k is Boltzmann's constant. Both d_{Ar} and d_{air} are of the order of 10^{-10} m. When the temperature T is 400°C , v_{Ar} is equivalent to 600 m s^{-1} and v_{air} is equivalent to 670 m s^{-1} . Thus, under Ar atmosphere, when pressure P is 4×10^3 Pa (30 Torr), the average collision frequency Z_{Ar} is 10^7 s^{-1} . While under vacuum, with the pressure 10^{-3} Pa, the magnitude of Z_{air} is 3 s^{-1} . It is evident that Z_{Ar} is much greater than Z_{air} .

Moreover, under low vacuum (Ar atmosphere), the chances that C₆₀ molecules come into collision with Ar molecules in the gas phase increase. Probably, C₆₀ molecules form clusters before depositing on the substrate. This enlarges the average size of particles deposited on the surface of substrate compared to vacuum atmosphere.

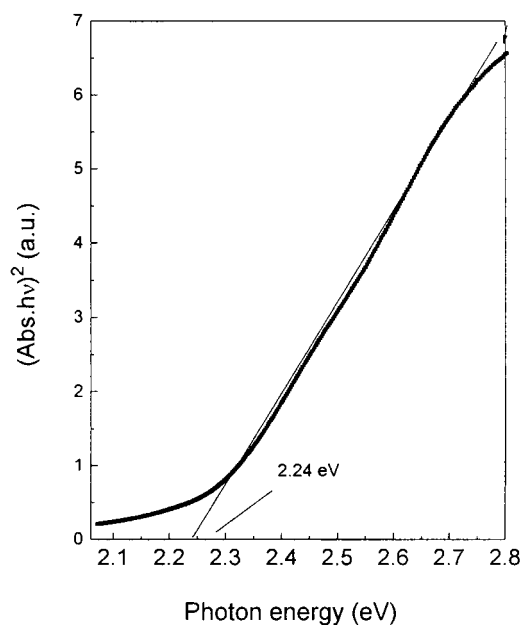
In our previous study [9], C₆₀ thin films had a lower potential barrier than amorphous diamond film, and need a lower threshold field for electron emission than amorphous diamond film. The surface morphology is a major factor responsible for the good emission characteristics, so the sharp surface of the C₆₀ film grown in Ar atmosphere may be very advantageous for using C₆₀ thin film for electron field emission.

3.2. UV/visible optical absorption spectroscopy

Figure 2 shows a comparison of UV/visible absorption spectra taken on a C₆₀ film prepared in Ar atmosphere (Ar gas C₆₀ film) and a C₆₀ film prepared under vacuum condition (vacuum C₆₀ film). The vacuum C₆₀ film (a) shows the well known solid C₆₀ UV/visible absorption spectrum. The Ar gas C₆₀ film (b) shows a weaker absorption in comparison with the vacuum C₆₀ film. The significant changes in the optical absorption spectrum are clearly observable for the Ar gas C₆₀ film. Firstly, a continuous red shifting of all feature peaks occurs. The data for

Table 1. The wavelength and correspondent energy of UV/visible optical absorption peaks of C₆₀ thin films in different conditions.

Preparation conditions	Corresponding C ₆₀ transition energy level		
	$h_g \rightarrow t_{2u}$	$h_u \rightarrow h_g$	$h_g \rightarrow t_{1u}$
Vacuum	218 nm (5.7 eV)	265 nm (4.7 eV)	342 nm (3.6 eV)
Ar atmosphere (30 Torr)	225 nm (5.5 eV)	305 nm (4.1 eV)	380 nm (3.3 eV)

**Figure 3.** Plot of $(\text{Abs. } h\nu)^2$ (where Abs. is the absorbance) against photon energy for the Ar gas C₆₀ thin film sample.

the wavelength and energy of absorption peaks are given in table 1. The effect of oxidation did not cause this spectral shifting [10]. Secondly, the absorption intensity decreases, and there is a selective loss of absorption intensity from some transitions, particularly from the allowed electronic transitions in the 200–400 nm region. The intensities corresponding to three major absorption peaks at 218, 265 and 342 nm respectively change dramatically compared with vacuum C₆₀ film. For example, the peak at 342 nm is the weakest among the three peaks in vacuum C₆₀ film, but this peak is the strongest among the three peaks in Ar gas C₆₀ film. This is the major result for C₆₀ thin films grown under Ar atmosphere according to our observations. The action of Ar gas is responsible for the variation in relative intensity of three UV/visible absorption peaks.

We have analysed the low energy part of the absorption spectrum according to the well known expression (3) derived for the fundamental absorption of the direct transition in semiconductors. The absorption coefficient as a function of photon energy can be expressed as

$$(\alpha h\nu)^2 = C(h\nu - E_g) \quad (3)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the bandgap energy and C is a constant. A plot of $(\text{Abs. } h\nu)^2$ (Abs. is the absorbance and is in direct proportion to α)

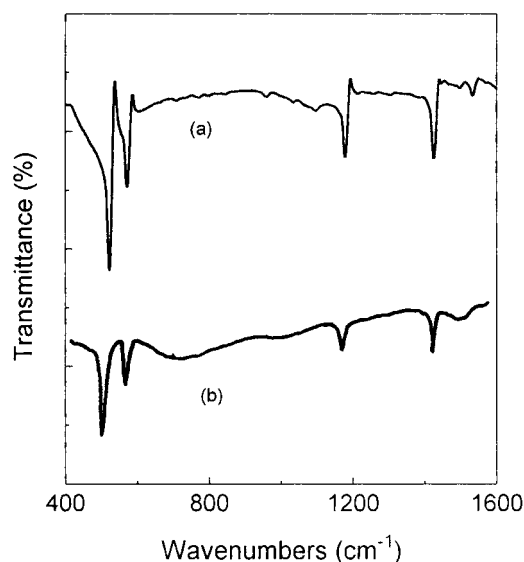


Figure 4. IR spectra of (a) vacuum C₆₀ and (b) Ar gas C₆₀ film.

against $h\nu$ is shown in figure 3. The optical bandgap E_g of the C₆₀ thin films between the HOMO (h_u) and the LUMO (t_{1u}) bands can be estimated by assuming a direct transition, so the above equation (4) allows us to infer a direct bandgap from the linear dependence observed and to evaluate a bandgap energy of 2.24 eV from the x -axis intercept in the extrapolated straight line. The graphs of $(\text{Abs. } h\nu)^{1/2}$ against $h\nu$ instead of $(\text{Abs. } h\nu)^2$ against $h\nu$ were not found to lead to straight lines over any part of the optical absorption spectrum: this supports the interpretation of a direct bandgap rather than an indirect bandgap for these C₆₀ thin films. Compared with our previous measurement of 2.02 eV for vacuum C₆₀ thin film in the fcc ordered structure, the result shows the bandgap energy of Ar gas C₆₀ thin film is larger than that of vacuum C₆₀ thin film. This may lead to a decline as a whole in absorption intensity.

3.3. Infrared spectroscopy

Figure 4 shows the IR spectra of an untreated C₆₀ film (vacuum C₆₀ film) (a) and a C₆₀ film grown in Ar atmosphere (Ar gas C₆₀ film) (b). The IR spectrum of the C₆₀ thin films prepared in Ar atmosphere shows the four typical IR active modes associated with the pristine C₆₀ solid (located at 527, 574, 1181, 1430 cm⁻¹). Except for absorption peak intensity, no spectral position changes between Ar gas and vacuum C₆₀ films are seen, which indicates that no chemical modification has taken place during the thermal evaporation of the C₆₀ powders in Ar atmosphere.

3.4. X-ray diffraction

UV/visible and IR measurements indicate that the effects of Ar atmosphere are not chemical in nature, but may be related to changes in structure. Indeed x-ray structural analyses of C₆₀ films grown in Ar atmosphere reveal significant changes compared with C₆₀ films grown in vacuum conditions. The vacuum C₆₀ film has been found to possess a face-centred cubic unit cell with $a = 14.172 \pm 0.003$ Å. Although the C₆₀ film is poorer in the overall crystalline than

C₆₀ powder, we can observe several new lines which can not be attributed to the cubic phase (fcc), but which is attributed to hexagonal phase (hcp). Three strongest diffraction lines for the fcc structure are at 20.3, 17.2 and 10.2 degree (2θ angle), which are respectively indexed as the (113), (022) and (111) lines of a face-centred cubic unit cell, with $a = 14.0175 \pm 0.004$ Å, while the three strongest diffraction lines for the hcp structure are at 24.1, 23.6, 21.2° (2θ angle), which are respectively indexed as the (014), (022), (004) lines of a hexagonal unit cell, with $a = 9.968 \pm 0.025$ and $c = 16.335 \pm 0.050$ Å [10].

A possible explanation of the obtained results is that Ar gas C₆₀ films consist of hcp phase and fcc phase. The hcp phase of C₆₀ film with a closer packed lattice, makes the interaction between C₆₀ molecules stronger. This variation in structure leads to an expansion for energy bands, and thus causes the red shifting of absorption peaks and an enhancement of the optical absorption in the low energy range.

Transmission electron microscopy (TEM) observation shows the average diameter of these spherical clusters is about 100 nm. Initial measurement of the electron diffraction pattern indicates that C₆₀ clusters are polycrystalline with lattice parameters $a = 1$ nm and $c = 1.6$ nm associated with the hcp structure. In Ar atmosphere, C₆₀ molecules collide with buffer gas molecules to form clusters: these C₆₀ clusters deposited on the substrate can probably lead to C₆₀ thin film with hcp structure, while change of structure may be the reasons for the red shifting of absorption peaks, dropped absorption intensity and expanded absorption peaks of UV/visible absorption spectra of Ar gas C₆₀ film.

4. Conclusions

AFM micrographs show the Ar gas C₆₀ films have much sharper and higher tips formed on the surface than vacuum C₆₀ films. IR and x-ray diffraction spectra indicate that C₆₀ thin films prepared in Ar atmosphere do not cause chemical changes, but cause a structural change. X-ray diffraction reveals C₆₀ thin films prepared in Ar gas to have a mixed phase of fcc and hcp: the data suggest that this film produces a closer-packed lattice of C₆₀ molecules. This lattice has a significant difference in optical properties compared with that of C₆₀ thin film prepared in vacuum.

Acknowledgment

This work is supported by Guangdong Provincial Natural Science Foundation of China.

References

- [1] Kroto H W *et al* 1985 *Nature* **318** 162
- [2] Hebard A F *et al* 1991 *Nature* **350** 600
- [3] Knize R J and Partaneu J P 1992 *Phys. Rev. Lett.* **68** 2704
- [4] Howard J B *et al* 1991 *Nature* **352** 141
- [5] Ebbesen T W, Tanigaki K and Kuroshima S 1991 *Chem. Phys. Lett.* **181** 501
- [6] Capozzi V, Casamassima G and Lorusso G F 1996 *Solid State Commun.* **98** 853
- [7] Katz E A 1999 *Solid State Phenom.* **67** 435
- [8] Sears F W, Zemansky M W and Young H D 1976 *Univ. Phys.* **2** 137
- [9] Chen Jun, Wei Aixiang, Zhang Haiyan *et al* 1997 *Chin. Phys. Lett.* **14** 949
- [10] AkseIrod L, Byrne H J, Sutto T E and Roth S 1995 *Chem. Phys. Lett.* **233** 436