On the Mechanism of Formation of Hydrocarbon Contamination on Surfaces Irradiated by a Narrow Electron Beam

Gl. S. Zhdanov, V. N. Vershner

1967

SovietRxiv

Abstract

Full Text

UDC 537.533.79 + 537.533.35

Physics

Gl. S. Zhdanov, V. N. Vershner

On the Mechanism of Formation of Hydrocarbon Contamination on Surfaces Irradiated by a Narrow Electron Beam

(Presented by Academician A. A. Lebedev, December 2, 1966)

According to present-day views ([1–3]), the formation of contamination on surfaces irradiated in vacuum by an electron or ion beam is explained by the condensation of residual hydrocarbons and their subsequent polymerization under the action of the irradiation. The rate of growth of the contamination layer depends on the size of the irradiated area and increases most sharply when the beam diameter is reduced to $2\,\mu$ and below. Thus, according to the data of ([3]), reducing the dimensions of the electron beam from 2 to $0.2\,\mu$, at a current density $j = 0.1$—0.3 a/cm^2, leads to a sixfold increase in the rate of contamination. The dependence of the contamination rate on the beam dimensions is explained by the fact that, as the beam diameter increases at constant current density, the temperature of the object rises and, consequently, the lifetime of adsorbed hydrocarbon molecules decreases.

Our measurements of the temperatures of objects in the electron microscope ([4]) showed that at $j = 0.1$ a/cm^2 and an irradiated-area diameter $d \leq 4\,\mu$, the temperature increase under the beam does not exceed 2—3°. An analogous conclusion had previously been obtained theoretically ([5]). It seems unlikely that such a small temperature increase could cause a change in the contamination rate by approximately an order of magnitude (the same effect is attained when objects are heated to 150—200° ([1])). As is seen from Fig. 1, an identical increase in the temperature of the object leads to a more noticeable decrease in contamination at a larger beam diameter. Thus, to explain the dependence of the contamination rate on the beam dimensions, it is insufficient to take into account only the change in the temperature of the object.

It was shown in ([1]) that, when a broad electron beam is used, migration of molecules over the surface plays no role in the formation of contamination. This conclusion was also unjustifiably extended to the case of narrow beams ([3]). We shall show below that, when the beam dimensions are reduced to a few microns,

Fig. 1

Figure 1: Fig. 1

the principal source of contamination becomes the flux of hydrocarbon molecules diffusing over the surface toward the irradiated region of the object.

Let ν be the number of hydrocarbon molecules incident on unit area per unit time, n the number of molecules adsorbed per unit area, and τ their mean lifetime on the surface. In the absence of an electron beam, equilibrium is established between the number of molecules arriving and desorbing during the time dt, i.e.,

$$\nu dt = n\frac{dt}{\tau} \quad \text{or} \quad n = \nu\tau. \tag{1}$$

Under the action of electrons, some of the molecules are ionized and polymerize. If τ_1 is the mean time interval between collisions of a molecule with electrons leading to the formation of an unsaturated bond and, as a consequence, to polymerization, then the number of molecules polymerized

Fig. 1. Contamination spots on a carbon film formed over 15 min under different irradiation conditions; 4500×.
1 —mean beam diameter $d = 4\mu$, current density $j = 0.1$ A/cm^2, increase of temperature under the beam (according to data from (4)) $\Delta T \approx 2°$, growth rate of the contamination layer $dh/dt = 4.5$ Å/s;
2 —$d = 4\mu$, $j = 1.3$ A/cm^2, $\Delta T = 30°$, $dh/dt = 2.2$ Å/s;
3 —$d = 10\mu$, $j = 0.3$ A/cm^2, $\Delta T = 30°$, $dh/dt = 0.9$ Å/s. Since $j \gg j_n \approx 0.1$ A/cm^2, the contamination rate does not depend on j (2).

···colliding during the time dt, is equal to $dp = n\frac{dt}{\tau_1}$. Denoting the cross section of such a collision by σ, we obtain $\tau_1 = e/\sigma j$ (e is the electron charge, j is the current density). In the steady state $vdt = dp + n\frac{dt}{\tau}$, i.e.

$$v = n\left(\frac{1}{\tau} + \frac{1}{\tau_1}\right). \tag{2}$$

An analogous result, but with a more complicated derivation, was obtained in [(2)].

It follows from formulas (1) and (2) that the number of adsorbed (but not polymerized) molecules n is greater on the nonirradiated areas than under the electron beam. The presence of a concentration gradient leads to the appearance of a diffusion flux of molecules directed toward the center of the irradiated region. In calculating this flux we shall assume that the current density j and the average

migration velocity of the molecules $\bar{v}$ do not depend on the distance r from the center of the beam.

Consider three rings of width a, whose centers coincide with the center of the beam, and whose radii are $r+a$, r, and $r-a$, where a is the average distance over which a migrating molecule is displaced in one jump. With sufficient accuracy it may be assumed that in the time $\Delta t = a/\bar{v}$ one quarter of the molecules in the outer ring pass into the middle ring and one quarter of the molecules from the middle ring pass into the outer ring. The same exchange of molecules occurs between the middle and inner rings. The change in the number of molecules in the ring of radius r during the time Δt is equal to:

$$dN_{\text{diff}} = \frac{1}{4}\, n(r+a)2\pi[r+a]a + \frac{1}{4}\, n(r-a)2\pi[r-a]a - \frac{1}{2}\, n(r)2\pi ra$$

Expanding the functions $n(r+a)$ and $n(r-a)$ in a Taylor series and referring the result obtained to unit area per unit time, we find

$$\Delta N_{\text{diff}} = \frac{dN_{\text{diff}}}{2\pi ra\Delta t} = \left(\frac{1}{4}\frac{d^2n}{dr^2} + \frac{1}{2r}\frac{dn}{dr}\right) a\bar{v}, \tag{3}$$

where ΔN_{diff} is the diffusion-caused change in the number of molecules on a unit area located at a distance r from the center of the beam, per unit time.

Adding ΔN_{diff} to v in equation (2) and carrying out simple transformations, we obtain

$$\frac{d^2n}{dr^2} + \frac{2}{r}\frac{dn}{dr} - \frac{n}{\rho^2} = -\frac{4v}{a\bar{v}}, \tag{4}$$

where

$$\rho = \sqrt{\frac{a\bar{v}\tau\tau_1}{4(\tau+\tau_1)}}. \tag{5}$$

Equation (4) can be reduced to Bessel' s equation. Its solution is expressed as a linear combination of exponential functions [(6)]. The constants of integration are determined from the conditions: $n(0) \neq \infty$ and $n(R) = v\tau$ (formula (1)), where R is the beam radius. Under these conditions the solution has the form:

$$n = \frac{v\tau\tau_1}{\tau+\tau_1}\left(\frac{\tau}{\tau_1}\frac{f(r/\rho)}{f(R/\rho)} + 1\right), \quad \text{where } f(r/\rho) \equiv \frac{\operatorname{sh}(r/\rho)}{r/\rho}. \tag{6}$$

Let us find the number of molecules polymerized per unit area per unit time:

Fig. 2

Figure 2: Fig. 2

$$\frac{dp}{dt} = \frac{n}{\tau_1} = \frac{v\tau}{\tau + \tau_1}\left[\frac{\tau}{\tau_1}\frac{f(r/\rho)}{f(R/\rho)} + 1\right]. \tag{7}$$

The growth rate of the contamination layer is

$$\left(\frac{dh}{dt}\right)_1 = V\frac{dp}{dt},$$

where V is the volume of a molecule. When thin objects are used, contaminants are formed at the same rate on both sides; therefore the total contamination rate is

$$\frac{dh}{dt} = 2\left(\frac{dh}{dt}\right)_1 = 2V\frac{dp}{dt}.$$

It should be noted that the function $f(r/\rho)$ increases as r varies from 0 to R; consequently, at constant current density in the beam, the contamination rate should increase from the center toward the edges of the beam. In reality the current density obeys a Gaussian distribution ([4,7]), and the decrease of j at the beam edges may completely or partially compensate the increase of $f(r/\rho)$. In practice, depending on which effect predominates, either a maximum or a minimum of contamination may be observed at the center of the irradiated region ([3]).

Fig. 2. Curve **1**–the function $\varphi(R/\rho)$, defined by formula (9). Curve **2**–experimental dependence of the growth rate of the contamination layer dh/dt on the beam radius R; open circles–data from ([3]), j = 0.1-0.3 A/cm^2, filled circles–our measurements, $j = 0.1$ A/cm^2.

Let us find the average growth rate of the contamination layer:

$$\overline{\frac{dh}{dt}} = \frac{1}{\pi R^2}\int_0^R 2\pi r\,\frac{dh}{dt}\,dr = \frac{2V\nu\tau}{\tau + \tau_1}\left[\frac{\tau}{\tau_1}\varphi(R/\rho) + 1\right] = \left(\frac{dh}{dt}\right)_\infty\left[\frac{\tau}{\tau_1}\varphi(R/\rho) + 1\right], \tag{8}$$

where the following notation has been introduced:

$$\varphi(R/\rho) \equiv \frac{2[\mathrm{ch}(R/\rho) - 1]}{R/\rho\ \mathrm{sh}(R/\rho)}, \tag{9}$$

$$\left(\frac{dh}{dt}\right)_{\infty} \equiv \frac{2V\nu\tau}{\tau+\tau_1}. \tag{10}$$

The quantity $(dh/dt)_{\infty}$ is the contamination rate for $R \to \infty$, when molecular diffusion plays no role. Formula (10) is a consequence of formula (2). The graph of the function $\varphi(R/\rho)$ is shown in Fig. 2.

Experiment shows ([1,3]) that the contamination rate in broad beams increases linearly with the current density at $j < 10^{-2}$ A/cm^2 and reaches saturation at $j = j_{\text{n}} \approx 10^{-1}$ A/cm^2. Since $\tau_1 \sim 1/j$, it follows from (10) that $\tau_1 \gg \tau$ for $j < 10^{-2}$ A/cm^2 and $\tau_1 \ll \tau$ for $j > 10^{-1}$ A/cm^2. With sufficient accuracy one may put $\tau \approx 10\tau_1$ at room temperature and $j = j_{\text{n}}$. This means (formula (8)) that, for a sufficiently narrow beam and $j \gg j_{\text{n}}$, the contamination rate due to molecular diffusion may increase by a factor of 10 or more in comparison with $(dh/dt)_{\infty}$.

Figure 2 gives experimental values of dh/dt, obtained in ([3]) and in the present work. The contamination rate was measured in an Elmiscope-1 electron microscope from the decrease in transparency of a carbon film. The transparency was estimated by the formula: $D = \ln(I_0/I) = -kh$, where h is the thickness of the contamination layer. The constant k, as in ([3]), was taken to be $5 \cdot 10^{-4}$ Å^{-1} at a voltage of 80 kV.

It follows from formula (8) that, for $\tau \gg \tau_1$ and small R,

$$R\,\overline{\frac{dh}{dt}} \sim \varphi(R/\rho).$$

Indeed, the experimental dependence agrees well with the theoretical one if one takes $\rho = 0.1\,\mu$ at $j = 0.1$ A/cm^2. For other values of j, somewhat different values of ρ may be obtained, since ρ depends on τ_1 (formula (4)), and consequently also on j.

Thus, the dependence of the contamination rate $\overline{dh}/dt$ on the beam radius R is determined by the ratio R/ρ, where ρ is a certain characteristic length determined by formula (4) and close to $0.1\,\mu$ at a current density j of the order of 0.1 A/cm^2. Four regions may be distinguished in which this dependence has a different character:

1. $R \leqslant \rho \approx 0.1\,\mu$. When R changes from 0 to ρ, $\varphi(R/\rho)$ changes by only 6%. Consequently, narrowing the beam at $R \leqslant \rho$ should not lead to an increase in contamination. Physically this means that most of the molecules pass through the irradiated region before colliding with electrons. The contamination rate increases with increasing j.

2. $\rho < R \leqslant 10\rho$. In this region $\overline{dh}/dt$ changes most strongly. The principal role in the formation of contamination is played by diffusion of molecules from unirradiated regions.

3. $10\rho < R \leqslant\approx 50\rho$. The contamination rate decreases with increasing R according to a hyperbolic law, asymptotically approaching $(dh/dt)_\infty$. In practice, because of the temperature increase when the beam is broadened, a sharper decrease may be observed.

4. $R > 50\rho \approx 5\,\mu$. Diffusion of molecules does not lead to any noticeable increase in contamination:

$$\overline{dh}/dt \approx (dh/dt)_\infty = \frac{2V\nu\tau}{\tau + \tau_1}.$$

This formula is confirmed experimentally [1,2].

Received
21 XI 1966

REFERENCES

[1] A. E. Ennos, Brit. J. Appl. Phys., **4**, 101 (1953).
[2] R. W. Christy, J. Appl. Phys., **31**, 1680 (1960).
[3] H. G. Heide, Zs. angew. Phys., **15**, 116 (1963).
[4] G. S. Zhdanov, V. N. Verdner, *Radiotekhnika i elektronika*, **11**, 1884 (1966).
[5] S. Leisegang, Proc. Intern. Conf. Electr. Micr., London, 1954, p. 176.
[6] E. Kamke, *Handbook of Ordinary Differential Equations*, "Nauka,"1965, p. 434.
[7] B. Gale, K. F. Hale, Brit. J. Appl. Phys., **12**, 115 (1961).

Note: Figure translations are in progress. See original paper for figures.