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Direct electron-beam-induced formation of nanometer-scale carbon structures in STEM.

I. Nature of “long-range” growth outside the substrate

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Abstract. — Long-range growth of carbon-containing structures beginning from the edge of the sample has been found to occur under the action of the electron beam passing outside the sample in the column of the microscope pumped down by an oil diffusion pump. The mechanism of the phenomenon is suggested.

1. Introduction.

It is well-known that the surface irradiated by electrons in the vacuum chamber pumped down by an oil diffusion pump is covered with a hydrocarbon layer [1]. This layer hinders conventional electron-microscopic studies [2, 3]. However, the phenomenon may be used, for instance, in microelectronics for the fabrication of protective masks on the surface of objects, since such layer formed by the electron beam prevents subsequent removal of the material upon chemical etching or ion bombardment, as is the case with the surface resists used in production of solid state microcircuits [4].

It was shown in [5] that a strip of hydrocarbon polymer grows in the horizontal plane following the electron beam if the beam moves slowly. The strip is not interrupted even if the beam keeps moving from the edge of the substrate into hole area. By this means rods and bridges were produced in the gap between the two edges of a silicon dioxide film [5-7].

The aim of the present work is to study the mechanism of the growth of electron-induced carbon-containing structures in the form of ledges and rods as well as to consider the possibilities for the formation of substrate-free nanometer carbon-containing structures in scanning transmission electron microscope (STEM).

2. Experiment.

The formation of carbon-containing structures and the measurements of the parameters of these structures were carried out in the VG HB501 STEM with an accelerating voltage of 100 kV and a field emission cathode. The substrates were kept at 80 °C for 10 min in the lock chamber pumped down to 10^{-5} Pa before they were placed into the microscope column to remove the hydrocarbon contaminations falling on the surface during preparation of the substrate and to increase the reproducibility of the results [8]. Then the samples were kept in the microscope column for 10 h to achieve the equilibrium between the oil vapours in the microscope column and the oil molecules adsorbed by the sample surface. The beam current in the microscope was up to 0.5 nA and the beam diameter was ≈ 1 nm. The accuracy of the determination of the beam position on the sample was ≤ 3 nm. The residual pressure in the microscope column pumped down by an oil diffusion pump was 3×10^{-7} Pa. The electron energy loss spectra were recorded by an electron spectrometer with a resolution of 1.0 eV and analyzed by the link-860 system. The substrates were 40-80 nm thick films of amorphous carbon or 40 nm thick Fe films sputtered on thin (≈ 60 nm) SiO₂ diaphragm on silicon [9].

3. Results.

Just as in the previous observations [10] the transmission images of thin foils point to the local growth of a carbon-containing layer on specimen surface owing to the action of the electron probe. Moreover, we have found that the passage of the stationary electron beam outside the film at a distance of ≤ 35 nm from its edge leads to the formation of a ledge on the film edge in the region adjacent to the electron beam. With further exposure the ledge increases reaching the beam. Figure 1a shows the edge of the Fe film and a circle indicating the passage of the electron beam (35 nm from the film edge). Figure 1b shows the same edge with a 30 nm wide ledge formed after 160 s exposure. A long rod protruding in the direction away from the substrate edge can be formed by successive movement of the electron beam at a certain distance from the ledge formed.



Fig. 1. — Images of the ledge and rod formed by the electron beam passing outside the film : a) the Fe film edge before the onset of the process; b) after 160 s exposure by the electron beam passing at 35 nm from the edge.

This technique enables the formation of strap bridges in the gap between two edges of the film as can be seen from figure 2. The width of the second, narrower, bridge in the figure does

not exceed 10 nm. Initially the width of the first bridge was the same, but it increased with the formation of the second one spaced at 70 nm from the first. The widening of the first bridge may result from the polymerization of the hydrocarbon molecules on its surface. The polymerization is likely to be induced by the secondary electrons emitted during the formation of the second bridge [11].

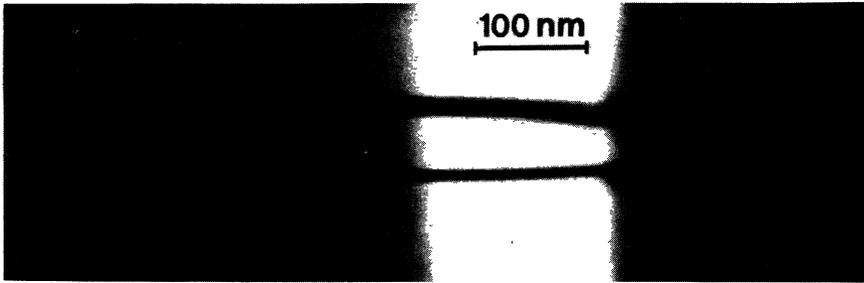


Fig. 2. — Bridges between two edges of the carbon film. The rate of electron beam movement is 6 nm/s.

Figure 3 shows EELS-spectrum of the electrons passed through the formed ledge (solid line). The presence in this spectrum of the 6 and 25 eV peaks in the region of low losses and the 284 eV absorption edge suggests that the spectrum corresponds to carbon [12]. Figure 3 also shows the EELS-spectrum recorded as the electron beam passed outside the preliminarily formed ledge at a distance of 10 nm from its edge (dotted line). (Throughout the recording period (2 s) the growing ledge had no time to touch the electron probe). It is seen that the peak of energy losses of the primary beam electrons corresponds to 18 eV, this value differs significantly from the maximum of the plasmon loss energy upon the beam passage through the ledge (25 eV). In our case this fact points to excitation of the surface plasmons whose maximum energy for amorphous carbon is 17.7 eV [12].

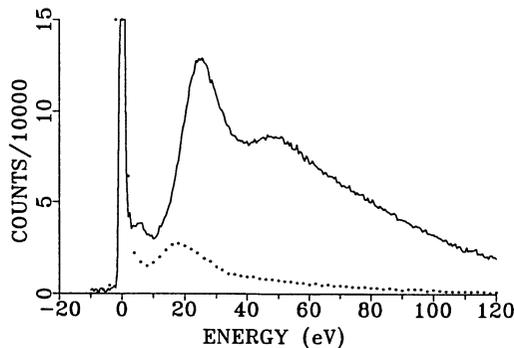


Fig. 3. — EELS-spectra of primary beam electrons passing through the ledge (solid line) and outside the preformed ledge at 10 nm from its edge (dashed line).

Figure 4a (asterisks) presents the time τ in which the growing carbon ledge reaches the electron beam initially spaced at 20 nm from the substrate edge as a function of the probe current i . It is seen that τ decreases with increasing probe current i and at large currents it approaches asymptotically a constant value. This suggests that the rate of formation of carbon ledges is limited by the diffusion rate.

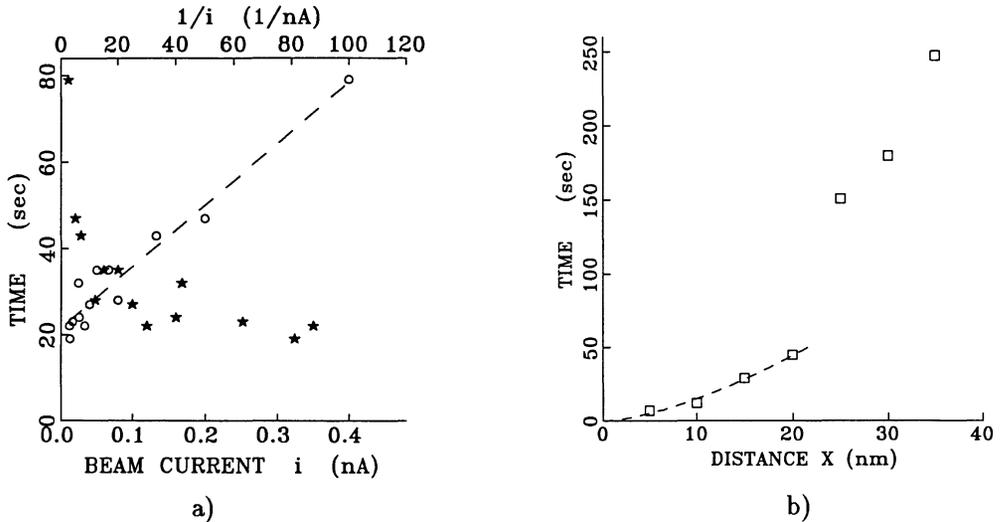


Fig. 4. — Dependences of the time τ in which the growing carbon ledge reaches the stationary electron probe on the probe current i (asterisks) and the inverse value of the probe current $1/i$ (circles) (a), and on the distance between the beam and the substrate edge x (b). In the case of (a) the probe-substrate distance is 20 nm; in the case of (b) the probe current $i = 1.6 \times 10^{-10}$ A.

The dependence of time τ on distance x of the beam from the substrate edge (Fig. 4b) is characterized by nonlinear increase of τ with increasing x .

4. Discussion.

It is possible to suggest that the hydrocarbon molecule dissociates on the substrate surface due to excitation of its valency electrons. Two channels of excitation of the hydrocarbon molecule are most probable. One of them is transfer of some part of the energy of the plasmon arising upon inelastic scattering of the beam electrons to the hydrocarbon molecule [13]; the other channel is direct resonance excitation of the molecule by the passing beam electron (on the analogy of excitation of surface plasmons on a small spherical particle by passing beam electron [14]). Excitation of the valency molecule shells may lead to the break of the chemical bonds up to ionization of the molecule [15]. As is known, dissociation products may polymerize losing their mobility and forming a hydrocarbon layer. A specific concentration gradient is created on the sample surface because of the mobile hydrocarbon molecule depletion in the electron beam region. This gradient determines the hydrocarbon diffusion flow into the irradiated zone which is a sink region [16].

To understand the experimental results, let us derive the quantitative functional dependence between the main growth characteristics of carbon-containing structures. Clearly, this calls for

simultaneous analysis of surface diffusion and the electron-induced process of molecule dissociation or polymerization.

Let an excitation zone of width 2α in which the hydrocarbon molecules are subjected to dissociation or polymerization be formed under the action of the electron beam passing at distance x from the edge of a flat substrate of thickness h (Fig. 5). The diffusion flow of molecules into the excitation zone may be conventionally divided into two parts: one-dimensional flow from the face surface J_t and two-dimensional flow from the upper and lower surfaces of the flat substrate J_s .

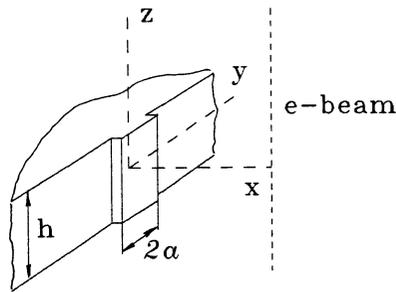


Fig. 5. — Scheme of the formation of a carbon-containing ledge on the substrate edge.

The relation between the flows J_t and J_s can be found from the solution of the corresponding continuity equations taking into account that $\alpha \ll \rho$ where $\rho = (D\tau_a)^{1/2}$ is the molecule diffusion length on a surface, D is the surface diffusion coefficient, τ_a is the lifetime of a molecule in the adsorbed state :

$$J_t/J_s = h \ln(\rho/\alpha)/(\pi\rho).$$

For $h = 100$ nm, $\alpha = 15$ nm and $\rho = 10$ μm [17] we find $J_t/J_s = 2.3 \times 10^{-2}$. Taking into account that $J_t/J_s \ll 1$, we may further neglect the contribution of the one-dimensional diffusion flow over the face surface and consider only the two-dimensional diffusion flow over both substrate surfaces. In essence, the mobility of hydrocarbon molecules is not limited when they pass from the lower or upper surfaces onto the face surface of the substrate and the diffusion flow to the reaction zone may be regarded as planar. This means that we may consider the two-dimensional diffusion flow into the reaction zone of width 2α and length h . Besides, assuming that in the present experiments $a \ll \rho$ and $h \ll \rho$, the rectangular reaction zone of area $2ah$ may be substituted for a round zone with an equivalent area of radius $R = (2ah/\pi)^{1/2}$ without changing the main features of the process.

In this case we may use the solution of the diffusion problem in which the formation of a hydrocarbon layer on the flat substrate is considered [16]. Assume that the dissociation of hydrocarbon molecules is the same in the whole reaction zone and directly proportional to beam current i and to effective dissociation cross-section σ . Then using the solution of the continuity equation obtained in [16] we find for $R \ll \rho$ the diffusion hydrocarbon flow to the reaction zone of radius R :

$$J = \frac{\nu\rho^2 (\rho_0^2/\rho^2 - 1) I_1(R/\rho_0)}{\rho_0 I_0(R/\rho_0) + R I_1(R/\rho_0) \ln(1.1 \rho/R)} \quad (1)$$

where $\rho_0 = \rho / [1 + i\sigma\rho^2/2eDah]^{1/2}$, I_0 and I_1 are the modified Bessel's functions of the zero and first orders, respectively, $\nu = \rho/(2\pi mkT)^{1/2}$ is the effective flow of the molecules coming from a

gas phase, ρ and T are the partial pressure and the temperature of a gas phase, k is the Boltzmann's constant, e is electron charge, m is the mass of a molecule. If one assumes that all the hydrocarbon molecules diffusing into the reaction zone take part in the formation of a hydrocarbon ledge, it is easy to find the relationship between the ledge growth rate v_x and the diffusion hydrocarbon flow J :

$$v_x = J \left(\frac{2\pi}{ah} \right)^{1/2} m_c \mu / \rho_c \quad (2)$$

where m_c is the carbon atomic mass, ρ_c carbon (graphite) density, μ the number of carbon atoms which form a ledge as a result of dissociation of a single hydrocarbon molecule. In further estimations we assume that the microscope column contains polyphenyl ether $C_{30}H_{22}O_4$ with an intrinsic vapour pressure of 10^{-7} Pa. In this case $\mu \leq 30$.

It may be expected that as the growing ledge approaches the electron beam, the probability of inelastic scattering of beam electrons will increase along with increasing effective cross-section of molecule dissociation. As a consequence, the dissociation rate and the linear rate of carbon ledge growth will increase. Then the exposure time required for the ledge to touch the beam may be determined from the following relationship

$$\tau(x) = \int_0^x v_x^{-1}(\xi) d\xi \quad (3)$$

where ξ is the distance between the edge of the ledge and the center of the electron beam. Substituting (1) into (2) and using expression (3), after simple transformations we obtain

$$\tau(x) = \frac{ah e \rho_c}{\nu \tau_\alpha i m_c \mu} \int_0^x \frac{d\xi}{\Sigma(\xi)} + \frac{x}{v_d} \quad (4)$$

where $v_d = \pi \nu \rho^2 m_c \mu / (ah \rho_c \ln [1.4 \rho (ah)^{-1/2}])$ is the limiting rate in the case of diffusion mechanism of growth, Σ the full dissociation cross-section. The experimental results represented by circles in figure 4a are well described by the linear dependence in the $\tau - 1/i$ coordinates (Fig. 4a, circles). Approximating by the least squares method, it was found that the intercept on the y-axis has the value $\tau = 21 \pm 7$ s and the tangent of the straight line slope is $\text{tg } \gamma = (0.59 \pm 0.05) \times 10^{-9}$ sA. Equating the second term of equation (4) to τ , we find $\rho = 7 \pm 2$ μm . The obtained value of ρ is typical of the hydrocarbon molecules migrating over the surface [17].

Let us analyse the above mentioned elementary acts of scattering and dissociation. Both main channels of energy transfer giving rise to molecule dissociation may be characterized by two main parameters, namely, the probability of electron excitation P and the cross-section of hydrocarbon molecule dissociation σ . Then the full dissociation cross-section $\Sigma(\xi)$ in equation (4) may be represented as

$$\Sigma(\xi) = \sigma_1(\xi) + \sigma_2(\xi) = P_s(\xi)\sigma_s + P_m(\xi)\sigma_m.$$

Here σ_1 and σ_2 are the cross-sections of dissociation for both main channels of energy transfer, P_s and P_m are the probabilities of electron beam excitation of the surface plasmon on the film face and the valency electrons of the hydrocarbon molecule, respectively; σ_s and σ_m are the corresponding dissociation cross-sections under the action of this excitation. Let us estimate the contributions of σ_1 and σ_2 to the total scattering cross-section. After differentiation of equation (4) with respect to x we obtain

$$\Sigma(x) = \frac{ah e \rho_c}{\nu \tau_\alpha m_c \mu i (d\tau/dx - 1/v_d)}. \quad (5)$$

Approximating the experimental dependence $\tau(x)' = \tau(x) - x \cdot v_d^{-1}$ by the third-degree polynomial (dashed line in Fig. 4b) and substituting $d\tau/dx$ into (5), we find

$$\Sigma(x) = (3.3 \pm 0.8) \times 10^{-22} x^{-2}$$

where x is the distance in nm. This dependence is plotted in figure 6 (solid line). The contributions of both dissociation channels may be separated by comparing the value $\Sigma(x)$ obtained from equation (5) and the theoretical probabilities of plasmon excitation on the surfaces of the semi-continuous medium P_s [12] and of the spherical particle P_c [18]. Integrating with respect to all the possible frequencies the expression for the probability of excitation of a plasmon with the energy $\hbar\omega$ on the surface of a semi infinite medium by an electron passing at distance x from the surface [12], we find full excitation probability P_s

$$P_s(x) = \frac{he^2\Gamma\omega_s^2}{2\pi^2\hbar\varepsilon_0v^2} \int_{\omega_0}^{\omega} K_0\left(\frac{2\omega x}{v}\right) \frac{\omega d\omega}{(\omega_s^2 - \omega^2) + \Gamma^2\omega^2} \tag{6}$$

where $v = 1.644 \times 10^8$ m/s is the electron velocity at the accelerating voltage of 100 kV, $\varepsilon_0 = 8.85 \times 10^{-12}$ Fm⁻¹ the dielectric constant, r the length of electron path at a distance x from the surface, $\hbar\omega_s = 17.7$ eV the energy of the surface plasmon loss peak for amorphous carbon, $\Gamma = 1.5 \times 10^{16}$ s⁻¹ the damping factor determined experimentally from the spectrum shown in figure 3 as the halfwidth of the plasmon resonance peak. Since we are interested in plasmons with the energy exceeding that of the chemical bond dissociation energy of organic molecules (≈ 3.4 eV [19]), we chose $\omega_0 = 5.14 \times 10^{15}$ s⁻¹ as the lower limit of integration in (6).

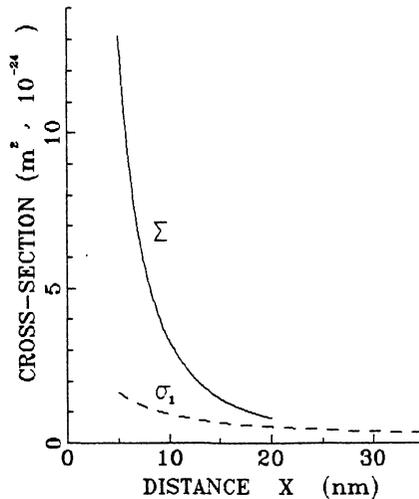


Fig. 6. — Dependences of effective cross-sectional $\Sigma(x)$ and $\sigma(x)$ on the probe substrate edge distance x .

The analysis of the dependence between $\Sigma(x)$ and the calculated values of $P_s(x)$ showed that the correlation coefficient close to unity is observed for $x > 25$ nm. We found $\sigma_s = (3.4 \pm 0.3) \times 10^{-24}$ m² from this dependence. This suggests that at large distances the contribution to the dissociation is made mainly by the surface plasmons. Their excitation probability is defined by equation

(6). Figure 6 shows the calculated dependence of $\sigma_1(x) = P_s(x) \cdot \sigma_s$ on the distance x in the 5 - 35 nm range (dashed line) plotted with regard to equation (5).

The fact that the values of $\Sigma(x)$ exceed significantly those of $\sigma_1(x)$ for small x indicates that the second channel of dissociation (direct resonance excitation of the molecule) is prevailing here. Let us analyze this process.

The action during the time 10^{-17} s of the external electrostatic field of electron passing on a distance r will cause collective displacement of the valency electrons in the molecule, the position of the atomic nuclei being unchanged. This will give rise to collective oscillations of the valency electrons showing up as a peak on the electron energy loss spectrum, the central part of the peak falling within at the 20-25 eV range [15]. Excitation of the valency molecule shells may lead to the break of the chemical bonds down to ionization of the molecule [15].

The calculation of energy losses on the basis of the free electron model by the formula

$$\hbar\omega_p = \hbar (ne^2/\epsilon_0m_s)^{1/2}$$

yields for organic molecules the typical value $\hbar\omega_p \cong 20$ eV [15] (n is the density of all outer shell electrons, e the charge, m_e the electron mass). This enables us to consider molecules as small spherical particles of the radius $R_m \cong 0.5$ nm. In this case, using equation (A10) from [14] in the approximation $R_m \ll r$, and assuming that the hydrocarbon molecule may be at any point with the coordinate y on the substrate face the averaged excitation probability in the whole reaction zone of the width $2a$ and the height h may be estimated by the following expression

$$P_m = \frac{2\alpha c}{av} \left(\frac{\omega_1 R_m}{v}\right)^3 \int_0^\infty \left[K_0^2 \left(\frac{\omega_1 (x^2 + y^2)^{1/2}}{v}\right) + K_1^2 \left(\frac{\omega_1 (x^2 + y^2)^{1/2}}{v}\right) \right] dy$$

Here $\alpha = 1/137$ is Sommerfeld's fine structure constant, c the velocity of light, K_0 and K_1 are the modified Bessel functions of orders 0 and 1, respectively, $\omega_1 = \omega_p \cdot 3^{-1/2}$.

From the closeness of the correlation coefficient to unity in the dependence between $\sigma_2(x) = \Sigma(x) - \sigma_1(x)$ and $P_m(x)$ calculated for the corresponding values of x we can conclude that at distances up to 20 nm from the edge of the substrate the main contribution to dissociation is made by the molecules excited directly by the bypassing electron. From the tangent of the dependence between $\sigma_2(x)$ and $P_m(x)$ we find $\sigma_m = (2.2 \pm 0.5) \times 10^{-18}$ m². Comparison of this value with geometrical cross-section $\sigma_M \simeq 0.8 \times 10^{-18}$ m² of the C₃₀H₂₂O₄ molecule suggests that each event of direct resonance excitation of hydrocarbon molecules leads to their dissociation.

The fact that σ_m turns out to be twice as large as σ_M may be related either to the roughness of some parameters used in the calculations or to the interaction of plasmon oscillations of neighbouring particles if the distances between them are sufficiently small. The mutual influence of collective excitations in different particles has been analyzed in [20]. Such collective resonance interaction is also probable in closely spaced hydrocarbon molecules adsorbed on the surface.

Attention should be paid to the low efficiency of hydrocarbon molecule dissociation under the action of surface plasmons. The small value of the cross-section of the process $\sigma_s = 3.4 \times 10^{-24}$ m² as compared to σ_M shows that at least 10^6 surface plasmon excitations are required for dissociation or polymerization of a single hydrocarbon molecule. This result may be explained taking into consideration the fact that the beam electrons may enhance not only the processes of dissociation of hydrocarbon molecules but also their desorption from the surface [21]. The excitation of the molecules adsorbed on the surface is also likely to occur at the expense of the resonance interaction between the surface plasmons and collective excitations of the valency electrons of the organic molecule lying on the surface since the corresponding characteristic frequencies are

closely spaced (15-20 eV) [12, 15]. Hydrocarbon molecule dissociation may be also affected by the secondary electrons produced by collective interactions of the solid-state electron plasma and the charge of the electrons of the passing beam. The presence of the secondary electrons in our experiments may be confirmed by the widening of the preformed bridge during growth of the second neighbouring bridge (Fig. 2).

It follows from the foregoing that it is most important to take into account the effect of the "long-range" electron beam-substance interaction upon the formation of nanometer structural elements. Indeed, even in the absence of the substrate when the "illumination" factor occurring at the expense of the secondary electrons emitted by the substrate is ruled out, the region of electron-induced dissociation of hydrocarbon molecules is about 20-30 nm in size (see, for instance, Fig. 1b) which exceeds considerably the diameter of the electron probe (≈ 1 nm). Therefore, to achieve the minimum size of structural elements it is essential that the parameters of the process are optimized with regard to "long-range" plasmon excitation.

5. Conclusions.

Electron beam-induced "long-range" growth of carbon-containing structures has been observed in the microscope column pumped down by an oil vapour diffusion pump. As the beam passes outside the substrate at a distance of $\lesssim 35$ nm from its edge, a carbon-containing ledge is formed on the substrate edge in the region adjacent to the electron beam. The electron energy loss spectra obtained during the ledge growth show a peak of 18 eV inelastic losses which may be related to collective electron excitation on the surface.

Within the framework of the model of hydrocarbon molecule surface diffusion the functional relationship has been found between time τ during which the growing ledge touches the stationary electron beam and the main parameters of the process, namely, beam current, the size of the dissociation zone, and the pressure of hydrocarbon vapours. Comparison between the calculated and experimental dependences of τ on the beam current made it possible to calculate the diffusion length ρ whose value ($\approx 7 \mu\text{m}$) is typical for hydrocarbon molecule surface diffusion.

It has been proposed that the dissociation of the hydrocarbon molecule on the substrate surface occurs due to the excitation of its valency electrons. Two possible ways of energy transfer to the molecule have been analyzed. One of them is direct resonance excitation of the molecule by the passing beam electron. The other is transfer of some energy of the surface plasmon produced by inelastic beam electron scattering to the hydrocarbon molecule. It is shown that the first process prevails at short distances and the second - at the distances over 20 nm. Estimation of the effective dissociation cross-sections revealed that each event of direct resonance excitation of the hydrocarbon molecule results in its dissociation whilst the efficiency of the transfer of surface plasmon energy to the hydrocarbon molecule is fairly low. The results obtained point to the necessity of taking into account the "long-range" effect in the interaction of the electron beam with the object, particularly, for the estimation of the limiting resolution in electron-beam lithography.

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