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Changes in crystal structure of fullerene films at alloying and radiation defect formation

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The crystal structure of the C_{60} fullerene films with their alloying by the oxygen molecules and copper atoms is studied and under the influence of high energy electron irradiation (E_e = 1.8 MeV) is investigated. It is shown that the crystal structure of the C_{60} and C_{70} films changes in the dependence on the concentration of impurity elements and radiation defects, inculcated in the interstitial positions. The presence of impurities, and also the radiation damages substantially influences the electronic and vibrational spectra of fullerenes and is the result of the appearance in this case of additional Coulomb intermolecular interaction.

Изучена кристаллическая структура пленок фуллеренов C_{60} и C_{70} при легировании молекулами кислорода, атомами меди, а также при воздействии высокоэнергетичным электронным облучением (E_e=1 эВ). Показано, что кристаллическая структура пленок изменяется в зависимости от концентрации примесных элементов и радиационных дефектов, внедренных в межузельные положения. Присутствие примесей, а также радиационных дефектов существенно влияет на электронные и колебательные спектры фуллеренов и является результатом возникновения при этом дополнительного кулоновского межмолекулярного взаимодействия.

The crystal structure of the C_{60} fullerene films at alloying with oxygen molecules and copper atoms has been studied. The influence of high energy electron irradiation (E_e = 1.8 MeV) on the changes in the crystal structure, optical conductivity, and vibrational spectra of C_{60} and C_{70} films under different absorbed doses has been investigated. It is shown that the crystal structure of the C_{60} and C_{70} films changes depending on the concentration of impurity elements and radiation defects introduced in the interstitial positions. The presence of impurities and radiation damage of molecules influences substantially the electronic and vibrational spectra of fullerenes and results from the appearance of an additional Coulomb molecular interaction, and manifests also different nature of the crystal structure change and mechanisms of its influence on the properties of C_{60} and C_{70} molecules.

The optical and electrophysical properties of the solid fullerene films depend substantially on the changes in their crystal structure due to alloying with impurities [1–4]. Of a special importance are the oxygen impurity atoms, which suppress the po-

lymerization possibility of fullerenes [5–6] due to the decrease of the fullerene excitation and formation of the cycle-attaching molecular bonds. On the other hand, it is known that fullerenes show a low ionization energy and high electron affinity energy, that contribute to a noticeable change in the electron structure of molecules when impurity atoms are introduced both into the fullerene molecules themselves and into the crystal lattice. The properties of fullerene films with the introduced exohedral alkali metal atoms [7, 8] are most widely studied. Other atoms introduced in the interstitial positions of the C_{60} molecule fcc structure influence essentially the optical conductivity, photoluminescence, and vibrational spectra of nanostructural molecules [4, 9, 10]. This influence is explained by the charge transfer between the fullerenes and impurity atoms, that provide an additional Coulomb interaction superimposed on the intermolecular Van der Waals forces [11].

It is obvious that it is impossible to study the influence of various alloying elements on the properties of the fullerene films without detailed studies of their crystal structure, since its changes determine the states of molecules themselves. However, there are essentially no such studies, except for alloying with alkali metals. Therefore, the influence mechanisms of non-alkali elements on the fullerene molecules are studied scarcely. The influence of radiation damages on the fullerene crystal structure and thus on the behavior of the molecules under electron irradiation at the bombarding particle energies exceeding the atomic displacement threshold, (when the fragmentation of molecules can be neglected) is even less investigated.

The purpose of this work is to study changes in the crystal structure of fullerene films at alloying by oxygen molecules and copper atoms, and also due to formation of radiation-induced defects during the high energy electron irradiation (electron energy 1.8 MeV) at various absorbed doses Q. Furthermore, the influence of C_{60} and C_{70} fullerenes radiation damage on their optical properties has been investigated. The crystal structure of the condensed C_{60} and C_{70} films was studied using X-ray diffraction, while optical conductivity and vibrational spectra of these molecules were investigated by spectral ellipsometry and Raman scattering, respectively. Oxygen alloying was carried out at various temperatures and annealing durations of the fullerene films in

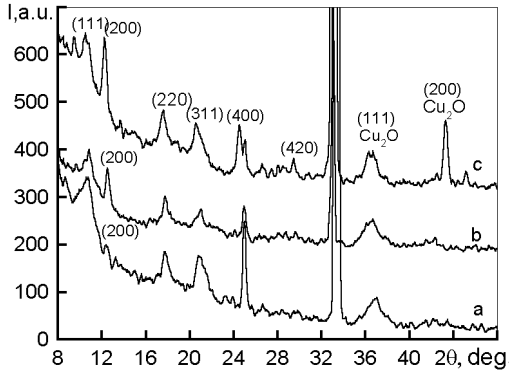

Fig. 1. X-ray diffraction patterns for Cu–C_{60} films with 20 mass% Cu: as-deposited (a); annealed at 353 K for 20 min (b); annealed at 473 K, 300 min (c). The substrate is Si (100), the film thickness 100 nm, λCuK_{α} emission.

air. The concentration of the introduced oxygen molecules was measured by Auger spectroscopy [9]. Copper-containing films were prepared using vacuum condensation at simultaneous spraying of copper atoms and fullerene molecules [2, 4]. The dose of electron absorption is varied from $Q = 0.5$ to 8 MGy.

The electron-diffraction and electron-microscopic studies of the C_{60} fullerene films testify about their fine-crystalline structure, average size of crystallites being ~25–40 nm [4, 9]. Amorphous component occupies an essential volume fraction in films of 700 to 2000 nm thickness. The X-ray diffraction patterns of the solid C_{60} crystalline films after different annealing temperatures and durations show that the diffraction peak (200), which should be observed in the fcc structures is absent even at significant annealing temperatures and times (T = 473 K, t = 300 min) (Fig. 1). The content of oxygen atoms in this case is 2.45 at.%. At the same time, as the annealing temperature and time increase, the lattice parameter increases from a = 1.414 nm in the initial state after sputtering (oxygen content 0.6 at.%) to a = 1.431 nm (T = 473 K). The observed lattice parameter increase indicates that a fraction of oxygen molecules enters the interstitial positions, although it is not possible to exclude a chemical reaction of the oxygen molecules with fullerenes. This conclusion is confirmed by the character of changes in the background of Raman scattering [9] and spectral emission of excitons [10] at thermal annealing of the C_{60} films.

As to copper-alloyed C_{60} films, the diffraction pattern, especially at a high Cu

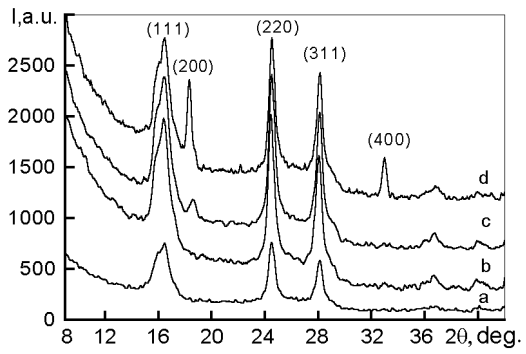

Fig. 2. X-ray diffraction pattern for C_{60} films: as-sputtered (unirradiated) (a) and electron irradiated at the absorbed dose (MGy): 1.5 (b); 4.0 (c); 8.0 (d). The substrate is Si (100), the film thickness 2000 nm, λCoK_{α} emission.

content (20 wt.%) differed from that for the film obtained by oxidation [4, 10, 13, 14]. Already in as-sputtered film prior to annealing, the (200) reflection appears in the X-ray scattering spectrum [15, 16], and its intensity grows due to annealing (Fig. 2). The crystal structure, as in the case of the C_{60} films, corresponds to the fcc phase. The lattice parameters of as-sputtered unannealed film both at low (4 mass%) and high (20 mass%) content of copper atoms are smaller than in the unalloyed C_{60} fullerene films and amount $a = 1.40$ and 1.406 nm, respectively. As the annealing temperature increases, the lattice parameters for both compositions the increase and at $T = 473$ K attain $a = 1.427$ and 1.430 nm, respectively, i.e. exceed the maximum value for C_{60} films [4, 12, 13], thus indicating the introduction of copper atoms into interstitial positions of the fcc lattice. The interstitial copper atoms cause a double effect. On the one hand, copper atoms, acting as donors, contribute to electron transfer to the fullerene molecules, ensuring the degeneration of rotational molecular degrees of freedom [11]; that is accompanied by the appearance of the (200) diffraction peak. The Coulomb interaction between the molecules and copper atoms appearing in this results in a decrease of the lattice parameter of the fullerene crystalline phase. On the other hand, increased concentration of the interstitial copper atoms causes expansion of the fcc lattice structure of the solid C_{60} films.

Thus, the alloying of C_{60} fullerene films with oxygen molecules or copper atoms is connected with the introduction of impurities into interstitial positions and results in appearance of an additional component of molecular interaction, which is a consequence of a change in the fullerene electron structure associated with the appearance of spatially spaced charges of opposite signs. Alloying with copper atoms, as in the case of alkali metals, a broad optical absorption band is observed in the energy gap due to electron transfer from copper atoms to the C_{60} molecules [14].

Similar transformations of the crystal structure evidenced by appearance of the (200) diffraction peak and by lattice parameter changes occur due to radiation damages of C_{60} and C_{70} fullerenes caused by high-energy electron irradiation. It is to note that in the as-sputtered C_{60} sample prior to irradiation, the hcp structure appears besides the fcc phase, which results in an asymmetry of (111) diffraction peak and in appearance of additional peaks corresponding to that phase. It is to assume that already in the course of the film precipitation, the chaotically distributed packing defects may be formed depending on the sputtering conditions, resulting in the appearance of hcp structure interlayers [17]. During the irradiation, the diffraction peak (200) appears, its intensity growing as the radiation dose increases.

As the absorbed dose Q increases, the lattice parameters of both phases also change. So at $Q = 1.5$ MGy the lattice parameter is $a = 1.425$ nm, that is higher than in the unirradiated sample ($a = 1.421$ nm). After a decrease, which occurs at $Q = 4$ MGy ($a = 1.420$ nm), a further rise of the absorbed dose up to $Q = 8$ MGy results again in the lattice parameter increase (up to $a = 1.430$ nm). An increase in the electron irradiation dose favors the increased c/a ratio in the hcp phase.

It is to note that as the radiation dose increases, a more essential reconstruction of the fullerene electron structure is observed. So at $Q = 4$ Mgy, the electron concentration in the region of the peaks associated with interband transitions increases. The optical conductivity peaks $\sigma(E)$ become smeared and equalized in values. Irradiation with the absorbed dose of $Q = 8$ MGy leads to the drop of $\sigma(E)$ and a noticeable displacement of its peaks. This behavior of $\sigma(E)$ cannot be connected with the polymerization of fullerenes, since the electron irradiation does not affect the displacement of the vibrational $A_g(2)$ mode lines. On the other hand, as the absorbed dose increases, an increased background of Raman scattering

is observed, and the smearing of lines of individual vibrational H_g modes starts. The results obtained evidence a change in the symmetry of C_{60} molecules caused by their radiation damage. Such damages contribute to the local static atomic displacement of carbon at the C_{60} molecular shell, and also to the transfer of expelled atoms to the interstitial positions of crystalline fcc lattice. The appearance of the charge exchanges between the impurity atoms and the fullerene molecules is accompanied by formation of additional Coulomb molecular interaction, which is evidenced also by reconstruction of electron spectrum.

The irradiation influence on the crystal structure of C_{70} films seems to be more complex. Fig. 3 shows the diffraction pattern for solid C_{70} films, subjected to electron bombardment at various radiation doses. It is seen that at the condensation, the C_{70} molecules form the hcp phase. In the as-sputtered film, the lattice parameters are a = 1.265 nm and c = 1.800 nm (c/a = 1.42). During the electron irradiation at absorbed doses Q = 0.5 and 1 MGy, the parameter a increases, while c remains unchanged up to Q = 2 MGy, while a takes its largest value (a = 1.324 nm) in the latter case. The packing density of the hcp lattice (c/a = 1.43) becomes the same as in the as-sputtered film. Thus, in the C_{70} fullerene films not only atomic displacement of carbon from the fullerenes to the interstitial positions occurs, but also a structure relaxation caused by the output of these atoms from the crystal lattice of the initial hcp phase. The appearance of the new diffraction reflections observed during irradiation evidences a possible appearance of new phases. An attention should be given also to a specific feature in the behavior of optical properties of C_{70} fullerene films as compared to the condensed state of C_{60} molecules. Although, as for the C_{60} molecules, the degeneration is removed for the majority of the of Raman scattering peaks, and an increase in its background appears, the symmetry reduction in the C_{70} fullerenes is less pronounced. Moreover, at the absorbed dose Q = 4 MGy, the Raman scattering spectrum becomes similar to that in the initial state. It is possible to assume that at increasing concentration of the introduced radiation defects in the hcp lattice of the C_{70} fullerene films, the electron structure reconstruction caused by atomic displacement of carbon results not only in the appearance of Coulomb molecular interaction, but also in

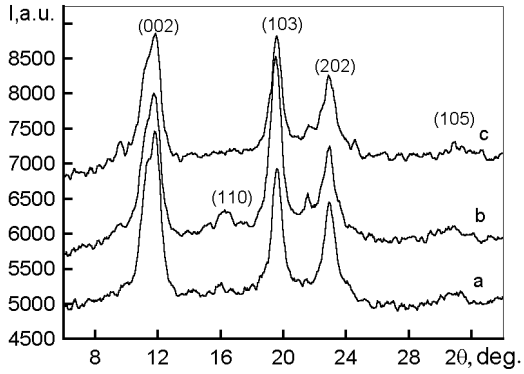

Fig. 3. X-ray diffraction pattern for solid C_{70} films: as-sputtered (unnirradiated) (a) and electron irradiated at the absorbed dose (MGy): 2 (b); 4 (c). The substrate is stainless steel, the film thickness 1800 nm, λCoK_α emission.

such redistribution of charges in the C_{70} molecular shell that provides a stiffening of C–C bonds in fullerenes.

The distinctions in the electron spectra changes for C_{60} and C_{70} molecules during irradiation are evidenced by the energy dependences of the exciton radiative recombination and optical conductivity. So, the irradiation which generates radiation defects in the C_{70} fullerene films causes appearance of X-centers favoring the nonradiative recombination processes and displacement of the localized electron states. The optical conductivity spectrum σE at Q = 4 MGy relaxes to the similar spectrum for the initial (unirradiated) state. This evidences a decreased influence of the displaced carbon atoms on the electron structure reconstruction of the C_{70} molecules in comparison with the case of lower radiation doses.

Thus, the alloying of fullerene films by the impurity atoms or molecules as well as creation of radiation defects during the damage of the locked molecular shells by the bombarding particles causes changes in the crystal structure and optical properties of C_{60} and C_{70} fullerenes. The appearance and intensity increase of diffraction reflection (200) (which is not observed at X-ray scattering from the fcc phase of solid C_{60}) under specific conditions of alloying and irradiation, is one of the important changes. As the copper atomic concentration and absorbed dose in the C_{60} fullerene films increase, the lattice parameter of the hcp structure changes in a complex fashion, thus reflecting the reconstruction of electron and vibration spectra caused by the

introduction of impurities, including the displaced carbon atoms, to the interstitial positions of crystal lattice and the additional Coulomb interaction occurring thereby. The irradiation of condensed C_{70} fullerene films also causes complex changes in the hcp structure parameters at increasing absorbed dose, thus indicating the radiation damages of molecules. However, the formation of radiation defects affects less the reconstruction of the electronic and vibrational spectra of C_{70} molecules in comparison with C_{60} fullerenes. This testifies about different nature of crystal structure changes and mechanisms of its influence on the properties of C_{60} and C_{70} molecules.

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Зміни кристалічної структури плівок фулеренів при легуванні та утворенні радіаційних дефектів

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Досліджено кристалічну структуру плівок фулеренів C_{60} при їх легуванні молекулами кисню та атомами міді та під впливом високоенергетичного електронного опромінення (E_e = 1,8 МеВ). Показано, що кристалічна структура плівок змінюється залежно від концентрації домішкових елементів та радіаційних дефектів, введених у міжвузлові положення. Присутність домішок, а також радіаційних дефектів істотно впливає на електронні та коливні спектри фулеренів і є наслідком виникнення при цьому додаткової кулонівської міжмолекулярної взаємодії.