IRRADIATION-INDUCED POLYMERIZATION AND DAMAGES OF FULLERITE C_{60} UNDER IRRADIATION WITH Fe IONS

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Results of thin fullerite C_{60} films irradiation with Fe⁺ ions, energy of which is E = 140 keV and doses varied from 1.2 \times 10^{12} to 0.66 \times 10^{13} ions/cm² are considered. Raman spectroscopy and XRD data show that after irradiation of fullerenes C_{60} with Fe⁺ ions dimmers and polymers with orthorhombic and tetragonal structures are formed that is similar to phases formed under high temperatures and pressure. At higher doses polymerized phases disappear because of destruction and formation of amorphous phase.

1. INTRODUCTION

In the condensed state C_{60} molecules form molecular crystals with Van der Waals interaction. High temperature face centered cubic structure has lattice parameter 1.4177 nm and at temperature T_c = 260 K it transforms into simple cubic lattice with lattice parameter 1.39 nm, at T = 100 K the amorphous phase forms. In the compressed fcc phase (density ρ = 1.72 g/cm³) distance between nearest molecules C_{60} - C_{60} is 1.002 nm. Due to that fullerenes have great octahedral pores with radius 0.207 nm and tetrahedral ones with radius 0.112 nm [1]. Due to that lattice parameter depends on method of preparing of the film and can vary, moreover hcp phase can be formed with lattice parameter a = 1.020 nm and c = 1.638 nm [2]. Structural transformations influence on the physical and chemical properties of fullerenes. More significantly properties of fullerenes change when dimmers are formed and Van der Waals interaction changes by covalent one. Appearance of covalent bonds is possible at photopolymerization [3], influence of pressure in region of 5...20 GPa and temperatures of 300...1800 °C [4], doping with alkali metals (K, Na, Rb, Cs) [5], electron irradiation with energy ~ 150 to 1500 eV [6], bombardment with heavy and light ions [7].

In all cases of polymerization covalent bonds are realized by [2+2] cycloaddition with formation of C – C intermolecular bonds linked by four-membered rings due to that the molecular dimer has dumbell-like shape [8]. Electron irradiation leads to more complicated covalent interaction in result of that form peanut-shaped dimers and polymers [9].

Each molecule can have one, two, four or six [2+2] cycloaddled bonds depending in that fcc phase transforms into: orthorhombic, tetragonal, rhombohedral or 3D polymerized phase with pseudotetragonal lattice. Due to appearance of chemical bonds between molecules along cube-face diagonal of fcc phase (1D-C_{60}) orthorhombic phase forms; appearance of four [2+2]-cycl addled bonds between molecules located at plane (100) or between six molecules located at (111) plane of fcc structure results in twodimensional net (2D-C_{60}), that leads to tetragonal and rhombohedral (point symmetry group D_{3h}, spatial group P3m1) structures [10]. Three dimensional structure (3D C_{60}) forms under application of high pressure (20 GPa) and temperature (~ 1200 °C) and has Immm spatial group with lattice parameters a = b = 0.99 nm and c = 1.070 nm.

Changes of structure influence properties of fullerites: for example hardness of 3D C_{60} structure is comparable with diamond, its electron structure has metallic nature with high density of states near Fermi level that is completely different from fcc phase that is semiconductor with band gap ~ 1.8 eV [11]. At low pressure (~ 5 GPa) and temperature in region 300...400 °C, as at high doses of ultraviolet irradiation takes place transformation from fcc phase to compressed fcc phase with lattice parameter 1.380 nm, at moderate conditions in fullerites dominates formation of dimers.

Ion irradiation also gives a variety of possibilities for modification of physical and chemical properties. Type of bombardment particles, their charge, fluence, temperature of target significantly influences mechanisms of interaction with fullerite target. Among the mechanisms is polymerization of C_{60} molecules and destruction, the latter leads to amorphization. This is accompanied by complicate processes intensity of which depends on different factors and none can be exactly forecasted.

In given work by methods of X-rays diffraction, Raman spectroscopy are studied mechanisms of radiation transformations in C_{60} films during irradiation with Fe ions, energy of which is 140 keV with different fluences.

2. MATERIALS AND METHODS

Films of C_{60} were prepared by vacuum sublimation of C_{60} powder (purity 99.99%) on heated up to 400 K Si (100) substrates (thickness of the films was d = 1000 nm) and irradiated with Fe⁺ ions, energy of which was E = 140 keV and fluences that changed from 10^{12} to 10^{14} ions/cm². Crystal structure was studied by methods of X-ray’s diffraction (λ = 1.7902 Å, CoKα irradiation), vibration structure was studied by Raman spectroscopy (Jobin Yvon T64000 spectrometer, Ar laser, λ_{exc} = 514.5 nm). Power of laser irradiation did not exceed 2 W/cm² to avoid photopolymerization.
effects. Analysis of vibration bands and XRD reflections was performed by numerical decomposition of experimental bands on elementary Lorenz constituents. Calculations of interaction of Fe irradiation with fullerites were performed with help of SRIM 2008 package.

3. RESULTS AND DISCUSSION

Passing of ions through silic C_{60} is accompanied by loss of energy on nuclear subsystem due to elastic collisions and on electron excitation due to inelastic interaction of the ions with electron subsystem. Increase of ions energy influences the losses in a different way. At higher energy of ions their losses due to nuclear interaction saturate, but electron excitation is proportional to energy. Taking into account that polymerization is caused by excitation of the electron subsystem, increase of the ions energy leads to formation of covalent bonds between molecules near track of passing ions. Together with decrease of the ions energy caused by electron deceleration increases contribution from energy that is transferred to nuclei of the atoms that leads to appearance of radiation defects, destruction of molecular cages C_{60} and, as a result, to amorphization of crystal structure. Due to that relation E/M is important, where E and M are the energy and mass of bombardment particles, because it determines loss of the energy on electron excitation S_e and nuclear subsystem S_n and therefore determines process of polymerization and amorphization of fullerites C_{60}. For the case of E/M \geq 1 MeV/amu S_e magnitude exceeds S_n and bombardment of C_{60} with swift heavy ions at low doses stimulates polymerization of fullerites [12].

More complicated are processes of structural modification of C_{60} films with heavy ions and moderate energies in the region of 100...200 keV. For this case losses on electron excitation have the same order of magnitude as losses on creation of radiation defects. Therefore, for Fe^+ ions with energy E = 140 keV according to calculations by SRIM programme

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S_e = (dE/dx)_e = 3.622 \times 10^{12} \text{eB/Å}, \quad S_n = (dE/dx)_n = 7.159 \times 10^7 \text{eV/Å}.
\]

Probability of polymerization and amorphization are the same. But it has been noted that not only bombardment ions interact with molecules. As is seen from Fig. 1, Fe^+ ions interact with fullerens on whole deep of penetration (128 nm), longitudinal (23.7 nm) and transversal (20.1 nm) scatters. Recoil energy of the carbon atoms is equal to 70...80 eV/(Å-ion) on whole deep of penetration (Fig. 2).

![Fig. 1. Deep of penetration (a), longitudinal (b) and transversal (c) scatters of bombardment ions \((E = 140 \text{keV})\) in C_{60} fullerites. (Thickness of the film 1000 nm, Si (100) substrate, modeling by SRIM package)](image1.png)

![Fig. 2. Distribution of the recoil energy of carbon atoms with deep of penetration of bombardment Fe^+ ions, \(E = 140 \text{keV}\) in fullerites C_{60}](image2.png)

![Fig. 3. Distribution of energy losses on ionization of the carbon atoms (straight line) and ionization caused by recoil ions (dashed line) at irradiation with Fe^+ ions, energy \(E = 140 \text{keV}\), of film C_{60}](image3.png)

Its important to note that bombardment Fe^+ ions don’t pass the whole deep of the film, due to that ions penetrate in the octahedral and tetrahedral pores of C_{60} crystal structure that also can lead to polymerization. PolymORIZATION and amorphization of different parts of the molecules at collisions with ions and knocked secondary atoms is accompanied with penetration of other ions in the pores. Polymerized molecules also can be destructed and probability of the process depends on the dose: with its increase part of molecules undergoes to polymerization and achieves saturated level; at high doses part of polymerized molecules starts to decrease due to damages. Amorphization rises and at high doses it saturates [13].

Fe^+ irradiation of C_{60} fullerite leads to structural changes that reveals in significant transformation of Raman spectra (Fig. 4).
At irradiation dose 1.2·10^{12} ion/cm^2 is observed general rise of the Raman scattering background in the region 1000...1600 cm^{-1}, and increase of intensity of H_g (8) band relative to A_g (2) vibration band. Similar behavior of Raman scattering characterizes spectra at higher fluence 1.2·10^{13} ion/cm^2. At this dose it is important to note that vibration band A_g (2) remains (it is the most sensitive band to the structural changes [14]), but its intensity falls. Moreover, widening of region near H_g (7) band is observed, H_g (7) disappears. In low frequency region vibrations of A_g and H_g type also remain. At fluence 6.6·10^{12} ion/cm^2 dramatical change of Raman spectrum is observed. It is characterized by full transformation at which vibration bands disapper and new wide bands proper to amorthous carbon and graphite nanoclusters are observed.

Transformation from crystal to amorphous phase under influence of ion irradiation as one important pecality of structural modification of carbon materials is observed for different ions and energies. But amorphization process for C_{60} fullerites has peculiarities due to simultaneous polymerization of molecules. Complicated processes, caused by covalent bonds formation during excitation of the electron subsystem and destruction of molecules due to radiation stimulated generation of vacancies on the molecular cage, determine irradiation conditions and respective influence on structural sensitive characteristics, including Raman scattering and infrared absorption.

At irradiation of C_{60} films with ions D_2^+ energy of which is 5 keV and doses to 7.4·10^{13} D^+/cm^2 at dose 5.6·10^{13} D^+/cm^2 the D and G modes of amorphous carbon (a-c) appear [15]. At rise of dose to the maximal one in the matrix of a-c phase form nanocluster layers of graphite, grains of which rise with increasing of dose. It is confirmed by changes of position and halfwidth of C_11 line. Vanishing of vibration bands of C_{60}, including most intense pinch-mode A_g (2), and appearance of D and G bands of a-c for irradiation with C_{12}^+ energy 7 MeV occurs at dose 1.1·10^{14} ion/cm^2 [16]. At lower doses fall intensity of A_g (2) line and in the vicinity of it A_g (2)-derived lines appear with frequencies lower than 1469 cm^{-1}, some of them overlap with H_g (7) mode, frequency of which for pure fullerites C_{60} is equal 1424 cm^{-1}. Disappearance of A_g (2) line and appearance of D and G bands of a-c phase at bombardment with boron ions, energy of which 50...80 keV takes place at 1·10^{14} ion/cm^2. Chemical modification of fullerens at this conditions is characterized by disappearance of all peaks at 527, 576, 1183, 1429 cm^{-1}, that are proper to pure nonirradiated fullerites C_{60}, at dose 1·10^{15} ion/cm^2. The latter results prove about destruction of molecules and formation of a-c phase. Analogous behavior of Raman and infrared spectra is observed for C_{60} films irradiated with ^{56}Fe^+, energy of which was 70, 1610 893, 980 MeV at fluences 5·10^{10}...8·10^{11} ion/cm^2. Increase of dose and lose by ions of energy on excitation of electron subsystem S_e leads to lowering of C_{60} icosahedral symmetry C_{60} due to polymerization and destruction of molecules at which fcc crystal phase of fullerites and polymerized structures have to be transformed into phase of amorphous carbon [15].

Because of dimerization and polymerization are accompanied by appearance of A_g (2)- derived lines, the dose dependence formation of the phases can be determined by detail study of A_g (2) line intensity (its frequency for initial pure state of C_{60} is 1469 cm^{-1}).

Fig. 5 shows decomposition of region in the vicinity of A_g (2) band for C_{60} film in the initial state before and after irradiation with Fe^+ ions with different doses.

At dose 1·10^{12} ion/cm^2 line A_g (2) has slight changes due to asymmetry that allows to decompose it on two components. One of the peaks corresponds to A_g (2) line with frequency 1469 cm^{-1}, the another one to A_g (2)-derived maximum with frequency 1466 cm^{-1}. Line A_g (2) is sensitive to the state of π-bonds, that are constituent parts of double bonds between carbon atoms, that are located between neighbor hexagons of the C_{60} molecules. Destruction of these bonds is accompanied by formation of covalent intermolecular links i.e. sp^3-hybridization changes by sp^3 states with formation of [2+2] cycloaddition between neighbor molecules. A_g (2) line shifts proportionally to the number of the intermolecular covalent bonds per molecule [8]. Partial redistribution of π-bonds on formation of dimmers leads to shift of A_g (2) by
Further dimerization into linear chains at which orthorhombic structure forms and each C₆₀ molecule has two covalent bonds results in shift of A₆(2) line by ~10 cm⁻¹. Polymerized nets proper to tetragonal and rhombohedral phases are characterized by further shift of A₆(2) band. This shift is observed at irradiation dose 1.2×10¹³ ion/cm². Fig. 5 shows that in spectrum of Raman scattering, numerical decomposition of region vicinity of A₆(2) band gives following lines at 1469, 1460, 1444, 1424 cm⁻¹, that can be attributed to nonpolymerized phase, orthorhombic and tetragonal ones. Intensity of A₆(2) band decreases to magnitude of H₁₂(8) line intensity. Moreover H₁₂(8) line broadens and new component appears at 1595 cm⁻¹, that points on graphite formation. Increase of the intensity and its broadening is caused by change of hybridization from sp² to sp³ i.e transformation of fullerite from crystal to amorphous with formation of nanographite. Peak H₁₂(8) at polymerization and amorphization also changes, but its intensity and broadening increase.

Therefore, irradiation with fluence 1.2×10¹³ ion/cm² is characterized by transformation to amorphous phase of fullerite and polymerization into different structures, typical to polymerization at high pressures and temperatures.

Dose 0.66×10¹⁴ ion/cm² is enough for full destruction of C₆₀ and transformation into amorphous phase, presence of that confirms appearance of D and G bands. According to numerical decomposition on components, these bands have constituents, one of which is at 1595 cm⁻¹ and can be assigned to nanographite formations [16].

XRD pattern confirms polymerization and amorphization of fullerites C₆₀ (Fig. 6).

As shown on the fig. 6, fcc phase remains for all doses. Passage of X-rays is deeper than penetration of Fe⁺ ions that's why XRD pattern corresponds to both implant and nonimplant layers of the fullerite film. Due to that reflection from polymerized and amorphpized structures overlap with initial fcc structure, that gives dominant contribution in the pattern. Despite of that detail analysis of the XRD pattern for irradiated states of the film allows to show that higher layers of the film undergo to structural transitions, confirmed by Raman spectroscopy. Lattice parameter of fcc phase decreases from a = 1.434 nm in initial state to a = 1.433 nm at dose 1.2×10¹² ion/cm², a = 1.430 nm at dose 1.2×10¹³ ion/cm², and a = 1.416 at dose 0.66×10¹⁴ ion/cm². Decrease of lattice parameter for fcc phase is due to changes in structure of surface layers C₆₀ fullerites cased by compression of fcc phase due to covalent bonds. Amorphization of structure leads to increase of background of X-rays diffraction and fall of intensity of diffraction peaks at dose 0.66×10¹⁴ ion/cm². New maximum at (200) peak of fcc phase points on polymerization of C₆₀ structure. Fig. 7 shows numerical decomposition of diffraction maximums in the initial state and after Fe⁺ irradiation.

Fig. 6. XRD pattern for fullerites C₆₀ before (1) and after irradiation with Fe⁺ ions, energy E = 140 keV for fluences 1.2×10¹² (2), 1.2×10¹³ (3) and 0.66×10¹⁴ ion/cm² (4). (Thickness of film 1000 nm, Si(100) substrate, CoKα, irradiation λ = 0.17902 nm, temperature T = 300 K)

In the initial state for line (111) two peaks are observed that are caused by presence of two phases from fcc and hcp phases. Irradiation causes transformation of all peaks and new components appear that can be attributed to orthorhombic and tetragonal phases. Lattice parameters for these phases are shown in table 1. For irradiation dose 1.2×10¹³ ion/cm² lattice parameters for the orthorhombic phase are a = 1.316; b = 1.458; c = 1.566 nm, for tetragonal phases a = b = 1.312; c = 1.450 nm. Increase of dose to 1.2×10¹³ ion/cm leads to the following magnitude of parameters a = 1.331; b = 1.417; c = 1.572 nm and
\(a = b = 1.336 \text{ nm}; \ c = 1.417 \text{ nm}, \) respectively. For fluence \(0.66 \times 10^{14} \text{ ion/cm}^2\) parameters are: \(a = 1.298; \ b = 1.433; \ c = 1.552 \text{ nm and } a = b = 1.305; \ c = 1.433 \text{ respectively.} \)

Observed lattice parameters differ from parameters received at applications of high pressure and temperature, electron bombardment [17] together with that was observed compression of fcc phase caused by ion implantation [18].

**CONCLUSIONS**

Irradiation of \(C_{60}\) fullerites with \(Fe^+\) ions, \(E = 140 \text{ keV}\) leads to polymerization due to creation of intermolecular bonds between neighbor \(C_{60}\) and to amorphization of structure because of collisions between bombardment particles and carbon atoms of molecular cage. Ion energy loss magnitude \(S_a\) is closed to magnitude of ion’s loss of energy on the electron excitation \(S_e\) due to that at low doses of irradiation destruction of the molecules takes place together accompanied by polymerization with formation of bonds that are more strong than Van der Waals ones. Polymerized and amorphous structures are revealed in changes of Raman spectra and XRD patterns that point on formation of phases similar to that is formed under high pressure and temperature ones and simultaneously on formation of a-c phase and nanocrystal layers of graphite.

**REFERENCES**


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наблюдаются формирования димеров и полимеров с орторомбической и тетрагональной структурами, присущими полимерным фазам, образующимся при высоких давлениях и температурах. С повышением дозы полимерная структура исчезает и появляется аморфная фаза углерода с включением нанокристаллических слоев графита.

РАДІАЦІЙНО-ІНДУКОВАНА ПОЛІМЕРИЗАЦІЯ І ПОШКОДЖЕННЯ ПЛІВОК ФУЛЕРИТІВ C₆₀ ІОНАМИ Fe

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Розглянуто результати опромінення тонких плівок фулеритів C₆₀ (d = 1000 нм) іонами Fe⁺ з енергією E = 140 кеВ і дозами від 1,2·10¹² до 0,66·10¹⁴ іон/см². Застосування методів раманівської спектроскопії і рентгенівської дифракції вказують, що в результаті бомбардування молекул C₆₀ іонами Fe⁺ мають місце формування димерів і полімерів з орторомбічною і тетрагональною структурами, властивих полімерним фазам, що утворюються при високих тисках і температурах. З підвищенням дози полімерна структура зникає і з'являється аморфна фаза углецю з включенням нанокристалічних шарів графіту.