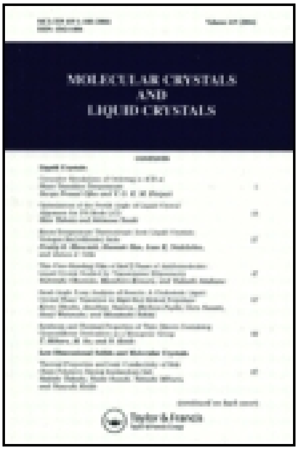

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Simulation of Fullerite C_{60} Polymerization Under Particle Beam Irradiation

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A model has been suggested, and the simulation of the fullerite C_{60} polymerization by electrons within the energy range $0.15 \div 1.5$ keV has been carried out. The number of created intermolecular bonds was assumed to be proportional (with a coefficient k) to the number of excited molecules. Polarization, exchange, and muffin-tin size were taken into account for elastic scattering. Ionization of deep atom levels was treated as a binary collision, and the inelastic scattering by valence electrons was described in the framework of the dielectric formalism. The comparison of results of the simulation with experimental data gave the coefficient of proportionality $k \sim (2 \div 5) \cdot 10^{-3}$.

Keywords: electron beam; electron spectroscopy; fullerite; polymerisation; simulation.

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INTRODUCTION

It is a common knowledge now that the particle beam irradiation stimulates the polymerization of fullerite essentially modifying its phonon and electronic structure. Polymerization can be performed with nanoscale resolution by using strongly focused particle beams. Studying this phenomenon seems promising because of a basic opportunity to purposely modify physical properties of fullerite by choosing the type of particles, their energy, dose and other parameters of beams [1].

EXPERIMENTS

To study the fullerite polymerization experimentally one needs a quantitative measure of the modification extent. Such a parameter has been suggested in the research of a fullerite C_{60} modification stimulated by electron beams [2–5]. The approach is based on the use of Electron Energy Loss Spectra (EELS), which shows two regions sensitive to the modification. The spectrum intensity of one of these regions (a low-energy anti-peak characterising the density of states near the Fermi level in the band gap) increases, whereas that of another one (a π-plasmon peak) diminishes in the course of the fullerite modification. The ratio of these intensities was taken as a very sensitive characteristic of the modification and its rate. The dependence of the polymerization rate on the primary electron energy was measured and compared with results of the computer stimulation described below.

MODEL

Let a primary electron with energy E create a cascade of secondary electrons inside some volume l^3 in the pristine fullerite. Hence, its fluence is $\Phi_1 = \lambda^{-2}$. Parts of polymerized and amorphized molecules in this volume are denoted as $p(\Phi)$ and $a(\Phi)$. The probabilities of the formation of a polymer bond and the amorphization of a polymeric molecule at this fluence well be denoted as $\alpha(E)$ and $\alpha(E)\cdot\beta(E)$, where $\beta(E) < 1$. Then we can write the balance equations as

$$\frac{dp(\Phi)}{d\Phi} = \alpha(1 - p - a) - \alpha\beta p, \quad \frac{da(\Phi)}{d\Phi} = \alpha\beta p. \tag{1}$$

Their solution at the initial conditions $p(0) = a(0) = 0$ is

$$\begin{aligned} p(\Phi) &= \frac{1}{1-\beta}\left(e^{-\alpha\beta\Phi} - e^{-\alpha\Phi}\right), \\ a(\Phi) &= \frac{1}{1-\beta}\left(1 - e^{-\alpha\beta\Phi} + \beta\left(1 - e^{-\alpha\Phi}\right)\right). \end{aligned} \tag{2}$$

In the case of a stable polymeric phase ($\beta = 0$), we obtain $p(\Phi) = \left(1 - e^{-\alpha\Phi}\right)$. Then the total polymerization is reached at the fluence $\Phi_{pol} \approx (2 \div 3)/\alpha$. In general, $p_{\max} = \beta^{\beta/(1-\beta)}$ at $\Phi_{\max} = -\ln(\beta)/\alpha(1-\beta)$.

As shown in [6], the covalent bond between two fullerenes can be formed if one of the molecular double bonds is excited or is an anion. The simulation showed that the number of anions is much less than the number of excited atoms. First, we suppose that any excitation of fullerene leads to the formation of such a bond. We did not take into account other mechanisms of relaxation of the excitation. Cascades of secondary electrons have been simulated by the Monte-Carlo method. For any k-th primary electron, the number of excited atoms $n_{k,ex}$ and the cascade volume $V_k = l_k^3$ were obtained. Then the part of excited molecules is $p(\Phi_k) = n_{k,ex}/\left(n_0 l_k^3\right)$, and the probability of polymerization is

$$\alpha_k(E) \equiv \frac{p(\Phi_k)}{\Phi_k} = \frac{n_{k,ex}(E)}{n_0 l_k(E)}, \quad \alpha(E) = \frac{1}{N}\sum_{k=1}^{N} \alpha_k(E), \tag{3}$$

where n_0 is the atomic concentration, $N = 5 \cdot 10^4$ is the number of primary electrons. According to our model, the quantity $\beta \equiv \Phi_{pol}^{\exp}(E)\alpha_{sim}(E)$ should be a constant.

The differential cross sections of elastic scattering by a separated carbon atom have been calculated as

$$\frac{d\sigma_e}{d\Omega} = |f(\theta)|^2, \quad f(\theta) = \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)\left(e^{i2\delta_l} - 1\right)P_l(\cos(\theta)), \tag{4}$$

where $f(\theta)$ is the scattering amplitude, θ is the scattering angle, $k = \sqrt{E/Ry}$ is the electron wave vector in terms of a_0^{-1}, E is the electron energy, $Ry = 13.6\,\text{eV}$, and a_0 is the Bohr radius. Phase shifts δ_l have been calculated according to [9] for the given electron-atom interaction $U(r)$. The influence of neighbor atoms has been taken into account by using the spherical symmetric muffin-tin model [10], where $U(r) = 0$ at $r > r_0$, and $U(r) = U_f(r) + U_f(2r_0 - r) - 2U_f(r_0)$ at $r \le r_0$, $2r_0$ is the distance between the fullerite atoms, $U_f(r) = U_S(r) + U_P(r) + U_X(r)$ is the interaction potential of an electron in a free carbon atom, $U_S(r)$, $U_P(r)$, and $U_X(r)$ are the screening Coulomb, polarization, and exchange potentials, respectively. The wave function, electron density, and screening function for a free carbon atom have been obtained by the *ab-initio* solution of the Hartree-Fock equation with the basis 6–31G* [11] and expressed as

$$\rho(r) = \frac{Z}{4\pi}\sum_{i=1}^{L} A_i \alpha_i^3 e^{-\alpha_i r}, \qquad U_S(r) = -\frac{Z}{r}\sum_{i=1}^{L} A_i\left(1+\frac{\alpha_i r}{2}\right)e^{-\alpha_i r}, \tag{5}$$

where the parameters A_i, α_i, and the number L were found by the methods of nonlinear programming. The accurate calculation of the polarization and the exchange is more difficult. We tested several approaches [13–15]. Differences in the cross sections were appreciable only at energies of about 1 Ry (see Fig. 1). We used the potential given in [13,14]:

$$U_P(r) = -\frac{\alpha_P r^2}{2\left(r^2+r_0^2\right)^3}, \quad U_X(r) = -\frac{k}{\pi}\left[\Pi - \frac{1}{\sqrt{1+\Pi^2}}\ln\left(\sqrt{1+\Pi^2}+\Pi\right)\right]. \tag{6}$$

Here, α_P is the polarizability of a free carbon atom, $\Pi = p_F(r)/k$, and $p_F(r) = \left[3\pi^2\rho(r)\right]^{1/3}$ is the Fermi momentum. At low energies, $\sigma_e \approx 4\pi a_{hs}^2$, where a_{hs} is the radius of a rigid sphere. Figure 1 shows that, at

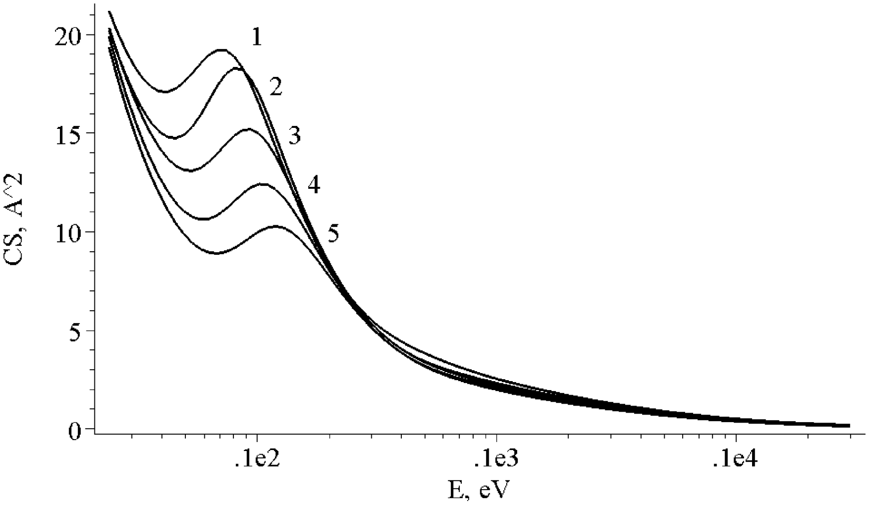

FIGURE 1 The total elastic cross sections of electron scattering on carbon atom at different interaction potentials: 1 – potential (5); 2 – potential (5,6) and muffin-tin (used in simulations); 3 – potential (5,[15]) and muffin-tin; 4 – potential (5,[13]) and muffin-tin; 5 – potential (5,[14]) and muffin-tin.

$E < 20\,\text{eV}$, $a_{hs} \approx 1 \div 2$ Å depending on the potential. The estimation obtained is close to $2r_0$. Therefore, the approximation of independent atoms is not justified here. The calculation [15] of the total elastic cross section for electrons scattered by a single C_{60} at energies $E < 30\,\text{eV}$ gives the value of about 150 Å^2. The total cross section over the all atoms in fullerene exceeds this value by $4 \div 8$ times. The inelastic scattering has been considered as the sum of electron scattering by the inner shell of a free carbon atom and by the valence electrons of fullerite. The ionization cross section of the carbon inner-shell at electron energies above the threshold has been evaluated by the approximation [16]:

$$\sigma_i = 4\pi a_0^2 \frac{n_i}{B_i^2} \frac{1}{t+u+1}\left(\frac{\ln t}{2}\left(1-\frac{1}{t^2}\right)+1-\frac{1}{t}-\frac{\ln t}{t+1}\right), \quad t \geq 1, \qquad (7)$$

where $t = E/B_i$, $u = U_i/B_i$, and the occupancy n_i, energy B_i, and kinetic energy U_i of i-th carbon level were determined together with (5). Other quantities have been determined according to [17].

The double differential cross section of the electron inelastic scattering by the fullerite valence electrons with losses of energy $T = \hbar\omega$ and momentum $\vec{p} = \hbar\vec{q}$ were calculated according to [7,8]:

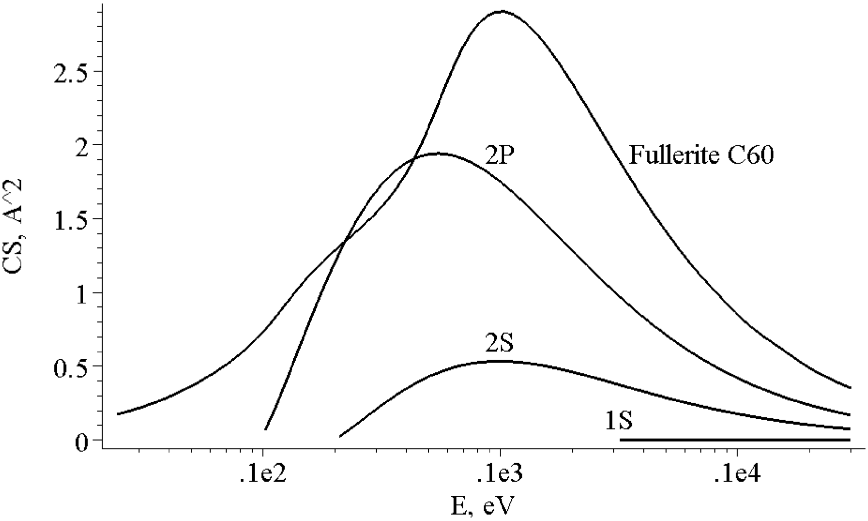

FIGURE 2 The total inelastic cross sections per atom: ionization of shells 1s, 2s, and 2p of free carbon atom; excitation of valence electrons in the C60 fullerite.

$$\frac{d^2\sigma_v}{dTd\Omega}=\frac{1}{2\pi^2 n_0 a_0}\frac{(T-q^2)\sqrt{E(E-T)}}{ETq^2}\mathrm{Im}\left\{\frac{-1}{\varepsilon(0,T-q^2)}\right\}, \tag{8}$$

where $q^2 = 2E - T - 2\sqrt{E(E-T)}\cos\theta$, and $\varepsilon(0,\omega)$ is the optical dielectric function which is composed from Lorentz curves for fullerite at $T < 30\,\text{eV}$ [5] and for carbon at $T > 30\,\text{eV}$ [18].

Figure 2 presents σ_i for a free carbon atom and σ_v for one carbon atom inside fullerite. According to [20], the cross section of ionization of a C_{60} molecule by an electron has a 22.4-Å^2 maximum at $E = 70\,\text{eV}$ and decreases to 14 Å^2 at$E = 1\,\text{keV}$. Figure 2 shows that the calculated cross section decreases rapidly with increase in energy and that it is overestimated near the maximum with a factor of $1.5 \div 6$ (curves 2 S, 2P) what makes the polymerization degree higher.

RESULTS AND DISCUSSION

Figure 3 presents the calculated $\alpha_{sim}(E)$ for a thick C_{60} fullerite film at various energies. Curve (3.1) is plotted for $l_k(E) \approx 500$ Å (it corresponds

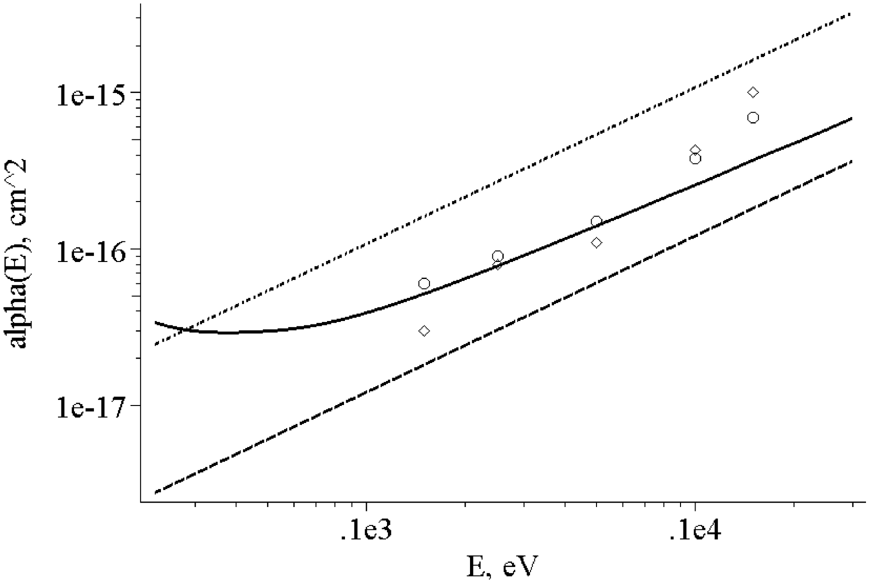

FIGURE 3 Energy dependence of polymerization probability α per one primary electron. Symbols: ◇ – the results of [3] multiplied by 1.10^{-16}; ○ – the MK simulation. Curves are obtained by the linear cascade theory: a dotted line is minimal values; a dot-dash line is maximal ones; continuous is for averaged energy losses.

to the electron energy $E \approx 2\,\mathrm{eV}$ since such electrons determine the value l) and for $n_{k,ex}(E) \approx E/2T(E)$ defined by the linear cascade theory. A rise of this curve at low energies is due to the overestimation of the cross sections. The lower and top curves give two limits for a part of excited molecules: $n_{ex,\min}(E) \approx E/(2B_{2s})$ with $B_{2S} = 10\,\mathrm{eV}$, and $n_{ex,\max}(E) \approx E/\left(2E_g\right)$ with $E_g = 2\,\mathrm{eV}$. Experimental data $\alpha_{exp}(E)$ taken from [3] show a nonlinear rise at high energies. The simulation gives a linear increase in the number of secondary electrons the primary electron energy, since most of them have the energy of several eV, and they excite fullerenes more efficiently. Therefore, the result of simulation for the high energy irradiation depends on the excitation cross sections at low energies. The quantity $\beta \equiv \Phi_{pol}^{\exp}(E)\alpha_{sim}(E)$, where $\Phi_{pol}^{\exp}(E)$ was calculated in [3], decreases from 580 at $E = 150\,\mathrm{eV}$ to 200 at $E = 1.5\,\mathrm{keV}$ and depends on energy as $E^{-1/2}$. Thus, only one of several hundred excitations leads to the formation of an intermolecular bond. The overestimated low-energy cross sections raise this value. Therefore, exact cross sections can help finding the type of collisions responsible for the formation of intermolecular bonds in a C_{60} fullerite.

In conclusion, the results of simulation of the irradiation of a C_{60} fullerite mainly confirm the model in which the number of intermolecular bonds created under irradiation is proportional to the number of excited molecules in the cascade of secondary electrons. The comparison of the results with experimental data allowed us to estimate the coefficient of proportionality which proves to be $k \sim (2 \div 5)\cdot 10^{-3}$ and is weakly dependent on the primary electron energy. This fact confirms the dominant role of secondary electrons in the fullerite polymerization.

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