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The behavior of the emission of the excitons localized at different X-centers at the radiation damages by electron beams with an energy of 1.8 MeV and argon ions in the plasma of glow discharge is studied. The nature of X-centers, which contribute to the emission of excitons near energies of 1.5 and 1.6 eV, is discussed. It is shown

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that the essential reconstruction of the energy spectrum of excitation is observed with increase in the radiation dose, as a result of the radiation damages of C_{60} molecules.

Keywords: Frenkel excitons; fullerene; radiative recombination

INTRODUCTION

The studies of the optical properties of isolated C_{60} molecules and properties of their solid films showed that C_{60} molecules in the crystalline state form the fcc phase which can be considered as an ideal molecular crystal [1–8]. The broadening and shifts of lines are observed in the spectra of optical absorption, photoluminescence and Raman scattering of solid films. Even more substantial changes in the crystal structure and optical properties occur with the polymerization of fullerene solid films by pressure [9–18]. The appearance of additional intermolecular bonds is possible with the excitation of fullerene molecules, which can be achieved also by alloying, oxidation, and doping of fullerene solid films [1,4–5,19–24].

The stimulated excitation of fullerenes, which can lead to their polymerization in the solid state, can occur during the irradiation by ions and electrons. Actually, the irradiation by low-energy electrons (37-1500 eV) even with the small doses leads to the formation of polymer chains for a noticeable number of fullerene molecules. The exciton special feature and a $(\sigma + \pi)$-plasmon with multipole structure are observed in the spectra of the elementary excitations of C_{60} fullerite under the electron influence. The energy of a π-plasmon, width of the forbidden band, and HOMO-LUMO transition energy are decreased with increase in the radiation dose. In this case, the quasi-continuous low-energy background considerably increases, that indicates an increase in the conductivity. Besides the formation of intermolecular chemical bonds, which testifies about an increase in share sp^3-hybridization of electrons, the "red" displacement caused by the collectivization of a part of π-electrons is observed [25]. It is obvious that a change in the electron structure of π-electrons and those near the Fermi level, which is achieved by electronic irradiation, contributes to the polymerization of C_{60} molecules.

The influence of the action of ionizing emission with the energies and the mass of particles capable of leading to the radiation damages of fullerene molecules is studied little. So, the irradiation by γ-quanta with doses from 10 to 1000 kGy leads to the polymerization of C_{60} molecules, which is manifested as a result of the "softening" of all vibrational Raman modes. So, the mode of $A_g(2)$ symmetry displaces from 1469 to 1458 cm^{-1}. The polymerization is entirely manifested

with a dose of 100 kGy, while, with a dose of 10 kGy, only the initial stage of the polymerization is observed, when the vibrational $A_g(2)$ mode coexists with both the indicated frequencies [26–27].

In this work, the behavior of the electron spectra of excitation and vibrational modes of C_{60} fullerenes in solid films is studied at the different dose loads of electronic irradiation and under the treatment by the plasma ionic discharge of argon.

SAMPLE AND METHOD

The samples were obtained with vacuum condensation of microcrystalline C_{60} powders on the substrate from a stainless steel and Si(100). The temperature of sublimation of C_{60} molecules was about 700 K, the thickness of films was equal to 700, 1200, and 2000 nm. The electronic irradiation was fulfilled with the use of a linear accelerator. The energy of electrons was equal to 1.8 MeV, the radiation doses were equal to 50, 100, 150, 200, 300, and 400 MRa. The temperature did not exceed 323 K. The energy of argon ions in the plasma discharge was equal to $\sim$1 keV, the dose load was selected to be 20 MRa. The emission of excitons was excited by the radiation of an argon laser with wavelengths of 514.5 and 488.0 nm and a power of $\sim$200 mW. The inverstigated samples were placed into a low-temperature cryostat, and the spectral measurement of radiative recombination was conducted at the temperature of liquid helium (4.2 K) or liquid nitrogen (77 K). The Raman scattering also was studied using the radiation of an argon laser with a wavelength of 514.5 nm.

RESULTS AND DISCUSSION

The spectra of radiative recombination for the solid C_{60} films at the temperature of liquid helium in the initial state of precipitation and after their irradiation by electrons with a dose of 200 MRa are given in Figure 1. The initial dose load practically does not influence the form of the photoluminescence spectra, revealing the presence of the volumetric emission of Frenkel excitons with a radiation energy of 1.69 eV and local emission of excitons, occupying X-centers of different nature [24]. With increase in the radiation dose, the peaks of radiative recombination of the excitons localized on the surface do not change. However, the essential reconstruction of the spectrum in the region of basic and low-energy peaks occurs. The broadening of the peak of volumetric emission and a noticeable increase of the peaks of local emission near the energies of 1.5 and 1.6 eV are observed. The emissive peak which corresponds to the position of $\sim$1.6 eV becomes a

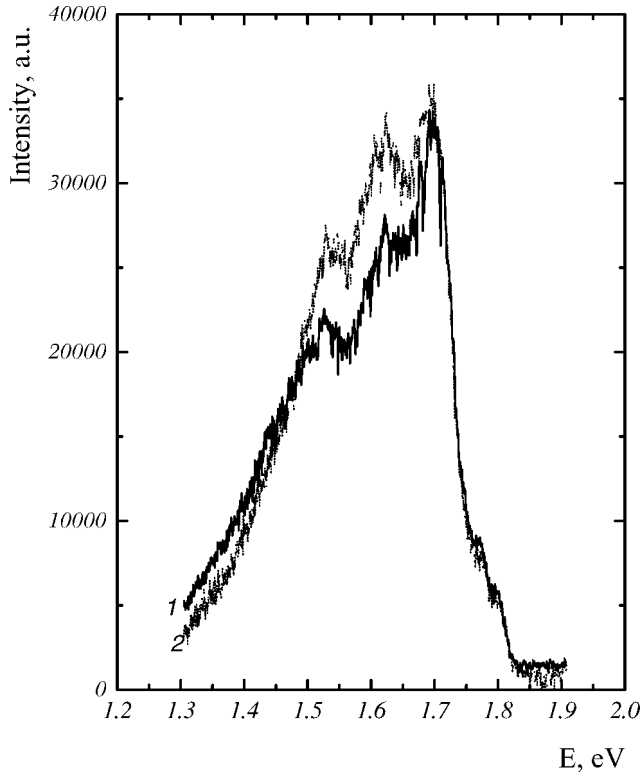

FIGURE 1 Spectra of the radiative recombination of excitons at the radiation damage by the electronic irradiation: 1 is the initial state of a solid C_{60} film; 2 is the irradiation at a dose of 200 MRa (d = 700 nm, the substrate is a stainless steel, T = 4.2 K, E_e = 1.8 MeV).

doublet. In the previously proposed model [24], it was assumed that the photoluminescence near the position of $\sim$1.5 eV is connected with the origin of $(C_{60}–O_2)^{-1}$ complexes, i.e. X-centers, which contribute to the increase of recombination of localized excitons on them. An increase of the intensity of radiative recombination in the region of this peak testifies to an increase in the chemical interaction of C_{60} molecules with oxygen. This becomes possible as a result of the break of the double bonds between hexagons, which is similar to the mechanisms of cycloattaching [4,5]. One of the possibilities of this break can be the radiation damage connected with the atomic displacement of carbon from the shell of molecules into the volume of the crystal lattice. As seen in Figure 2, initially with a dose of 100 Mra, the electron transitions over a wide range of energies near of

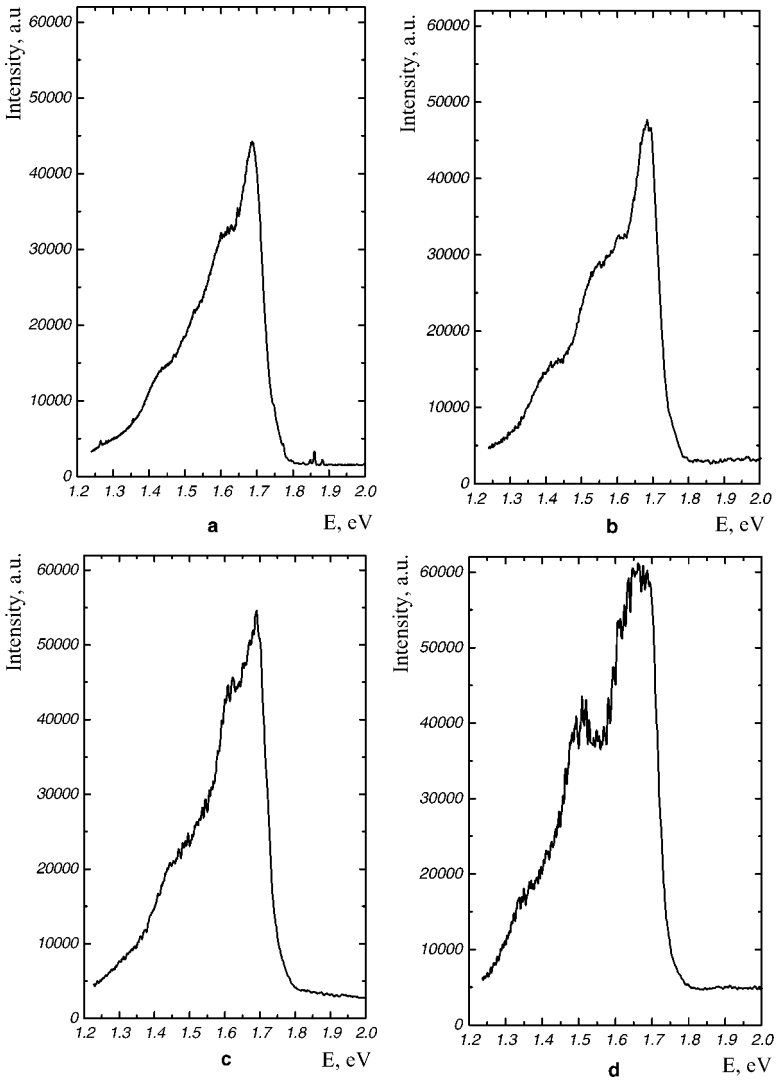

FIGURE 2 Spectra of the radiative recombination of excitons at the radiation damage by the electronic irradiation: a is the initial state of a solid C_{60} film; b is the irradiation at a dose of 100 MRa; c-300 MRa; d-400 MRa (d = 2000 nm, the substrate is Si(100), T = 77 K, E_e = 1.8 MeV).

1.5 eV occur. The peak in the region of 1.6 eV remains practically constant as the maximum of the volumetric emission of excitons. With increase in the radiation dose to 200 and 300 Mra, the intensity of

photoluminescence insignificantly increases in the region of 1.5 eV. More noticeably, it increases for the localized excitons at the X-center (1.6 eV). If we use the assumption that the X-centers, which correspond to the local radiative recombination of excitons, are impurity atoms [24] inculcated in the octa- and tetrahedral interstices of the fcc crystal lattice, then the increase of emission in this region is a consequence of the displacement into the crystal volume of carbon atoms formed at radiation damages. The basic peak width remains constant and, therefore, an improvement in the microcrystalline structure is absent. The subsequent increase of the dose to 400 MRa leads to a sharp increase of the emission of excitons in the region of both considered X-centers.

Thus, from one side, the bond breaking between the carbon atoms on a molecule itself occurs, which is accompanied by an increase in the number of sp^3-hybridized states, and, from another side, the accumulation of impurity carbon atoms in the crystal lattice takes place. The last fact is also confirmed by the doublet nature of the peak near of 1.6 eV which is observed at the temperature of liquid helium and can corresponds to two types of the existent interstices.

An increase in the intensity of the peaks of local emission near of 1.5 and 1.6 eV occurs also with annealing [24] (see Fig. 3). The difference from the irradiated samples in this case consists in the introduction of oxygen into the crystalline interstices. It is evident that even

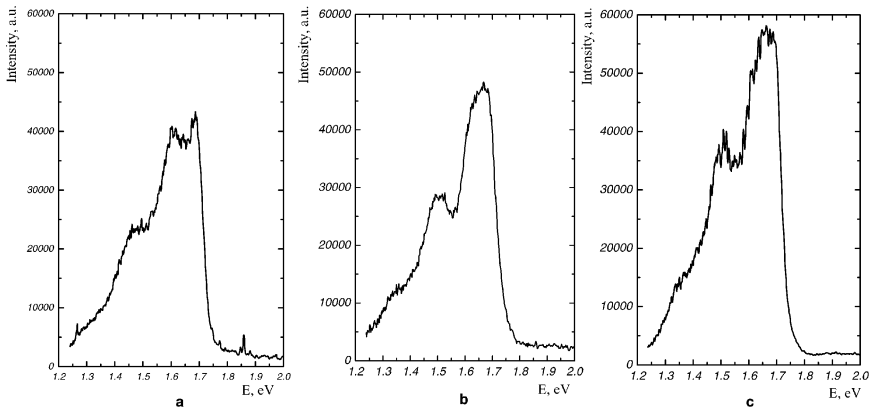

FIGURE 3 Spectra of photoluminescence of excitons at the annealing and the radiation damages by the electronic irradiation: a is the annealing of a solid C_{60} film at 393 K during 20 min; b is the subsequent irradiation at a dose of 150 MRa; c–400 MRa ($d = 2000$ nm, the substrate is Si(100), $T = 77$ K, $E_e = 1.8$ MeV).

the small-term annealing at 393 K during 20 min generates the noticeable maximum of emission at the X-centers which are the introduction sites. The electronic irradiation strengthens the processes of radiative recombination at X-centers of both types, especially with an energy of ~1.6 eV as a consequence of radiation damages and the connected reconstruction of the energy states of excitation.

The analogous processes occur with the use of ionic radiation by argon in the plasma of glow discharge even with small radiation doses. As seen in Figure 4, with a weak change in the peak caused by the emission of localized excitons at the X-center with an energy of ~1.5 eV, a number of special features is observed in the energy range from 1.60 to 1.69 eV. The increase in their intensity within the framework of the proposed model for X-centers is a consequence of the introduction of displaced carbon atoms with the radiation effect (peaks with an energy of ~1.6 eV) and the possible introduction of argon ions.

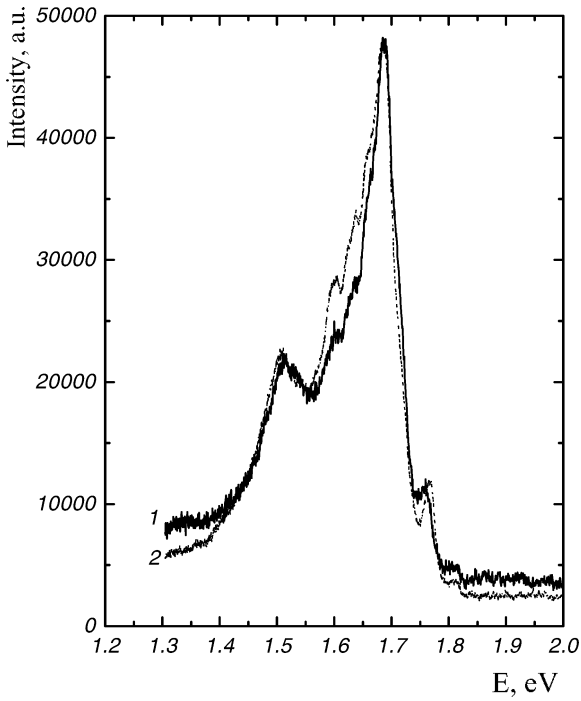

FIGURE 4 Spectra of the emission of excitons at the radiation damages by argon ions in the plasma of glow discharge: 1 is the initial state of a solid C_{60} film; 2 is the irradiation at a dose of 20 MRa (d = 1200 nm, the substrate is a stainless steel, T = 4.2 K, E_{Ar} = 1 keV).

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