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The Structure and Mechanical Properties of C_{60} Fullerite

S.O. Rudchenko*, A.T. Pugachov, V.E. Pukha, V.V. Starikov

National Technical University "KPI", 21, Frunze Str., 61002 Kharkov, Ukraine

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The fullerite films with texture (110) were prepared by the condensation of C_{60} molecules on KCl, LiF, and Si substrates. The hardness (H = 0.42 GPa) and Young's modulus (E = 14.1 GPa) of the fullerite films were determined by nanoindentation method at continuous scanning in depth. The results were compared with theoretical estimates of elastic modules and previous works on measurements of elastic characteristics and hardness of crystalline C_{60}.

Keywords: Fullerene, Fullerite, Microdiffraction, Nanohardness, Elastic modulus.

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1. INTRODUCTION

During the last decade one can observe an increasing interest of the researchers to the study of the physical properties of fullerites, i.e. molecular crystals, in whose lattices large hollow carbon molecules of fullerene of the general formula $C2n$ ($10 \le n \le 120$) are located.

Intermolecular interaction of the most studied fullerites, consisting of C_{60} molecules, is characterized by weak Van der Waals bonds with a small "impurity" of covalency. Orientational phase transition from the close-packed fcc-phase Fm3m to the simple cubic Pa3 is observed at $T \cong 260$ K and transition to the state of orientational glass – at $T = 90$ K.

Internal structure of C_{60} molecules is not actually changed in the formation of fullerite crystals, and intermolecular distances are found to be approximately an order of magnitude larger than the interatomic ones. As well as in usual molecular crystals, binding energy of molecules in fullerite is much lower than the intramolecular one, and, as a result, frequencies of the translational and librational oscillations of its lattice are considerably lower than the oscillation frequencies of carbon atoms in C_{60} molecule.

At the same time, fullerites are unique in that they allow doping by atoms of any sizes (from hydrogen to uranium), whereupon they are considered as promising materials for a new generation of devices of micro- and nanoelectronics, superconducting electronics, molecular traps for atoms including radioactive, high-capacity light rechargeable batteries, etc.

Elastic, plastic and strength properties are traditionally ascribed to the fundamental properties of crystalline solids. Elastic properties depend on the quantum-mechanical state of material particles which form a crystal – atoms, ions or molecules, i.e. on the character of the chemical bond.

The first experimental measurements of the elastic constants of fullerite were performed on the basis of measurements of ultrasonic velocities (frequency of 5 MHz) in monocrystalline samples of different crystallographic orientations [1]. However, such measurements are only possible after the production of monocrystalline C_{60} of a rather large size and high quality. Elastic constants of monocrystalline C_{60} were determined by the X-ray diffraction data; theoretical calculation of elastic constants of monocrystalline C_{60} was performed based on realistic force models; hardness and elastic modulus of monocrystalline C_{60} were measured along the direction (111) of the fcc-lattice by the nanoindentation method [2-4]. It is understandable that measurements on monocrystals give more complete information, however, very small sizes and irregular geometric shape of monocrystals does not allow to perform measurements with high accuracy. Currently, there are papers on measurements of the elastic properties of polycrystalline, and, more precisely, compacted samples of fullerite [5] and measurements on polycrystalline films by the method of surface acoustic waves [6].

Experimental and calculated values of the elastic mo-dulus presented in the mentioned works are sometimes significantly different. The situation is more ambiguous when object is not a monocrystal, but is a polycrystal. The aim of the given work is the experimental determi-nation of the elastic modulus and hardness of polycrystalline fullerite using the nanoindentation technique.

2. INVESTIGATION MATERIALS AND TECHNIQUES

Powder of C_{60} fullerene of the purity of 99.5 % (NeoTechProduct, Saint-Petersburg, Russia) was used for the production of C_{60} films. Fullerene powder was cleaned before use by the vacuum distillation.

Films of C_{60} fullerite of the thickness of 4.3 μm were obtained by the method of thermal vacuum deposition (pressure in the vacuum chamber was $P = 5 \times 10^{-6}$ Torr, deposition rate – 1 Å/s) on KCl, LiF, and Si monocrystals at the substrate temperature of 50 °C.

Microscopic investigations of the structure of the obtained C_{60} films were carried out on the transmission electron microscope PEM-125K with resolution of 0.2 nm. Preparation of the samples for TEM was performed by dissolution of alkali halide crystals after film deposition; then films were washed in deionized water and placed on a copper grid.

Nanohardness and elastic modulus of C_{60} films were measured by nanoindenter MTC G200 using Berkovich

* sveta_rud87@mail.ru

diamond point ($R < 20$ nm). The technique of continuous scanning in depth was used and this allowed to register the elastic modulus and hardness versus the indenter penetration depth. The values of E and H were defined at the indenter penetration depth of 10-15 % of the film thickness. Results were averaged after 5 measurements for the given sample.

3. RESULTS AND DISCUSSION

Use of the continuous stiffness measurement (CSM) method allows to register the nanohardness H and elastic modulus E as the function of the indenter penetration depth. Mechanical tests were performed for films of C_{60} fullerite of the thickness of 4.3 μm deposited on Si, KCl and LiF plates at the substrate temperature of $Ts = 50$ °C. Different substrates and thick films were used in the experiment in order to exclude the influence of the substrate on the real values of nanohardness and elastic modulus of fullerite.

Electron microscopic investigations of fullerite films on KCl and LiF substrates indicate that films have the face-centered cubic (fcc-) lattice with the lattice parameter of 1.42 nm and grain size of 1 μm. Electron diffraction patterns contained reflections of (111), (220), (311), (420), etc. types typical for (211)-orientation in the fcc-lattice (Fig. 1). Non-uniform distribution of the intensity over the ring (220) implies that planes (220) of the majority of grains are oriented along the primary beam, and texture (110) is realized in the studied films.

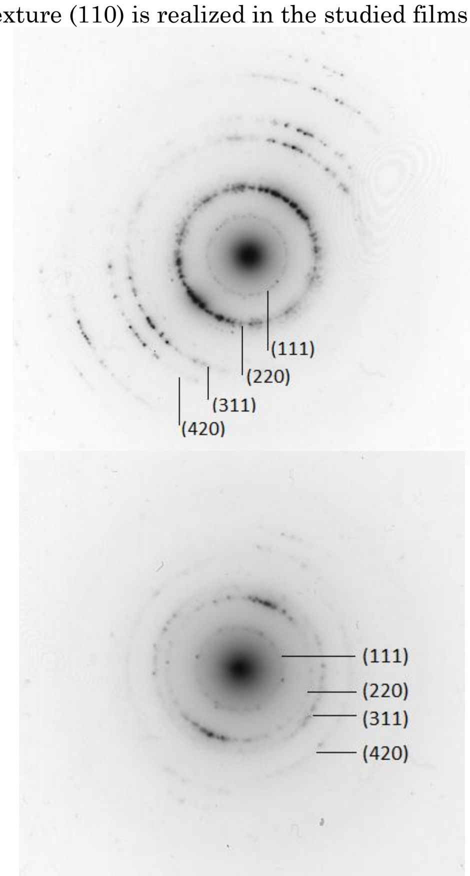

Fig. 1 – Patterns of microdiffraction of thin C_{60} fullerite films on the substrate: a – KCl and b – LiF

Trihedral diamond pyramidion – the Berkovich indenter with the grinding angle of 65° and point radius of 10 nm – was used for the indentation. Loading occurred automatically at room temperature. Loading and unloading diagrams are represented in Fig. 2.

Maximum loading was equal to 3.7-3.9 mN, indenter penetration depth at maximum loading – 600 nm, and after unloading – 550 nm. We should pay attention to a large area between loading and unloading curves which is proportional to the irreversible energy loss during the indentation. At unloading residual plastic deformations in the film are substantial and elastic restoration is insignificant (< 10 %).

In Fig. 3 and Fig. 4 we show the dependences of E and H on the indenter penetration depth. In Table 1 we present the measured values of the elastic modulus and nanohardness of fullerite film on different substrates.

As seen from Table 1, at the film thickness of 4.3 μm substrate does not considerably influence the values of E and H, and, based on the results of nanoindentation, hardness and elastic modulus of the fullerite film are $H = 0.42$ GPa and $E = 14.1$ GPa, respectively. The value of elastic modulus coincides well with the data obtained at the theoretical calculation of the elastic modulus for the direction (110) in the fcc-lattice of monocrystalline fullerite ($E_{110} = 14.7$ GPa) [3], calculations performed on the basis of measurements of sound speed in monocrystalline C_{60} ($E_{110} = 13.2 \pm 1$ GPa) [1], and value of elastic modulus of polycrystalline C_{60} ($E = 12.6 \pm 0.45$ GPa) calculated from the values of moduli C_{ij} for monocrystal [1, 3, 6]. At the same time, the value of hardness significantly exceeds the values presented in [7], but agrees well with the data obtained on polymerized fullerite [8]. This data is given in Table 2.

It is known that during irradiation of C_{60} films by the visible or ultraviolet radiation, as well as during the interaction with oxygen, polymerization (photopolymerization and formation of oxypolymer film on the fullerite surface) is observed in the near-surface layers of fullerene [9-11]. The films we have studied were stored without special measures to guard against the influence of oxygen and illumination; and therefore we suppose that the polymerization processes took place on our samples as well.

Table 1 – Elastic modulus and hardness of C_{60} fullerite film on different substrates

Substrate	E, GPa	H, GPa
Si	14.159 ± 0.642	0.411 ± 0.036
KCl	13.995 ± 0.359	0.419 ± 0.057
LiF	14.23 ± 0.755	0.421 ± 0.049

Table 2 – Results of nanoindentation of C_{60} fullerite

	E, GPa	H, GPa
Experimental data	14.1	0.42
C_{60} (110) (literature data)	14.7[3]; 13.2 [1]; 12.6 [1, 6]	0.024
Polymerized C_{60} (literature data)	–	0.4-0.65

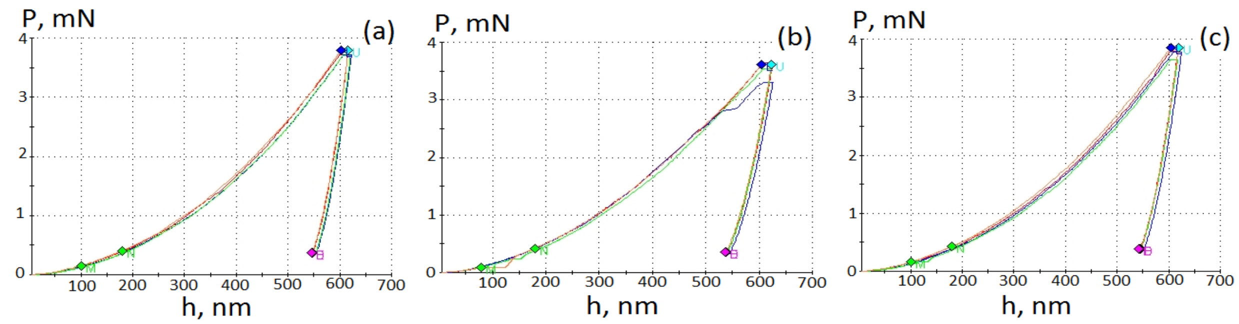

Fig. 2 – Loading curves of C_{60} fullerite films on different substrates: a – Si, b – KCl, c – LiF

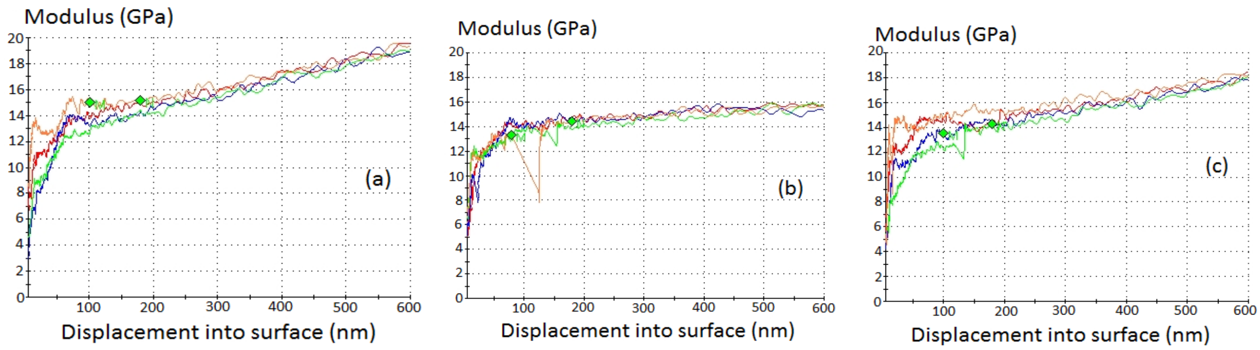

Fig. 3 – Elastic modulus of C_{60} fullerite films on different substrates: a – Si, b – KCl, c – LiF

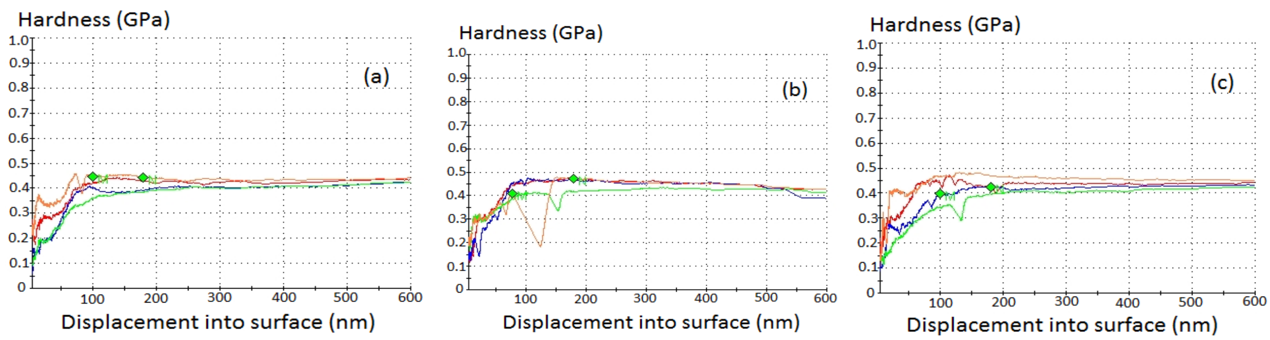

Fig. 4 – Nanohardness of C_{60} fullerite films on different substrates: a – Si, b – KCl, c – LiF

4. CONCLUSIONS

Polycrystalline C_{60} fullerite films for which texture (110) is realized were prepared in this work. Using the nanoindentation technique for the obtained objects, we have measured the elastic modulus ($E = 14.1$ GPa) and hardness ($H = 0.42$ GPa). Results of our measurements agree with the results of the majority of previous estimates of the elastic properties of solid C_{60}. At the same time, the value of hardness considerably exceeds the values presented in other works (0.024 GPa), but agrees well with the data obtained on polymerized fullerite ($H = 0.4$-0.65 GPa).

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