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# On the temperature dependence of the deposition rate of amorphous, hydrogenated carbon films

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The temperature behavior of the deposition rate of amorphous, hydrogenated carbon films is analyzed both experimentally and theoretically. A reactor based on the supersonic expansion of an arc plasma is used. The film thickness is measured using *in situ* He–Ne ellipsometry. The surface temperature is measured with thermocouples. Comparison of the presented model with the experimental results suggests that the deposited atoms and radicals diffuse over the surface in a weakly bound, adsorbed layer before they are incorporated in the film. Direct incorporation upon chemisorption is improbable.

## I. INTRODUCTION

Plasma deposition is an effective way to grow thin films. It has received increasing attention during the last decades because plasma-deposited films have a number of industrial and scientific applications. Many of these applications are important for microelectronics or for the improvement of surface properties.[1-3]

The interaction between plasma and substrate is very complex and at present only some first steps in modeling of this interaction exist. The plasma–wall interaction includes the deposition of materials derived from a reactive gas as well as the erosion of these substrates by the plasma (etching). Sometimes etching and deposition can occur at different positions in a reactor at the same time.[4]

According to the mechanism of plasma deposition one can distinguish between direct incorporation of particles from the gas phase (flow-in model) and deposition from an adsorbed layer (adsorbed-layer model).[5] Direct incorporation is closely linked to the chemisorption of particles on a surface characterized by the Rideal process. The adsorption model is based on chemical reactions between the substrate or the film and particles physisorbed in a weakly bound layer. The latter mechanism is similar to the Langmuir–Hinshelwood mechanism.[6]

The temperature dependence of the deposition rate allows the distinction between these two different mechanisms. The temperature behavior of etch rates has been investigated previously,[7,8] but the model developed for that application can also be used for plasma deposition.

## II. MODELING

Plasma–wall interactions involve a large number of phenomena, and it is difficult to account for all of them. Volume processes (plasma) and surface processes (substrate) of growth or erosion are both important. The plasma plays an important role not only in the production of reactive particles but also in the transport of the species towards the substrate. A number of investigations have been reported [9,10] which are concerned with the formation of reactive particles in the gas phase.

In this study we consider a flux of condensible particles.

The flow depends on the partial pressure of the particles and their temperature. We start with the several flow densities $j_i$ of the relevant species

$$j_i(\mathbf{r},t) = V_{pl} n_i(\mathbf{r},t) \tag{1}$$

in which $\mathbf{r}$ and $t$ are the usual coordinates for space and time ($n_i$ = volume concentration of the species $i$; $v_{pl}$ = flow velocity of the plasma). The particle flux towards the substrate and the behavior of the substrate in relation to the incident plasma particles together result in the measured deposition rate. The substrate behavior is essentially influenced by its structure, chemical state and temperature. The incoming particles may be (partially or completely) reflected, implanted, adsorbed, or bound on the surface. Which process dominates will depend on the properties of the substrate and on the energy of these particles. For each species the following expression is valid:

$$\epsilon^{st} + \epsilon^{refl} + \epsilon^{impl} + \epsilon^{inc} = 1, \tag{2}$$

where $\epsilon^{st}$ = probability of physisorption (sticking coefficient); $\epsilon^{refl}$ = probability of reflection; $\epsilon^{impl}$ = probability of implantation; $\epsilon^{inc}$ = probability of direct incorporation (chemisorption at the surface).

The character of the deposition process depends on the distribution of these probabilities. In reality all processes may occur at the same time. In most cases however, one process will be dominant and the others can be neglected.

### A. Direct incorporation

The flow-in model is based on the assumption that the probability of incorporation $\epsilon^{inc}$ dominates. The deposition rate $P$ only depends on the flow of particles which are relevant for deposition and their probability of incorporation

$$P(\mathbf{r},t) = \sum_i \epsilon_i^{inc} j_i(\mathbf{r},t) = \sum_i P_i(\mathbf{r},t). \tag{3}$$

The flux $j_i(r,t)$ is connected with pressure, flow rate and temperature of the feeding gas in case of neutrals and radicals and with the substrate voltage in case of ions as dominant species. The growth rate $W(\mathbf{r},t)$, which is the experimentally measured quantity (in m s$^{-1}$), is proportional to the deposition rate $P$ (in m$^{-2}$ s$^{-1}$):

$$W = \frac{1}{L} \sum_i V_i P_i = \frac{1}{L} \sum_i n_i V_i \, \epsilon_i^{inc} \, v_{pl} \qquad (4)$$

with $V_i = M_i/\rho$ which represents the mean volume per incorporated particle. ($\rho$ = density of the deposited film: $L$ = Avogadro's number, $n_i$ = density of species $i$, $v_{pl}$ = plasma flow velocity, $M_i$ = molecular mass of species $i$). The incorporation probability $\epsilon_i^{inc}$ can be considered as a product of the concentration of bounding sites $n_0$ and a cross section of the process investigated:

$$\epsilon_i^{inc} = n_0 \sigma_{0i}^{inc} \exp(-E_i^{inc}/kT), \qquad (5)$$

where $\sigma_{0i}^{inc}$ is a prefactor, $E_i^{inc}$ is the activation energy of direct incorporation and $T$ the temperature. Because direct incorporation is a (spontaneous or induced) unidirectional chemical reaction its cross section can be written in the exponential form.[11] Besides the temperature also steric factors and the excitation state of the surface atoms (e.g., via ion mixing) influence the cross section of incorporation. The deposition rate is concluded to increase with increasing temperature in the temperature regime where direct incorporation is dominant.

## B. Deposition from an adsorbed layer

Another type of growth is the deposition of a layer due to interaction between the surface of the substrate and a physically adsorbed monolayer. During a characteristic residence time $\tau$ the particles either diffuse over the surface or they react with the substrate to be incorporated in the film. Such a reaction may occur under the influence of other particles from the discharge (ions, electrons).[12] The mechanism of deposition caused by an adsorbed layer was discussed in detail by Deutsch et al.[13] Here we only mention that the degree of coverage $\theta_i$ with adsorbed particles $i$ is

$$\theta_i = \frac{j_i \, \epsilon_i^{st}}{j_i \, \epsilon_i^{st} + n_\theta (1/\tau_i + \sigma_i j_x)}, \qquad (6)$$

where $\sigma_i$ = cross section of bonding aided by particle bombardment; $j_x$ = impingement rate of these particles. If there is no flux of energetic particles to the surface which can crosslink the adsorbed species we only have an equilibrium between adsorption and desorption and $\theta_i$ reduces to the Langmuir isotherm.

The deposition rate $P(r,t)$ now takes on the form

$$\sum_i P_i = P(r,t) = \sum_i n_i^{ads} \sigma_i j_x = \sum_i n_0 \theta_i \sigma_i j_x \qquad (7)$$

and combining this with Eq. (6) gives

$$P(r,t) = \sum_i \frac{n_0 \sigma_i j_x j_i(\mathbf{r},t) \, \epsilon_i^{st}}{j_i(\mathbf{r},t) \, \epsilon_i^{st} + n_0(1/\tau_i + \sigma_i j_x)}. \qquad (8)$$

The growth rate itself is given according to Eq. (4).

The residence time $\tau_i$ of the adsorbate depends on the surface temperature $T$ in accordance with the Frenkel equation

$$\tau_i = \tau_{0i} \exp(E_i^{des}/kT), \qquad (9)$$

where $\tau_{0i}$ = preexponential factor: $E_i^{des}$ = desorption energy. Naturally, also the surface diffusion and/or the surface reactivity will be influenced by the substrate temperature.

These effects are implicitly included in $\sigma_i$, but if $\tau_i$ dominates in Eq. (8), as it is the case at sufficiently high temperatures, the temperature behavior of the deposition rate follows a negative slope. At low temperatures ($\tau_i \to \infty, \theta_i \to 1$) the rate is determined by the other parameters, and may even be constant.[13] If we are in a mass transport limited situation then $j_i$ is dominant and the deposition rate is nearly independent of the surface temperature.

Summarizing it is concluded that it is possible to determine how the particles are incorporated into the film by evaluation of the temperature dependence of the deposition rate. A positive temperature slope indicates that the particles are directly incorporated in the film upon chemisorption. A negative slope indicates that the incorporation is intermediated by an adsorbed layer.

## III. EXPERIMENTAL RESULTS

We discuss the deposition of carbon layers in a supersonic reactor. The reactor is described more extensively elsewhere.[14] In this device a geometric separation has been realized for the three principal processes occuring in plasma deposition. The plasma production, plasma transport, and the plasma treatment, here the deposition, are in separate sections of the apparatus.

A thermal plasma generated with a cascaded arc is employed to dissociate and ionize molecular gases. The complete arc system is fixed to an anode supporting flange which is attached to a large vacuum system.

Since the gas expands into vacuum the transport velocity and the effective area in the expanding plasma beam increase. Opposing the arc an electrically floating and water-cooled sample support is mounted. The methane dissociation in the arc is nearly complete[15] and the products are deposited at the surface: a carbon film is growing. A schematic view of the system is given in Fig. 1. The dependence of the deposition rate on macroscopic parameters such as gas flow, pressure, and arc current has been discussed elsewhere.

It is of interest to verify the effect of the substrate temperature on the deposition rate. The construction of the reactor permits a high velocity of ions and neutrals. When they collide with the surface these particles will transfer their kinetic energy into heat energy of the sample. Therefore, we investi-
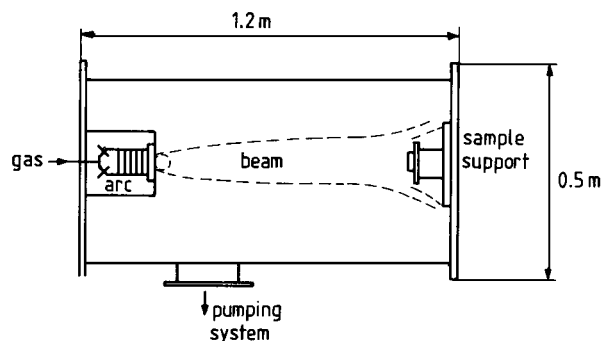
FIG. 1. Outline of the reactor used in the present experiments. The gas is fed through a cascaded arc and emanates in the vacuum system where an intense plasma beam is created. The thus created reactive particles are deposited on the substrate which is mounted on the sample support.
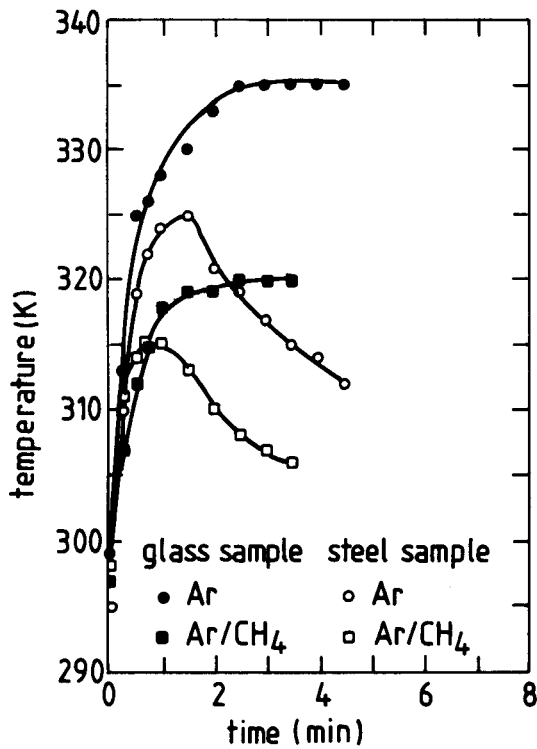
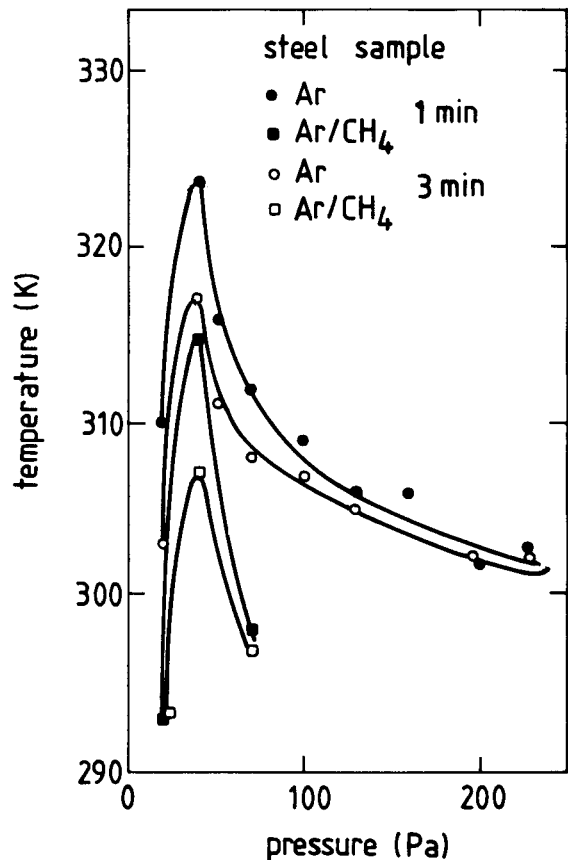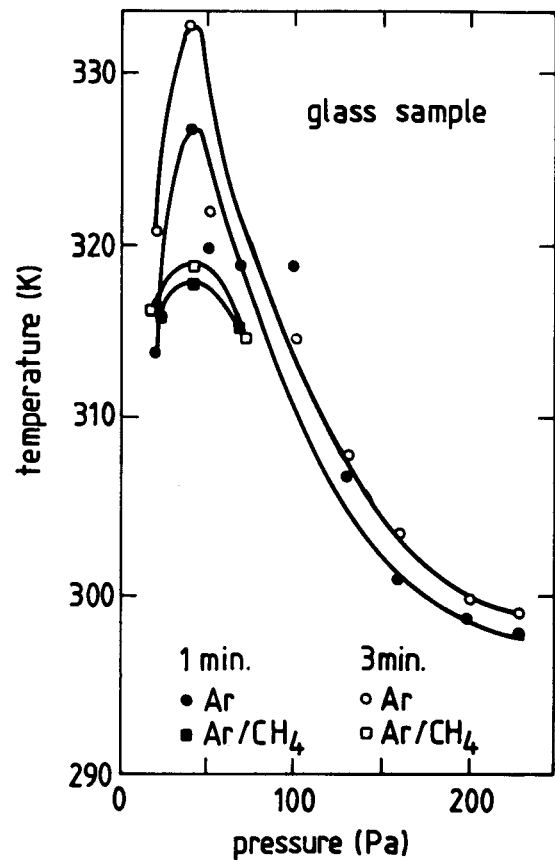FIG. 2. The temperature of the surface exposed to the plasma as a function of time. The pressure is 40 Pa.

gate the substrate heating due to incident particles.

Small glass or steel plates coated with a thin gold layer served as substrates. The standard conditions used were the following:

arc current: $I_{arc}$ = 50 A,
arc voltage: $V_{arc}$ = 85 V,
arc pressure: $p_{arc}$ = 4.7×10⁴ Pa,
gas flow, argon: $\Phi_{Ar}$ = 100 std. cm²/s (scc/s),
gas flow, methane: $\Phi_{CH_4}$ = 1.86 scc/s,
background pressure: $p \sim 10^{-3}$ Pa,
process pressure: $p$ = 20...250 Pa.

The temperature was measured by the thermocouples which were connected with the substrate and shielded from the plasma by a small cover. The surface temperature was recorded as a function of process duration (Fig. 2). In each run the discharge was operated for 4.5 min.

Because steel samples have a higher heat conductivity than glass samples, the heating curves for both substrates were recorded. In case of steel substrates the temperature maximum is reached after ~ 1 min and then a decrease due to the heat transfer to the water cooling occurs. This behavior is caused by the high heat conductivity of metal. After switchoff of the discharge the temperature fell down quickly to the value of the cooling water. As expected, glass samples show quite a different time dependence. At the same conditions a glass substrate reaches a higher temperature than a steel substrate.

Furthermore, the surface temperature was measured as a function of the gas pressure in the system (Fig. 3). From the $T(p)$ plots one can see that there is a certain pressure (40





FIG. 3. The equilibrium surface temperature in dependence on the gas pressure for two different substrates (glass and steel, respectively).
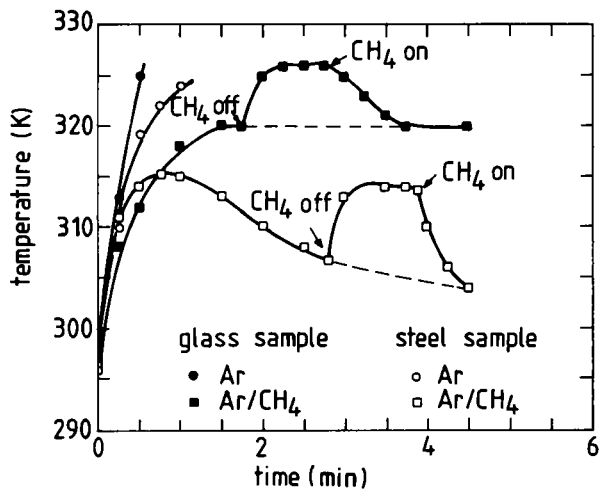
FIG. 4. The surface temperature as a function of time for several plasma conditions including the conditions that are used during deposition.

Pa) where the heating of the sample (due to the impinging particles flux) is most effective. Measurements were performed not only in pure argon but also under deposition conditions, i.e., with admixture of $CH_4$ (Fig. 4). It is clear that with methane injection the surface temperature of the samples is lower than when only argon is used. This is a consequence of the energy the plasma has to supply to dissociate and ionize methane; the plasma is observed to quench when methane is injected. The results are confirmed by the increase of temperature if the $CH_4$ flow is switched off and again only Ar flow exists.

Combining the measured film thickness versus time with the temperature versus time it is possible to get a relation between the deposition and the surface temperature.

The rates were calculated from the thickness of the coated films, which was obtained by in situ ellipsometry. Laser ellipsometry (He–Ne–laser, $\lambda = 632.8$ nm) is a suitable means for the measurement of thin-film growth, for detailed descriptions of this procedure see for instance Ref. 16.

A typical example of a $\Psi$–$\Delta$ plot obtained by ellipsometry is given in Fig. 5. From Fig. 6 one can see that the thickness and therefore the deposition rate depends on the substrate temperature. The temperature varies with increasing process duration as shown above. The deposition rate appears to decrease gradually because of heating of the surface of the (in this case glass) substrate. When thermally conducting substrates are used, this decrease is not observed to such an extent.

The derived growth rate $W$ versus substrate temperature $T$ is plotted in Fig. 7. The slope implies an exponential decrease of the rate according to Eq. (8). Because the rate is decreasing one can assume that the residence time $\tau$ is the dominant factor and the expression for the growth results in

$$W = \frac{1}{L} \frac{M_C}{\rho_C} \sigma j_C j_{Ar} \epsilon_C^{st} \tau_{0C} \exp(E_C^{des}/kT). \tag{10}$$

The subscripts C and Ar denote the carbon and argon atoms or ions respectively, which are the only particles that participate in the formation of the layers.[15] As the plasma beam consists mainly of energetic (1 eV) argon atoms (99%) and no high-energy ions are present like in conventional discharges, it is assumed that the energy needed for the incorpo-
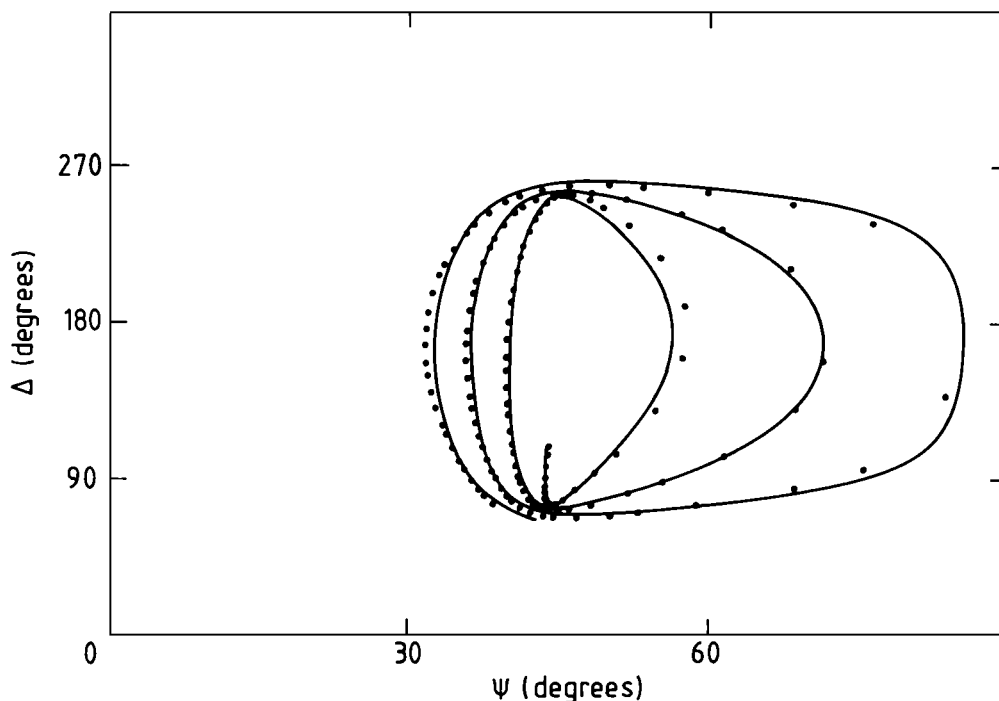


FIG. 5. An example of $\Psi$–$\Delta$ curves as measured (points) with in situ ellipsometry during the deposition of amorphous carbon films on gold. The simulation used to determine the film thickness is also shown (full curve).
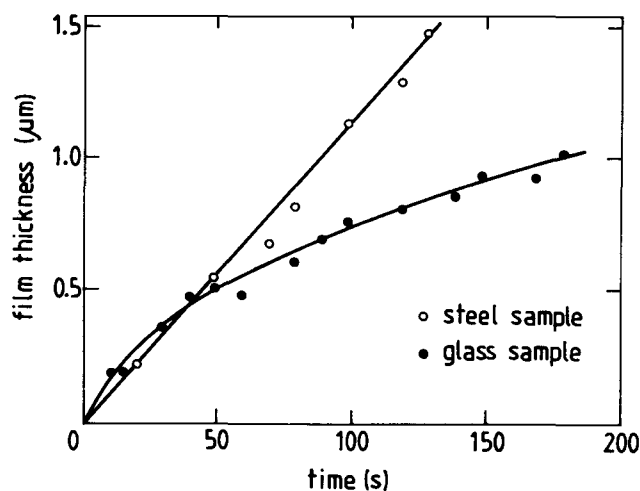
FIG. 6. Film thickness vs time for two sample materials.

ration of the carbon atoms into the film is mainly supplied by the argon atoms. From Fig. 7 we obtain an activation energy of $E_C^{des} = 0.58$ eV and a prefactor of $2.7 \times 10^{-15}$ cm$^{-2}$ s$^{-1}$. Taking the values for $L$, $M$, and $\rho_C$ into the equation we can find

$$\sigma j_C j_{Ar}\ \epsilon_C^{st} \tau_{0C} = 4.1 \text{ cm}^{-2} \text{ s}^{-1}. \tag{11}$$

With a carbon flux $j_C = 5 \times 10^{17}$ cm$^{-2}$ s$^{-1}$ and an argon flux of $2.5 \times 10^{19}$ cm$^{-2}$ s$^{-1}$ measured in the expanding beam[15] we find for the product of the cross section for cross linking, the prefactor of the residence time and the sticking probability a value of $\epsilon_C^{st}\ \sigma\tau_{0C} = 3.2 \times 10^{-29}$ cm$^{-2}$ s. If we assume a
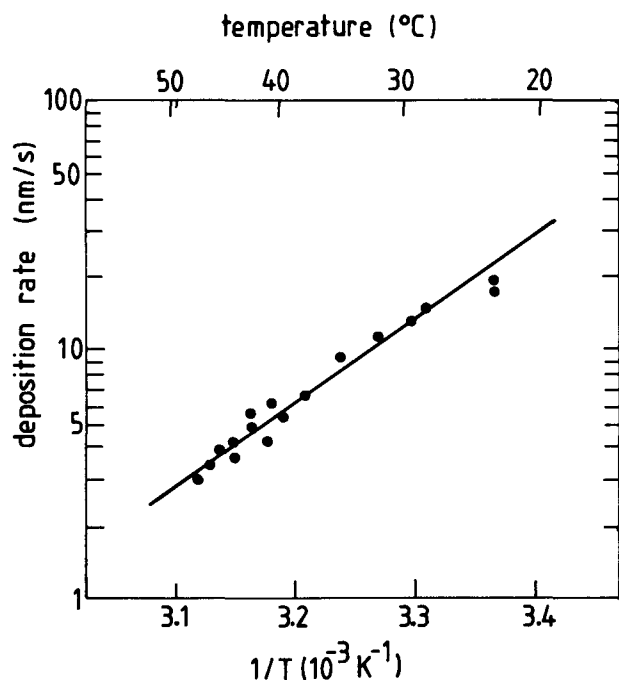


FIG. 7. Growth rate in dependence on the substrate temperature. The points represent the experiments, the line an exponential regression.

sticking probability $\epsilon_C^{st}$ for carbon atoms of 1 and a residence time $\tau_{0C} \cong 10^{-12}$ s[17] then we obtain a value of $3 \times 10^{-17}$ cm$^2$ for the cross section of crosslinking the C atoms by Ar bombardment.

## IV. CONCLUSION

For the deposition of amorphous carbon coating from a $CH_4$–Ar plasma in a supersonic reactor we obtain a negative slope of the temperature dependence of the deposition rate. This result indicates that an adsorption–desorption equilibrium is the rate limiting process in the temperature range studied. A relatively small variation of the temperature leads to a remarkable decrease of the growth rate. After reaching the temperature equilibrium of the sample the rate is stable.

Summarizing we can conclude that the investigations performed indicate that the incorporation of reactive particles into the growing film may be intermediated by an adsorbed layer.

## ACKNOWLEDGMENTS

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