Volume 3, Number 5 ACTA PHYSICA SINICA May, 1994
1004-423X/94/03050360-06 (Overseas Edition) © 1994 Science Press

# A DOUBLE-TEMPERATURE-GRADIENT TECHNIQUE FOR THE GROWTH OF PURE $C_{60}$ SINGLE CRYSTALS FROM THE VAPOR PHASE

WANG GANG(王 刚), XIE SI-SHEN(解思深), LIU WEI(刘 维),
FU CHUN-SHENG(傅春生)†, LI CHAO-RONG(李超荣), WANG CHANG-QING(王昌庆),
LI NAN(李 楠), QIAN SHENG-FA(钱生法), ZHANG ZE-BO(张泽勃),
YU YU-DE(俞育德), and ZHOU WEI-YA(周维亚)
*Institute of Physics, Academia Sinica, Beijing* 100080, *China*
†*Beijing Institute of Technology, Beijing* 100081, *China*

(Received 4 October 1993)

Pure $C_{60}$ single crystals were grown by a sublimation-condensation method in an evacuated closed quartz tube situated in a double-temperature-gradient furnace. Large $C_{60}$ single crystals, up to a size of 0.6 mm×1.0 mm×2.0 mm with quite smooth and shiny faces, were obtained. X-ray diffraction, electron diffraction and X-ray morphology were carried out and showed that the quality of large $C_{60}$ single crystals grown by the double-temperature-gradient technique is excellent. In this paper the experimental results of the growth of large $C_{60}$ single crystals are reported and the morphological and structural characterizations are discussed in detail.

**PACC:** 6150C; 8110; 6110

## I. INTRODUCTION

In the past few years, the investigation on all-carbon molecules has become one of the most interesting topics in condensed matter physics, chemistry and materials science. Recent researches focus on the preparation, magnetic properties, phase transition and superconductivity of new fullerites. And most of the studies so far have been done on polycrystalline powder samples or thin films. However, a thorough understanding of the underlying nature of fullerene molecules can only be achieved through studies of single crystals of this kind of material. Hence, it is desirable to obtain highly pure single crystals of sufficiently large size for various properties measurements.

To grow defect-free single crystals of pure $C_{60}$ with large size from the vapor phase needs not only to minimize the interactions between the crystal interface and the mother phase as well as those between crystals and supporting quartz tube[1], but also to keep sufficiently high vapor pressure of $C_{60}$ inside the quartz tube simultaneously. Therefore, we have developed a furnace with double, instead of single, linear-temperature-gradients for the preparation of pure and large monocrystalline $C_{60}$ from a sublimation-condensation process in the middle of an evacuated closed quartz tube.

In this paper the experimental results of the growth of $C_{60}$ single crystals by the double-temperature-gradient technique from the vapor phase are reported. The morphological and the structural characteristics of pure $C_{60}$ crystals are discussed in detail.

## II. EXPERIMENTAL

### A. Preparation of $C_{60}$ powder

The starting powder of $C_{60}$ with a purity of 99.9% was separated by toluene extraction and liquid chromatography from the soot produced by arc discharge. Details of the preparation have been described elsewhere[2].

### B. Growth of $C_{60}$ single crystals by double-temperature-gradient technique from the vapor phase

The $C_{60}$ powder was placed at the closed end of a 60 cm long quartz tube with an inner diameter of 8 mm. The tube with the powder was evacuated to $10^{-3} - 10^{-4}$ Pa and heated at 523 K for 4 h to remove all the aromatic solvents initially present in the $C_{60}$ powders formed after solvent evaporation of the chromatographically separated solution. Then the temperature was gradually increased to 873 K in order to sublimate the $C_{60}$. After six hours about two thirds of the $C_{60}$ powder was sublimated to the colder part of the tube, and the segment of the tube between hotter end and the colder part was sealed off. This process was repeated two or three times in order to effectively separate the low-vapor-pressure fragment from the impurities and the pure $C_{60}$ material was isolated. Finally the high purified $C_{60}$ was placed at one end of the quartz tube (about 30 cm long) and the other sealed end of the tube was empty.

The repeated sublimation process could be simplified by substituting small $C_{60}$ single crystals for $C_{60}$ powder as a starting material sealed into a 30 cm long evacuated quartz tube with an inner diameter of 8 mm, i.e., the small $C_{60}$ single crystals was at one end of the tube and the other end of the tube was empty.

The quartz tube with the source material was placed in a horizontal resistance-heated furnace with double-temperature-gradient (V-shape temperature profile), which was developed from a furnace with single linear-temperature-gradient adopted previously[2]. The hot (863 K) and the cold (823 K) regions of the tube were controlled by two DWK-702 precision temperature controllers, respectively. These conditions were maintained for three days. Then the temperature of the hot end was decreased down to 823 K and subsequently both regions were slowly cooled from 823 K to room temperature at a rate of about 43 K/h.

### C. Electron diffraction, X-ray morphology and X-ray diffraction

Samples for electron diffraction were prepared with the crushed single crystal powder. Electron diffraction experiments were performed on a JEM 200 CX microscope.

X-ray morphology experiments were carried out with a RU-200 12 kW rotating anode, operating at 40 kV, 50 mA. Mo$K\alpha$ radiation was used. The divergence angle of the incident X-ray beam was about 0.02°. The transmission Lang patterns were taken by making use of the diffraction from (110) plane and recorded by the high-resolution emulsion film with exposure time of 5 h.

Powder X-ray diffraction data of smashed $C_{60}$ crystals were obtained at room temperature using a Guinier-de Wolff focusing camera with Cu$K\alpha$ radiation, and high purity silicon powder as an inner calibration standard.

## III. RESULTS AND DISCUSSION

The large pure $C_{60}$ crystals were grown in the center of a double-temperature-gradient furnace by adjusting the temperatures of the hot regions (two ends of the quartz tube) and the cold region (the center of the tube). It was observed with an optical microscope that the majority of $C_{60}$ single crystals were polyhedra exhibiting clean and shiny {111} or {100} faces and the average edge length of the single crystals was 1 mm. A few of the large single crystals have the size about 0.6 mm×1.0 mm×2.0 mm.

The X-ray morphology pattern of a $C_{60}$ single crystal is shown in Fig. 1.

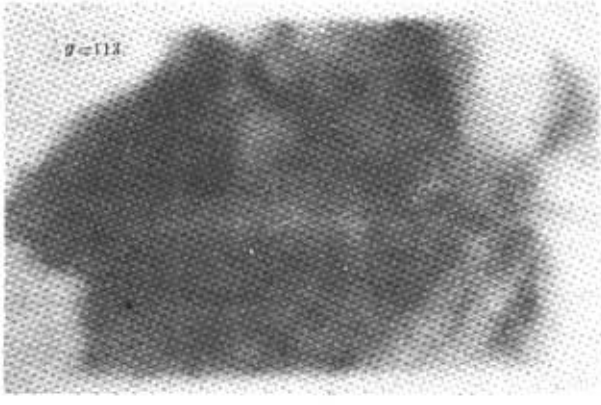

**Fig. 1.** X-ray morphology pattern of the $C_{60}$ single crystal.

As shown in Fig. 1, almost the entire sample contributes to the diffraction, which indicates an excellent monocrystalline character of the sample. Different contrast in different ranges is also shown in Fig. 1. This contrast difference is due to the different orientation of the crystal,

i.e., Bragg diffraction condition cannot be simultaneously satisfied at different parts of the crystal because of the small mis-orientation. In other words, there exists mis-orientation or mosaic structure in the crystal.

The electron diffraction patterns and the high-resolution electron microscopic (HREM) images are shown in Figs.2–5.

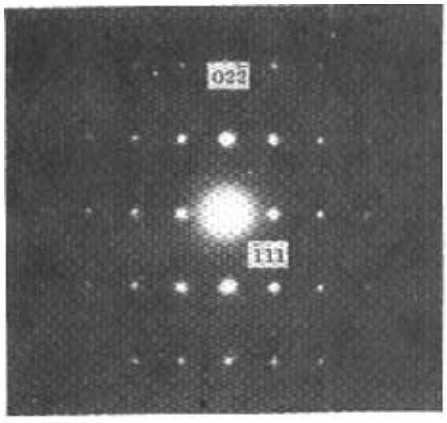


**Fig. 2.** Electron diffraction pattern along the [211] zone.

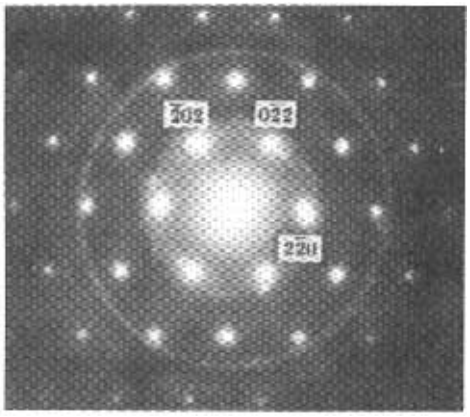


**Fig. 3.** Electron diffraction pattern along the [111] zone.

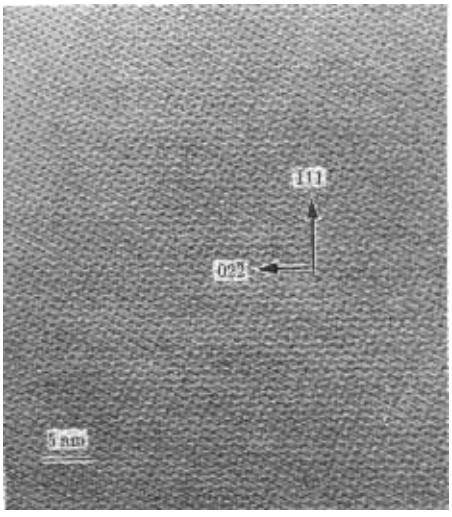


**Fig. 4.** High-resolution electron microscopic image corresponding to the diffraction pattern shown in Fig.2.

The shape and quality of $C_{60}$ crystals grown by the double-temperature-gradient technique depend on the conditions in the cold region (crystal growth region). A sharp concave minimum of the V-shaped temperature profile promoted the formation of a large single crystal. A temperature plateau in this region causes numerous nucleation centers and thus more crystals of different quality, size, shape and surfaces were observed. The occurrence of twinned and multiply-twinned particles were frequent. These crystals are different from those grown by the linear-temperature-gradient technique[2].

Just as the general features of fcc crystals, in the case of $C_{60}$ different kinds of defects like twins and stacking faults can be easily introduced especially in the (111) plane[1,3], as shown in Fig.5. Usually the twins result from strain during the crystal growth process. Some origins that a crystal may grow as a twin are known to be: growth of twins from a twinned nucleus; developing of two crystals in close proximity so that they finally overlap; influence of impurities; generation of stacking faults;

mechanical deformations, etc.

The twinning occurs in the form of two or more individual crystallites with the twin boundaries visible under an optical microscope. In the case of rather large crystals it was possible to separate the parts of the twinned crystal mechanically by cutting the sample with a blade. The faces thus obtained were quite smooth and shiny with a triangular shape.

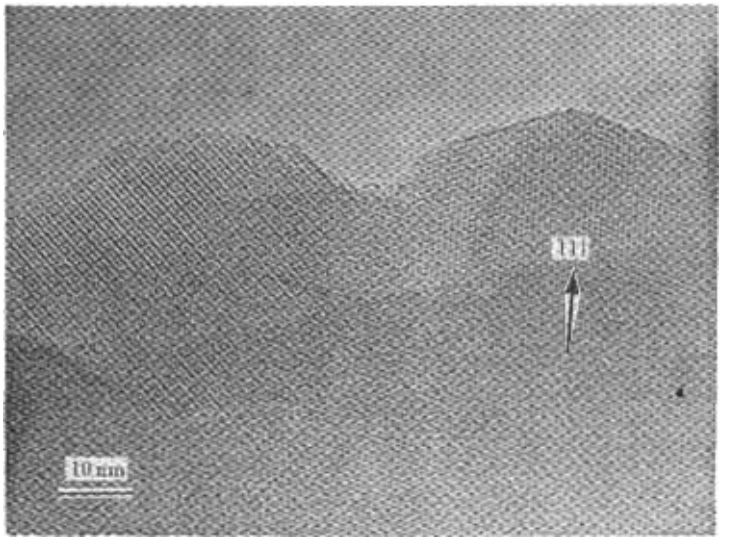


**Fig. 5.** High-resolution electron microscopic image viewed along the [110] zone.

In some cases the surface could be characterized as dendrites. Dendrites can grow in two seemingly independent process. One is the steady-state propagation of the dendrite main stem and the other is the non-steady-state evolution of dendrite branches.

Other types of surfaces with a sharp "barrier" on the edges of the crystal planes were observed at the positions with higher temperatures (i.e. places closer to the source of powder or smaller crystals of $C_{60}$). This kind of surface probably developed during the decrease of temperature from 863 to 823 K at the end of the growth process and the steady state was disturbed. Thus, near the end of the quartz tube the crystals would grow with a "barrier", whereas in the center of the tube the crystals would grow with a smooth surface.

Since the {111} faces have a higher stability than {100} faces in an fcc structure, if conditions of the crystal growth are not optimized {100} faces would not be perfect, whereas {111} faces are still shiny. When the growth conditions are even worse both (100) and {111} faces will be roughened.

To ensure good quality of monocrystals these influences inducing the twins mentioned above must be suppressed or eliminated. The following precautions could be taken: cleaning the crystal growth region of the quartz tube; stabilizing crystal growth conditions including

the temperature gradients; using high purity $C_{60}$ powder; adjusting suitable supersaturation such that untwinned nuclei may preferably grow in a barely saturated vapor.

The advantage of the double-temperature-gradient technique for the growth of single crystals is due to the absence of crystal deformation caused by the conical geometry at the end of the tube. Thus the crystals grown by this method generally show clean and shiny faces and the size of the crystals can be made large. Different from the linear-temperature-gradient technique, the size of $C_{60}$ crystals grown by this technique are virtually determined by the amount of source material and by the time the temperature gradient can be maintained.

## IV. CONCLUSIONS

Large crystals of $C_{60}$ (up to the size of 0.6 mm×1.0 mm×2.0 mm) can be grown from the vapor phase by the double-temperature-gradient technique. The results of X-ray diffraction and electron diffraction confirm the expected fcc structure of $C_{60}$ single crystals with the lattice parameter of $a = 1.4205$ nm at room temperature. X-ray diffraction, electron diffraction and X-ray morphology indicate that the quality of the $C_{60}$ crystals grown by the described technique is excellent. Though the twinning easily occurs during the growth of $C_{60}$ crystal, it is possible to obtain larger size $C_{60}$ single crystal provided that the origin of the twinning could be suppressed.

## REFERENCES

[1] M. Haluska, H. Kuzmany, M. Vybornov, P. Rogl and P. Fejdi, *Appl. Phys.*, **A56**(1993), 161.
[2] Wang Gang, Xie Si-shen *et al.*, *Acta Physica Sinica*, to be published (in Chinese).
[3] M. A. Verheijen, H. Meekes, G. Meijer, E. Raas and P. Bennema, *Chem. Phys. Lett.*, **191**(1992), 339.