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SELF-COOLING OF A GAS, ABSORBING LASER RADIATION, DUE TO THE INTENSIFICATION OF PHOTOABSORPTION CONVECTION

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The effect of decrease in the temperature of an absorbing gas in a volume occupied by the beam of a continuously operated laser with decrease in the beam diameter has been investigated experimentally for the case of constant radiation power. Based on theoretical evaluations it has been inferred that the intensification of photoabsorption convection is the reason for the temperature decrease. It has been shown that an optimum diameter of the beam exists for which (for a given radiation power) the temperature of the absorbing gas attains its maximum (accordingly the maximum is attained by the yield of the reaction of thermal decomposition of the gas in the case of its pyrolysis). When the diameter is optimum the heat loss from the beam volume by heat conduction is equal to the heat loss by photoabsorption convection. It has been inferred that in constructing an adequate theoretical model of laser-induced chemical vapor deposition it is necessary to take into account the convection.

Behind the method of laser-induced chemical vapor deposition [1, 2] (Fig. 1) is the idea of utilizing the energy of laser radiation for dissociation of the initial gas instead of either heating it to the dissociation temperature through the substrate or the reactor walls (as in the case of chemical vapor deposition) or initiating plasma discharge in it (as in the case of plasma-enhanced chemical vapor deposition). It is clear that the rate of dissociation of the gas under the action of continuous laser radiation depends on the power of the radiation and the absorptivity of the gas. But in what manner is the dissociation rate related to the diameter of a laser beam? In particular, what diameter must the beam have to attain the maximum rate of deposition? The model proposed in the most detailed investigations of laser-induced chemical vapor deposition [3, 4] provides no answer to these questions. However, the fact of the dependence of the deposition rate on the beam diameter has already been reported in [5]; this rate increased 1.5–2.5 times when the diameter of the beam was increased from 4 to 7.5 mm for 77 W continuous radiation.

Experiment and Results. To elucidate the question posed we conducted the following experiment. The beam of a continuously operated CO_2 laser (line (R(20) 10.591 μm, power 70 W) was focused to the chamber of a unit of laser-induced chemical vapor deposition of amorphous silicon under the following conditions (Fig. 2): distance "beam axis–substrate" 5.3 mm, substrate temperature 340^oC, and composition of the argon–silane mixture $[SiH_4]/[Ar] = 5.2/94.8$ for a total pressure of 36 mm Hg and a pumping rate of 10 standard cm^3/min.

The powdered deposit produced on the substrate which was located under the waist of the focused beam is shown in Fig. 3. It is well seen that at the center of the substrate, above which the radiation intensity was maximum, the deposit has the minimum thickness (optical density) and width, whereas at the edges of the substrate (on the left and on the right), i.e., in the regions above which the radiation intensity was minimum, its thickness and width are maximum. The optimum density in equidistant cross sections perpendicular to the longitudinal axis of the deposit was measured using a microphotodensitometer. Setting the thickness of the deposit proportional to its optical density, we took the obtained curve density as the geometric profile of the deposit in the cross section. Measuring the area between the *X* axis and the optical-density curve for a certain cross section, we obtained the mass of the deposit of this cross section in relative units. The transverse dimension of the laser beam corresponding to this cross section of the deposit was measured from the size of the holes melted by the beam in a 120-μm-thick lavsan film.

The dependence of the mass of the deposit (in relative units) on the cross-sectional area of the beam which is obtained in such a manner is presented in Fig. 4. It is seen that the ratio *M/S* is not constant. This fact rejects one

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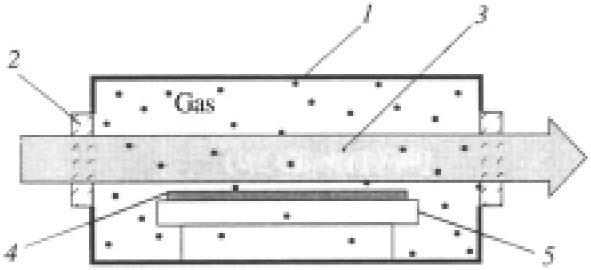


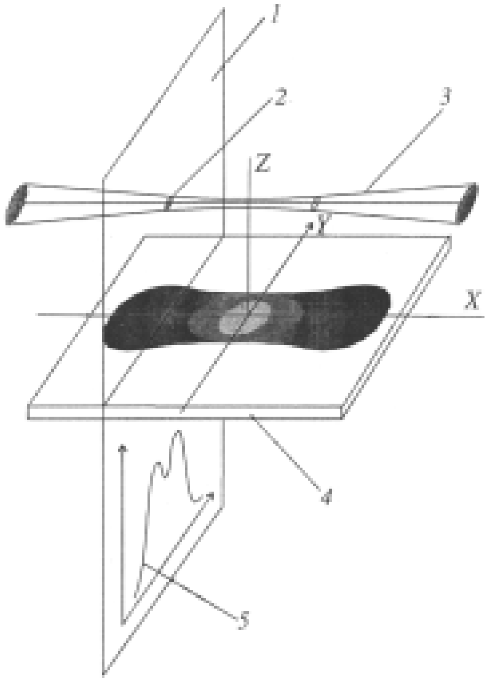


Fig. 1. Principle of laser-induced chemical vapor deposition: 1) chamber with a reactive gas; 2) window to introduce laser radiation; 3) laser beam; 4) plate (substrate) on which the film is deposited; 5) heater of the substrate.

Fig. 2. Circuit of measurement of the deposition rate as a function of the cross section of the laser beam: 1) plane in which the mass of the deposit and the cross section of the beam are compared; 2) cross section of the beam; 3) focused laser beam; 4) glass substrate with a deposit; 5) curve of the optical density of the deposit; *X*, *Y*, *Z*) coordinate axes; the origin is on the substrate under the beam waist.

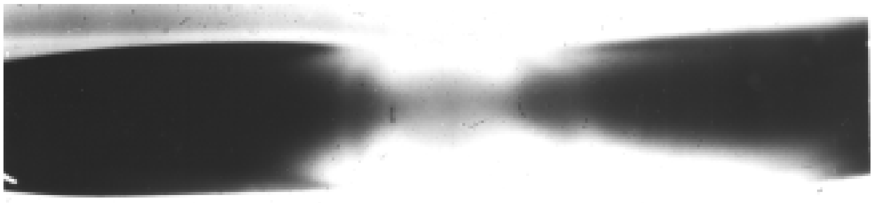


Fig. 3. Photograph of a powdered deposit produced under the focused beam.

explanation of the effect considered in [4], i.e., an increase in the deposition rate due to the increase in the number of dissociated molecules with increase in the beam size.

The final result of the absorption of continuous laser radiation by a dense gas (36 mm Hg) is the increase in its temperature [3]. Consequently, in our case the rate of dissociation of monosilane and the rate of increase of the deposit on the substrate are determined by the temperature in the reaction zone in accordance with the Arrhenius law [3, 5]. With this in mind we measured the distribution of the gas temperature around the focused laser beam in the vicinity of the waist. For this purpose we introduced a moving thermocouple into the chamber of the unit of laser-induced chemical vapor deposition. Before the measurement we evacuated the chamber, switched on the laser beam, and determined the boundaries of the region around the beam where the thermocouple does not contact the beam yet. Then we closed the beam, switched on the channel of the reaction mixture, and after the establishment of the steady-state pressure in the chamber opened the beam again and measured the end of the thermocouple at a given point. The thermocouple was calibrated *in situ* against the melting points of grains of such metals as In, Sn, Pb, and Al.

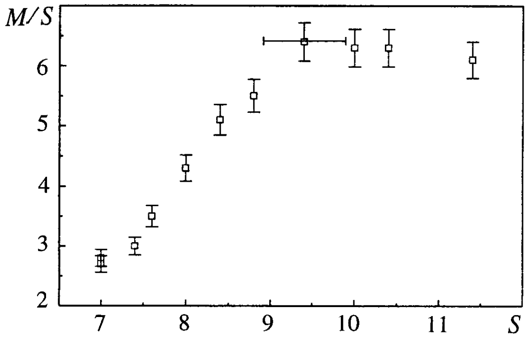


Fig. 4. Ratio of the mass of the deposit to the area of the beam cross section vs. size of this cross section. *M*, rel. units; *S*, m^2.

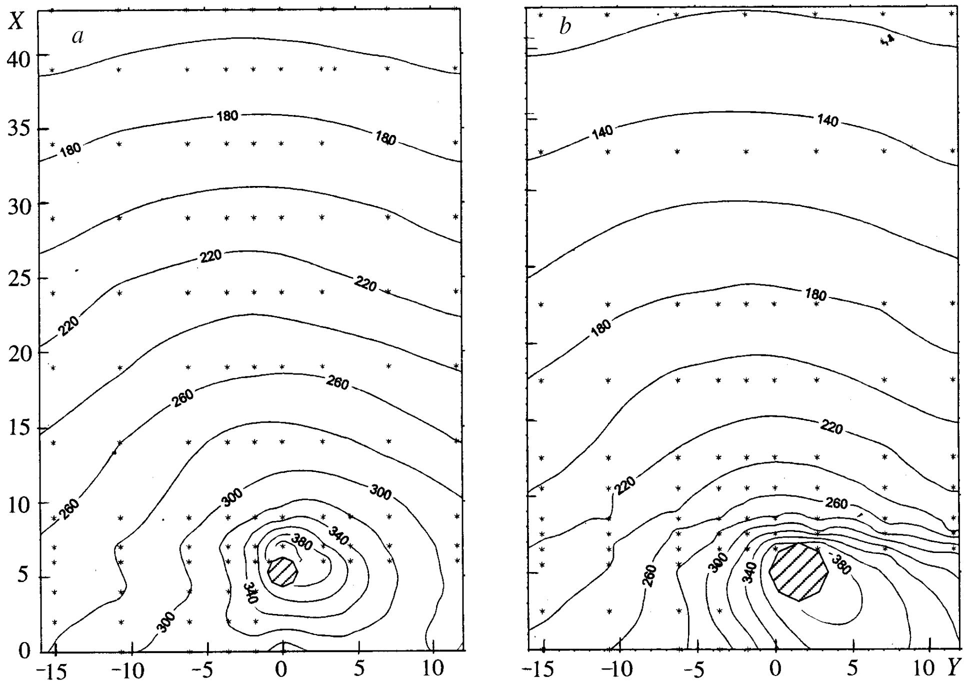
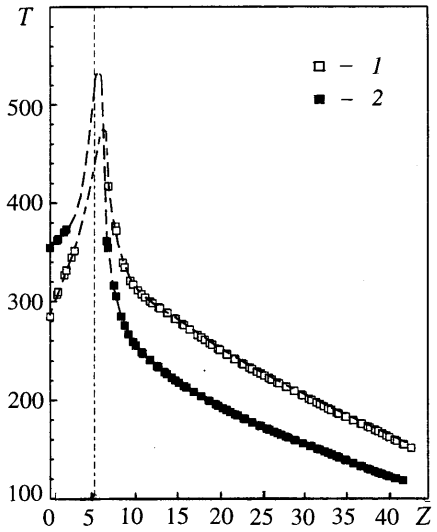


Fig. 5. Isotherms of the temperature distribution in the plane perpendicular to the beam axis and intersecting the waist of the focused laser beam (a) and the beam before the waist at the point where the diameter of the beam is twice as large as in the waist (b). *X*, mm; *Y*, mm.

It should be said the temperature was measured for a somewhat lower power of the beam than the power for which the deposit was produced (see Fig. 2), i.e., when no marked dissociation of monosilane occurred yet. Otherwise, the powder formed would have been deposited on the thermocouple and this would have led to the distortion of the value of the measured temperature. However, the mechanism of heating of the gas is the same in both the case of heating with the dissociation of monosilane and without dissociation, since the products of dissociation of monosilane do not absorb the radiation of the CO_2 laser [6].

The distribution of the gas temperature around the laser-beam waist obtained in such a manner is shown in Fig. 5a. The analogous distribution for the cross section where the diameter of the beam is twice as large as in the waist is presented in Fig. 5b. The asterisks on the plots denote the sites where the temperature was measured. The isotherms are obtained as a result of computer interpolation (temperature in ^{o}C). The position of the laser beam is marked by the hatched polygon. For the cross sections in question, the temperature distributions in the vertical plane which passes through the beam axis are presented in Fig. 6.



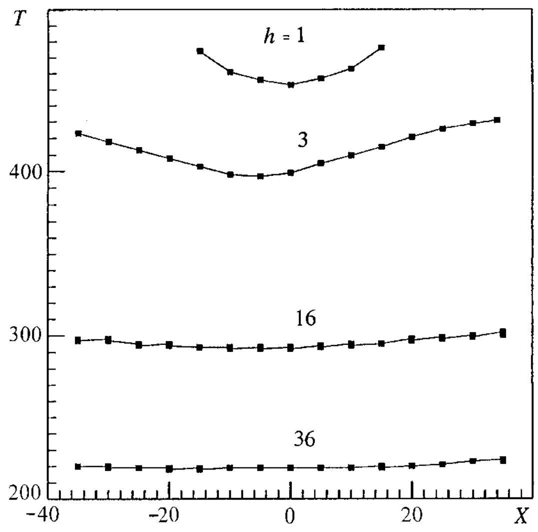


Fig. 6. Distribution of the gas temperature on the Z axis in the plane $Y=0$ (see Fig. 3) for two values of the diameter of the convergent laser beam (the dashed vertical line shows the beam axis): 1) diameter of the beam is 1.8 mm (waist); 2) 3.7 mm. T, ^{o}C; Z, mm.

Fig. 7. Distribution of the gas temperature above the waist of the focused laser beam at different distances h from its axis in the vertical plane ($Y=0$) passing through the beam axis. T, ^{o}C; X, mm.

The thermocouple gives no way of measuring the gas temperature directly in the beam, but on the basis of the obtained data on the temperature distribution around the beam one can qualitatively extrapolate the curves of Fig. 6 into the beam. For this purpose the dependences already obtained were supplemented with a measurement of the behavior of the temperature of the gas above the laser beam along its axis at different distances from the beam (Fig. 7). It is seen that as the waist is approached the gas temperature decreases monotonically; the closer to the beam axis, the larger this decrease is. It can be inferred that inside the beam the difference between the gas temperature in the waist and at the periphery of the caustic must be even larger. Therefore, the curves (see Fig. 6) into the laser beam must be extrapolated in a such a manner, as is shown by the dashed line.

The isotherms in the vicinity of the beam axis (it is precisely here that the dissociation of monosilane occurs) are nearly circles (Fig. 5). It follows that a decrease in the gas temperature which is analogous to that given in Fig. 7 occurs throughout the volume of the beam waist. Thus, in the experiment in question, the temperature of the gas, which absorbs laser radiation, decreases with decrease in the beam size, leading to a decrease in the rate of dissociation of monosilane and the rate of deposition on the substrate.

The right-hand wing of the temperature distribution (Fig. 6) for the smaller diameter at large distances from the beam axis lies higher than the same wing for the larger diameter of the beam; however, the contribution of this region to the dissociation–reaction yield is negligibly small as compared to the high-temperature region because of the exponential dependence of the dissociation rate on the temperature.

Discussion. The decrease in the temperature of the absorbing gas with decrease in the diameter of the beam (with its power being preserved) seems strange if the process of laser-induced chemical vapor deposition is considered on the basis of the models proposed. Thus, according to [7], the increase in the gas temperature, caused by the absorption of laser radiation, is equal to

$$\Delta T = \frac{\ln(b/a)}{2\lambda} P\alpha . \tag{1}$$

This expression is obtained when the laser beam is considered as an isothermal cylinder of radius a whose axis runs at a distance b from the isothermal plane approximately realized by the substrate surface. In the case of the heat flux with the power per unit length of the cylinder F_0, the temperature distribution in the radial direction is determined from the relation

$$F_0 = -2\pi r \lambda dT/dr\,, \quad a \le r \le b\,, \tag{2}$$

where λ is the thermal conductivity of the medium [8]. Next, the power of the flux F_0 is equated to the power of the laser radiation absorbed by the gas $P\alpha$ and expression (2) is integrated from the temperature of the substrate T_s to the maximum temperature of the gas T_g after which we obtain (1). Here the heat loss, caused by convection and the initiation of the reaction of decomposition of monosilane, is set negligibly small, as is done in [3] and the previous works of Meunier et al. Thus, according to the model considered, the behavior of the maximum temperature of the gas must be opposite to the behavior observed in our experiment. Correct analysis of the temperature distribution in the initially isothermal medium in a cylindrical cell upon the introduction of a Gaussian beam into it and reaching the steady state yields qualitatively the same behavior of the temperature as a function of the beam radius, as does (1) [9].

A numerical solution of the steady-state equation of heat conduction where the source of heating of the gas is laser radiation also yields an increase in the gas temperature in the volume of the beam with decrease in its diameter. Thus, in [10] for the same conditions it is shown that the peak temperature (on the beam axis) increases from 570°C for a diameter of 4.2 mm to about 700°C for a diameter of 2 mm.

Now we try to take into account photoabsorption convection by means of the following simplified analysis. Let there be a gas-filled horizontal cylinder with radius a (i.e., a volume occupied by the laser beam) uniformly heated due to the absorption of laser radiation. Then the heat loss, caused by convection, per unit time per unit length of the cylinder is equal to

$$Q_v = 2\rho_0 a V_c C_p \Delta T\,. \tag{3}$$

The heat loss by heat conduction (per unit length) Q_c can be evaluated using expression (2). We set $r = a$; since the laser beam, filled with the gas, is approximated by the isothermal cylinder, we can approximate dT/dr as $-\Delta T/(b-a)$ or $dT/dr \approx -\Delta T/b$ for $b >> a$. Then

$$Q_c = 2\pi\lambda\Delta T\, a/b\,. \tag{4}$$

We equate the total loss to $P\alpha$, i.e., to the energy absorbed by the gas per unit time (heat loss by decomposition of monosilane is disregarded, as previously, by virtue of its low concentration):

Thus, we obtain

$$\Delta T = \frac{P\alpha}{2\pi\lambda \frac{a}{b} + 2aV_c\,\rho_0 C_p}\,. \tag{5}$$

According to [11], in the general case the characteristic velocity of photoabsorption convection (i.e., of that caused by the heating of the medium by laser radiation) is determined by the expression $\tilde{V} = C(\mathrm{Pr})q^N$. We have three regimes of photoabsorption convection, which change from one to another as q increases: weak convection ($N = 1$), moderate convection ($N = 1/2$), and developed convection ($N = 1/3$). The coefficient $C(\mathrm{Pr})$ depends on the regime. Only two regimes — of weak and developed convection — exist for gases ($\mathrm{Pr} \approx 1$). This has been established by means of the dimensionless analysis of Navier–Stokes equations in the Boussinesq approximation. Numerical integration of these equations for a horizontal Gaussian beam, directed along the axis of a long square tube, confirms the dependences of [12], where q is determined as $q = \alpha I_0 L^5 \beta g/(\rho_0 C_p \nu^3)$.

To determine the convection regime we must calculate q. We set

$$I_0 \approx P/\pi a^2\,. \tag{6}$$

In our case, the distance "substrate axis–substrate" b (5.3 mm) is much smaller than the diameter of the chamber (180 mm) and the distance between the substrate and the cover of the chamber (69 mm). It is clear that we should take b

as the dimensional parameter determining convection. There is another argument in favor of this assumption. In certain experiments, one more substrate was placed above the laser beam at the distance $2b$ from the lower substrate; however, the appearance of the deposit did not change. Therefore, we take $2b$ as L. The optical absorption of the silane–argon mixture $\alpha \cong 10^{-2}\ \text{cm}^{-1}$ was measured in the course of the experiment. As the remaining parameters we took the properties of pure argon at the substrate temperature (600 K) and a pressure of 36 mm Hg: $\rho_0 = 3.8\cdot 10^{-2}\ \text{kg/m}^3$, $C_p = 5.21\cdot 10^2$ J/(kg·K) [13], $\nu = 4.6\cdot 10^{-2}\ \text{m}^2/\text{sec}$, and $\beta = 3.67\cdot 10^{-3}\ \text{K}^{-1}$ [14]. Thus, for a laser beam with a radius of about 1 mm we obtain the maximum value $q \approx 10^2$. This corresponds to the regime of weak convection [12] which extends to the values of $q = 10^5$–10^6. The fact that the convection is weak is confirmed by the form of the isotherms around the laser beam (Fig. 5) near which they represent nearly regular circles, which is the characteristic feature of the regime of weak photoabsorption convection [12].

Now we can write $\tilde{V} = C(\text{Pr})q$. Since, according to [12], the dimensional velocity of convection is $V_c = \tilde{V}\nu/L$ and $L = 2b$, with account for (8) we obtain

$$V_c = C_1 \frac{16\alpha P b^4 \beta g}{\pi \rho_0 C_p \nu^2} \frac{1}{a^2} = \frac{A}{a^2}, \tag{7}$$

where

$$A = 16 C_1 P \alpha \beta b^4 g / (\pi \rho_0 C_p \nu^2), \tag{8}$$

C_1 is the weak-convection constant [12]. Upon the substitution of (7) into (5) the increase in the gas temperature in the beam as a result of the absorption of radiation can be written as

$$\Delta T = \frac{P\alpha}{2\pi\lambda \dfrac{a}{b} + 2\rho_0 C_p \dfrac{A}{a}}. \tag{9}$$

From the above it is seen that $\Delta T \propto a$ for low values of a and $\Delta T \propto 1/a$ for high a. Thus, (9) adequately describes (at least, qualitatively) the yield of the pyrolysis reaction of monosilane and the behavior of the deposition rate as functions of the beam radius (Fig. 4).

By equating the derivative $d(\Delta T)/da$ to zero one can obtain the condition where ΔT attains its maximum:

$$\frac{\pi\lambda}{\rho_0 C_p b} \approx \frac{A}{a^2}. \tag{10}$$

The left-hand side of (10) characterizes the intensity of heat transfer by heat conduction, whereas the right-hand side characterizes the intensity of heat transfer by convection (see (7)). Thus, the maximum increase in the gas temperature in the zone of the beam is attained for such size of it for which the intensity of the heat loss by heat conduction is equal to the intensity of the heat loss by photoabsorption convection. This "optimum" value of the beam radius a_{opt} can be evaluated from (10) by the order of magnitude:

$$a_{\text{opt}} \approx \left(\frac{A \rho_0 C_p b}{\pi\lambda} \right)^{1/2}. \tag{11}$$

For $a >> a_{\text{opt}}$ the heat loss by heat conduction predominates and $\Delta T \propto 1/a$, whereas for $a << a_{\text{opt}}$ this role is played by photoabsorption convection and $\Delta T \propto a$.

If to roughly evaluate a_{opt} we substitute $\lambda = 30.7\cdot 10^{-3}$ W/(m·K) (thermal conductivity of pure argon at the substrate temperature (600 K) and a pressure of 36 mm Hg) [13], $C_1 \approx 4\cdot 10^{-5}$ [12] (this value is approximate since in the case of the weak regime the convection constant depends on the ratio L/a [12]), and the values of the remaining parameters given earlier into (11), we obtain $a_{\text{opt}} \approx 0.5$ mm by the level of 1/e, where e is the natural logarithmic

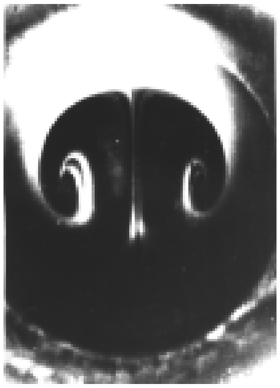


Fig. 8. Photograph of the powdered trace of convective flows on the entrance window of a cylindrical cell.

base, or $a_{opt} \approx 1$ mm by the level of 0.95, which can be assigned to our measurements of the beam cross section. In order of magnitude, the value $a_{opt} \approx 1$ mm corresponds to the value of 1.7 mm obtained in the course of the experiment (Fig. 4).

In closing, we will touch upon the question of the presence of convection in photochemical experiments; this question has been investigated in [15] in detail. From this work it follows that the realization of the presence of convection in photochemical systems dates back to 1912. The criteria which guarantee the absence of photoabsorption convection are: 1) strictly horizontal lower and upper walls of the reaction cell; the lateral walls are heat-insulated; 2) the light directed either vertically upward or vertically downward in such a manner as to ensure the illumination of the entire cross section of the cell. It seems clear that in actual experiments on laser-induced chemical vapor deposition, these conditions are not satisfied or, at least, we always have weak photoabsorption convection. To illustrate the above we can give the photograph of a powdered deposit left on the entrance window of a cylindrical cell with a silane–argon mixture after the short-duration action of continuous laser radiation for $q \approx 10^8$–10^{10} (Fig. 8). This deposit is actually a "portrait" of photoabsorption convection resulting from the absorption of laser radiation.

CONCLUSIONS

1. In the case of weak photoabsorption convection, a range of diameters of the laser beam exists where the heat removal from the zone of the beam exceeds the heat removal by heat conduction. In this case, a decrease in the beam diameter leads to a decrease in the average temperature of the gas in the beam zone because of the intensification of photoabsorption convection.

2. An optimum value of the laser-beam diameter exists for which the total heat loss from the beam zone is minimum and the gas temperature (deposition rate) attains its maximum value. It is shown that for this diameter the heat loss by heat conduction is equal to the heat loss by convection.

3. Photoabsorption convection plays an important role in laser-induced chemical vapor deposition, and one must take it into account in constructing a mathematical model of the process.

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NOTATION

a, radius of the laser beam, mm; a_{opt}, radius of the beam for which the convection heat loss is equal to the loss by heat conduction, mm; b, distance from the beam axis to the substrate, mm; F_0, heat release power per unit length of the cylinder in approximation of the laser beam by an isothermal cylinder, W/m; λ, thermal conductivity, W/(m·K); C_p, specific heat of the gas at constant pressure, J/(kg·K); β, coefficient of thermal expansion of the gas, K^{-1}; ρ_0, density of the gas flowing into the laser beam, kg/m^3; ν, kinematic viscosity, m^2/sec; α, coefficient of optical absorption of the gas, cm^{-1}; P, laser-radiation power, W; I_0, intensity of the laser beam on its axis, W/cm^2; T_s, substrate temperature, ^{o}C; T_g, maximum temperature of the gas, ^{o}C; ΔT, increase in the gas temperature as a result of the absorption of laser-radiation energy, K; Q_v, power of the heat loss by heat conduction per unit length of the beam, W/m; q dimensionless rate of heating due to the absorption of laser radiation; L, width of the tube in modeling of photoabsorption convection in a tube of a rectangular cross section, mm; g, free-fall acceleration, m/sec^2; V_c, dimensional velocity of the convection flow, m/sec; $\tilde{V}$, dimensionless velocity of convection, $V_c = \tilde{V}\nu/L$; C(Pr), convection constant; Pr, Prandtl number; N, index of convection. Subscripts: opt, optimum; 0, on the (beam) axis; s, substrate; g, gas; v, velocity; c, convection; p, pressure.

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