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Advanced mathematical models for simulation of radiative heat transfer in CVD reactors

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Abstract

The effect of radiative heat transfer, in horizontal chemical vapor deposition reactors, on the upper wall temperature and the formation of parasitic GaAs and As deposits is studied in detail. A multi-band model is developed, including the interference of thermal radiation. It is shown that the interference phenomenon leads to a significant additional decrease of the wall temperature that, in turn, results in a substantial diminution of the deposition rate of the GaAs layer. The As film deposited on the reactor wall results in a more significant decrease of the wall temperature, of about 130 K.

1. Introduction

Radiative heat transfer in reactors used for chemical vapor deposition (CVD) of epitaxial layers significantly influences the mass transport of species and chemical reactions during the growth and, what is especially important, determines the formation and composition of wall deposits. In Ref. [1], an experimental and numerical study of the formation of wall deposits during the metalorganic chemical vapor deposition (MOCVD) of GaAs was performed and it was observed that the variation of the intensity of the wall cooling changes the composition of the deposit from a condensed As film to a deposited polycrystalline GaAs layer. It was also found that the rate of deposition of GaAs on the quartz wall varied by more than one order of magnitude at a temperature range of 180 K [1].

In earlier publications devoted to the numerical study of the radiation processes in CVD reactors, the rather simple gray-diffusive models [2–4] or two-band [5] models were used to describe the radiative heat exchange between the solid parts of the reactor. A detailed analysis of the wall emittance, reflectance and transmittance in dependence of its optical thickness, the kind of reflection (diffuse or specular) and the thickness and composition of the wall deposit was performed in Ref. [6]. Using these results a numerical study of heat transfer in a horizontal CVD reactor was conducted in Ref. [7]. The significant effect of the film deposited on the surface of the reactor wall and susceptor on the upper wall temperature distribution was shown. It was found that the effect of the polycrystalline GaAs film has a dual character. On the one hand, the deposited film in-

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creases the reflection of the incident radiation flux coming from the susceptor and, therefore, tends to decrease the upper wall temperature. On the other hand, a sufficiently thick film, in which absorption of the radiation becomes tangible, results in an additional heating of the reactor wall and leads to an increase of its temperature.

In the up to now published studies the radiative heat transfer inside a film was considered using the well-known geometrical optics approximation. This approach is justified until the coherence length of thermal radiation remains far less than the film thickness. In reality, this condition is often violated, especially at the initial stage of the deposition process. Since at temperatures of practical importance, the main part of the black-body radiation in vacuum is in the wavelength range of 2–13 μm, it becomes apparent that, for a more accurate simulation of radiative heat transfer in CVD reactors, it is necessary to use models based on wave optics, that take into account the interference of thermal radiation inside the film.

In the present paper an advanced model for simulating radiative transport is presented and a numerical study of the interaction between radiative heat exchange in a horizontal reactor and the formation of parasitic GaAs and As deposits on the reactor wall during metalorganic chemical vapor deposition (MOCVD) is performed. The effect of GaAs and As deposits on the wall emittance, reflectance and transmittance are discussed in Section 2, while the influence of these deposits on the upper wall temperature is studied in detail in Section 4.

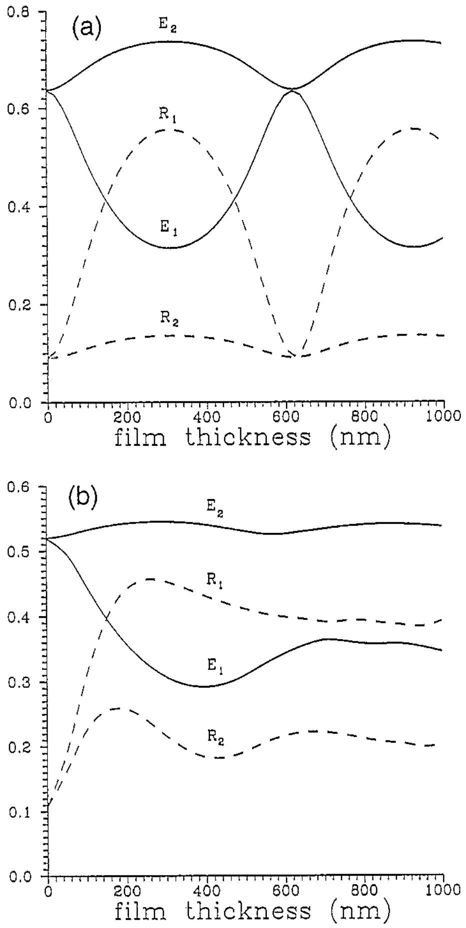

Fig. 1. Emittance and reflectance of a 2 mm quartz wall covered by a film. (a) At 4 μm wavelength; (b) averaged over the whole wavelength range of the black-body radiation. Indices 1 and 2 correspond to the radiative exchange with the reactor volume and with the ambient, respectively.

2. Emittance, reflectance and transmittance of the wall covered by a film

It is well known that interference phenomena occur when monochromatic radiation passes through a thin film, which results in the fact that the radiative properties of the film turn out to be oscillating functions of the wavelength and the film thickness [8]. This is illustrated in Fig. 1a, where the emittance and reflectance of a 2 mm thick quartz plate covered by a polycrystalline GaAs film are shown as functions of the film thickness for a wavelength of $\lambda = 4$ μm. Indices 1 and 2 in Figs. 1a and 1b correspond to the radiative exchange with the reactor volume and with the ambient, respectively. In this case, radiation is completely coherent and, therefore, for the calculation of the radiative properties of the layered structures, the relations of thin film optics have to be used. But, if the wavelength of radiation is within a finite range, the electromagnetic waves start to interact with each other. This results in a decrease of the radiation coherence degree and the radiation intensity oscillations. In the limits of a wide spectrum, one can obtain completely incoherent radiation, which means that the geometrical optics approximation must be used.

The coherence degree of the radiation can be characterized by the coherence length:

$$l \approx \frac{\lambda_{\max}^2}{2\pi\Delta\lambda \operatorname{Re}(n_f)}, \tag{1}$$

where $\lambda_{\max}$ is the wavelength associated with the maximum spectral density, $\Delta\lambda$ is the effective spectrum width, and $\operatorname{Re}(n_f)$ is the real part of the film refractive index. If the spectral density is a step function of the wavelength, then, as it was shown in Ref. [9], radiation can be considered as completely coherent if $d/l < 0.8$, and completely incoherent if $d/l > 9$, where d is the film thickness.

For the spectrum of thermal radiation, similar estimations are not available. In Fig. 1b, the emittance and reflectance for the same system including a quartz plate and a GaAs film are presented after averaging over the whole wavelength range of black-body radiation at the temperature 1000 K. One can see that the emittance and reflectance oscillations are decaying quite quickly, and that, once the thickness of the GaAs deposit exceeds 0.7–1.0 μm, radiation becomes nearly completely incoherent and the geometrical optics approximation can be used. It is possible to estimate the effective width of the spectrum $\Delta\lambda$ and the coherence length l at $T = 1000$ K. Because in the considered case the refractive index of GaAs is $n_2 = 3.3$ and $\lambda_{\max} = 2.9$ μm, we obtain $\Delta\lambda \approx 3.7$ μm and $l \approx 0.11$ μm.

Unlike GaAs, arsenic is characterized by a complex refractive index, with high values of the real and imaginary parts, that in turn depend on wavelength. For example, at $T = 500$ K, the electrical conductivity of solid arsenic is $\sigma = 2 \times 10^4$ (ohm · cm)$^{-1}$ [10]. Hence, we obtain

$$\operatorname{Re}(n) = \operatorname{Im}(n) = \sqrt{\frac{\sigma}{2\omega\epsilon_0}} = 7.7\sqrt{\lambda}. \tag{2}$$

Here, ω is the radiation angular frequency and ϵ_0 is the universal dielectric constant. The wavelength λ in (2) is taken in terms of microns. Thus, the coherence length of the As film is significantly less than that of GaAs. The main difference between these films is due to the very high absorption coefficient of arsenic. Therefore, interference phenomena in the As film take place only until its optical thickness does not exceed unity, that is if

$$4\pi \operatorname{Im}(n)\frac{d}{\lambda} \le 1, \tag{3}$$

or, by using relation (2), if

$$d \le \tfrac{1}{96}\sqrt{\lambda} \quad \mu\text{m}. \tag{4}$$

So, interference effects in the As deposit can be neglected if its thickness is larger than 15–25 nm.

It is assumed by calculating the emittance, reflectance and transmittance of the wall that radiation inside the quartz wall is completely incoherent due to its large enough thickness. As a result, for example, the wall reflectance relative to the radiation incident under an angle θ on the side of the reactor volume takes the form

$$R_1 = R_{f1}^{\nu} + \frac{\rho_2 (\mathrm{Tr}_f^{\nu})^2 \exp(-2\tau/\mu_1)}{1 - \rho_2 R_{f2}^{\nu} \exp(-2\tau/\mu_1)}, \tag{5}$$

where ν is the wavenumber, ρ_2 is the quartz reflectivity, R_{f1}^{ν} and R_{f2}^{ν} are the film reflectances on the side of the reactor chamber and the quartz wall, respectively, Tr_f^{ν} is the film transmittance, τ is the optical thickness of the wall, and μ_1 is defined by the relation $\mu_1 = \sqrt{n_2 - \sin^2\theta}/n_2$, where n_2 is the quartz refractive index. Similar expressions can be written for the other radiative characteristics of the wall.

For a GaAs film, due to its transparency, one can write

$$R_{f1}^{\nu} = R_{f2}^{\nu} = 1 - \mathrm{Tr}_f^{\nu}. \tag{6}$$

The transmittance Tr_f^{ν} is defined by the well-known expression [8]

$$\mathrm{Tr}_f^{\nu} = \frac{(1 - r_{10}^2)(1 - r_{12}^2)}{[1 - r_{10} r_{12} \exp(-2i\beta)][1 - r_{10} r_{12} \exp(2i\beta)]}, \tag{7}$$

where r_{10} and r_{12} are Fresnel intensity reflection coefficients of the two boundaries: the film–vacuum and the film–quartz, respectively. The phase lag β is equal to $2\pi/\lambda n_f d \cos\theta_f$. The interference effect in Eq. (7) is manifested through the terms including the phase lag β. By integrating this relation over β from 0 to infinity, we obtain the expression for the film transmittance corresponding to the geometrical optics approximation.

For As films in the opaque domain, one can neglect the angle dependence of the film reflectance and obtain the relations

$$\mathrm{Tr}_{\mathrm{f}}^{\nu}=0; \quad R_{\mathrm{f}1}^{\nu}=1-\frac{2}{\mathrm{Re}(n_{\mathrm{f}})};$$

$$R_{\mathrm{f}2}^{\nu}=1-\frac{2n_2}{\mathrm{Re}(n_{\mathrm{f}})}. \tag{8}$$

Resulting expressions for the wall emittance and reflectance are obtained by integrating expression (5) and the corresponding one for emittance over the incident angle θ, and by averaging over both polarization components of radiation.

3. Model of the radiative heat transfer in the reactor

In Refs. [6,7], a three-band model based on the analysis of the wavelength dependence of the absorption coefficient of quartz was introduced to describe the radiative heat exchange between the solid parts of the reactor. In the present study, there is a need to use a multi-band model, due to the very strong dependence of interference phenomena on wavelength. It is also important for the As film, due to the significant dependence of the refractive index of arsenic with respect to wavelength, as shown in the present study. Therefore, in the present paper, a 14-band model is developed for a more accurate modelling of radiative heat transport in CVD reactors. For the calculation of radiative fluxes, the approximation of diffuse reflection is used. As a result, the net radiative flux absorbed inside the reactor wall can be calculated using the following expression:

$$q_{\mathrm{net}}^{\nu}=\sum_{k=1}^{14}\left[\left(E_1^{\nu_k}+E_2^{\nu_k}\right)\Delta_k(T_w)\sigma T_{\mathrm{w}}^4-E_1^{\nu_k}q_{\mathrm{in}}^{\nu_k}-E_2^{\nu_k}q_{\mathrm{out}}^{\nu_k}\right]. \tag{9}$$

Here, $\Delta_k(T)$ is the fraction of black-body radiation in the kth waveband, T_{w} is the wall temperature, while $q_{\mathrm{in}}^{\nu_k}$ and $q_{\mathrm{out}}^{\nu_k}$ are the effective radiative fluxes coming to the inside and outside surfaces of the reactor wall, respectively.

Expressions (5)–(9) are introduced into the numerical procedure developed in Ref. [11], and applied here to the simulation of heat transfer in the widely used horizontal-type CVD reactor (see Fig. 2).

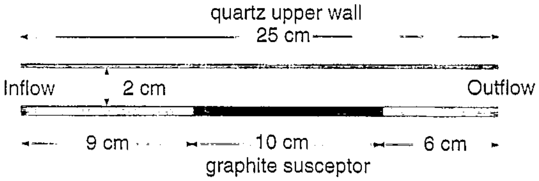

Fig. 2. Schematic view of the horizontal CVD reactor.

4. Numerical results

The mathematical model we have developed is used in the present work for modelling the effect of the kind of the wall deposits on the temperature distribution on the surface of the reactor wall. Calculations are conducted for typical growth conditions used for MOCVD of GaAs: the inflow gas temperature is 300 K, the susceptor temperature is 1000 K, the total pressure is 0.1 atm, and the inflow velocity is 1 m/s. To demonstrate the basic effects of the deposits formation, it was assumed for simplicity that the thicknesses of the As and GaAs films on the reactor wall are uniform. The GaAs deposit is assumed to be present only on the part of the upper wall of the reactor just above the susceptor, whereas for the case of the As deposit, it is assumed that it covers the whole upper wall.

In Figs. 3–6, the influence of the GaAs deposit is demonstrated. The dependencies of the maximal temperature along the surface of the upper wall upon the GaAs film thickness obtained by using the present model and the geometrical optics approximation are shown in Fig. 3. One can see that interference effects on the transport of radiation result in a more significant decrease of the wall temperature in comparison to the geometrical optics approach. It is also interesting to note that the curves in this figure are similar to the curves in Fig. 1b. In Fig. 3 also, the effect of the emissivity of the susceptor surface is demonstrated. It has to be noted that GaAs substrates are placed on the susceptor, and that its surface is covered by a polycrystalline GaAs layer. In this way, the susceptor emissivity can be changed from the emissivity of pure graphite, equal to 0.9, to the emissivity of pure GaAs, which is equal to 0.5 at

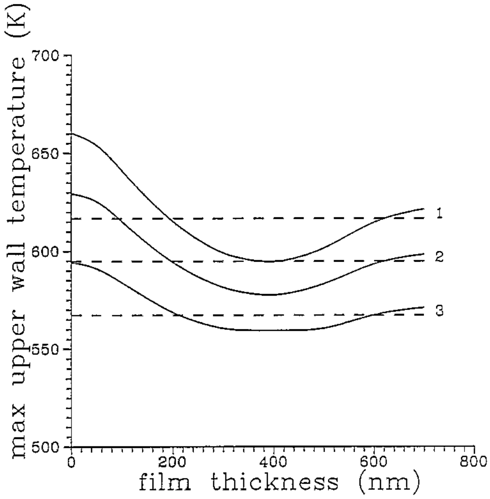

Fig. 3. Dependence of the maximal temperature of the upper wall on the thickness of the GaAs deposit and the susceptor emissivity. (1) Emissivity 0.9; (2) 0.7; (3) 0.5. Dashed lines correspond to the geometrical optics approximation.

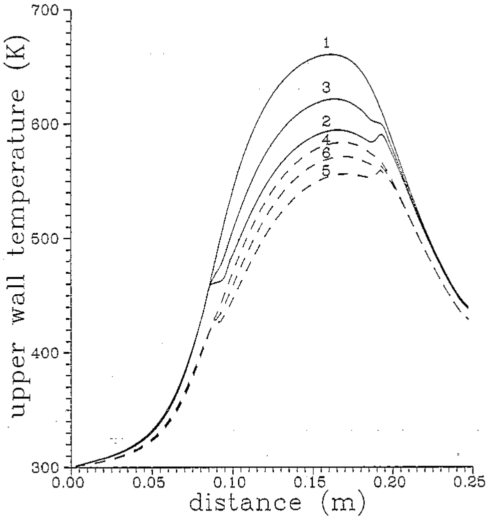

Fig. 4. Temperature distribution along the upper wall of the reactor for different values of the GaAs deposit thickness and the susceptor emissivity. (1)–(3) Emissivity = 0.9, (4)–(6) emissivity = 0.5; (1) thickness 0 nm, (2) 400 nm, (3) 700 nm, (4) 100 nm, (5) 400 nm, (6) 700 nm.

high temperatures. Therefore, calculations are performed for the following three values of the emissivity of the susceptor surface: $E = 0.9$, $E = 0.7$, and $E = 0.5$. One can see that the variation of the susceptor emissivity results in significantly lower wall temperatures. After the simulation work was completed the company AIXTRON provided experimental data on variation in the upper wall temperature with time during MOVPE of GaAs in the horizontal reactor AIX 200/4 [12]. The variation in the wall temperature predicted in Fig. 3 is confirmed in these experiments, where at typical growth conditions a decrease in the upper wall temperature of around 35 K followed by its increase has been observed.

The temperature distribution along the upper wall is shown in Fig. 4 for several values of the film thickness and the emissivity of the susceptor. The non-smooth temperature behavior near the point $x = 0.09$ m, and the small local maximums in the vicinity of the point $x = 0.19$ m are due to a stepwise change of the radiative properties of the upper wall because of the abrupt boundary of the GaAs film in the domain of maximal radiative heating. This effect disappears when the film covers a larger domain of the wall and the edge of the GaAs film is shifted to the less heated region (Fig. 5). Besides, in practice, the thickness of the deposit is non-uniform, and the optical properties of the wall are functions of the position, which can lead to some smoothing of the mentioned peculiarities.

The obtained decrease of the wall temperature due to the formation of a GaAs deposit on the reactor

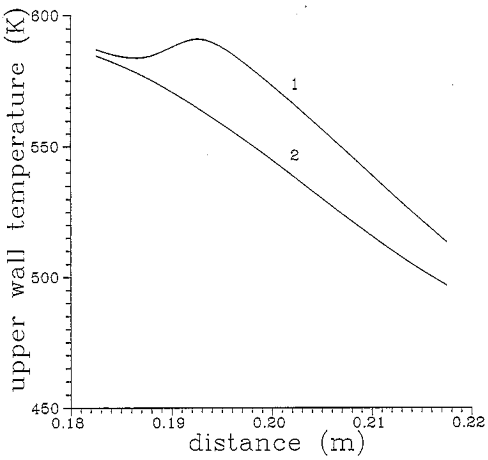

Fig. 5. Effect of the length of the GaAs film on the temperature distribution along the upper wall. (1) The film is located from $x = 9$ cm to $x = 19$ cm; (2) the film covers an increased domain from $x = 9$ cm to $x = 22$ cm.

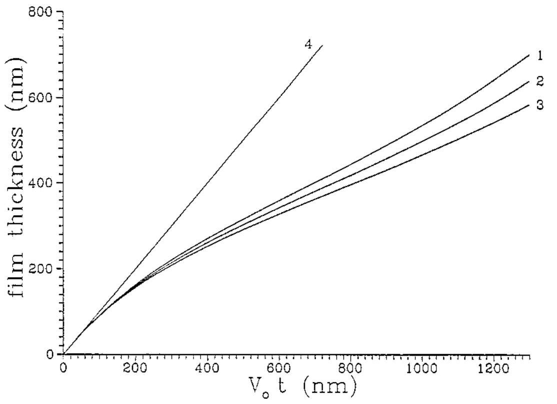

Fig. 6. Dependence of the maximal film thickness on the duration of the growth process for different values of the kinetic constant B. The susceptor emissivity is 0.9, and v_0 is the film deposition rate at $t=0$. (1) $B=8$; (2) 9; (3) 10; (4) describes the film deposition with a constant rate v_0.

wall results in a lowering of the rate of deposition of the polycrystalline layer.

The temperature of the reactor wall is usually significantly lower than the typical temperatures when mass transport limited growth of GaAs is observed [13]. We can assume a kinetically limited mechanism of deposition of the GaAs layer on the reactor wall. In this case, the deposition rate v can be calculated using the following expression:

$$v = v_0 \exp[-B(T(0)/T - 1)]. \tag{10}$$

Here, v_0 is the deposition rate on the surface of the pure quartz wall of the reactor at the start of the growth process, i.e. when the thickness of the GaAs deposit is equal to zero (it is assumed that the reactor is heated up to the working temperatures before starting to introduce the metalorganic precursor, for example, the trimethylgallium), $T(0)$ is the temperature of the pre-heated pure quartz wall before the start of the growth process, and $B = A/RT(0)$ is a non-dimensional constant.

Using the results shown in Fig. 2, we can calculate the evolution of the thickness $h(t)$ of the GaAs deposit. With $v = \mathrm{d}h/\mathrm{d}t$, we obtain

$$t = v_0^{-1} \int_0^h \{\exp[-B(T(0)/T(h) - 1)]\}^{-1} \, \mathrm{d}h. \tag{11}$$

The dependencies $h(t)$ calculated for the three values of the kinetic constant B are shown in Fig. 6, together with the direct line, which corresponds to a deposition process under a constant wall temperature T_0 and with a constant deposition rate v_0. The results of the calculations show the significant slowdown of the film deposition due to the decrease of the wall temperature, because of the interference effects discussed in the present work. This phenomenon, in combination with the effect of the GaAs layer deposited on the susceptor, can suppress the parasitic deposition of a GaAs layer on the reactor wall and result in stationary growth conditions in the reactor after some transient process. To model these transients, the consistent consideration of heat transfer and mass transport in the reactor is necessary, taking into account the evolution of the kind of the deposit and of its thickness and optical properties, which result in changes in the radiative heat transport in the reactor.

The effect of the As film is shown in Fig. 7 for the cases of a pure graphite susceptor and a susceptor covered by a GaAs layer. One can see an unexpectedly large decrease of the wall temperature, which is due to the high reflectivity of the As film, resulting in a decrease of the radiative heat transport toward the wall, in comparison with a pure quartz surface.

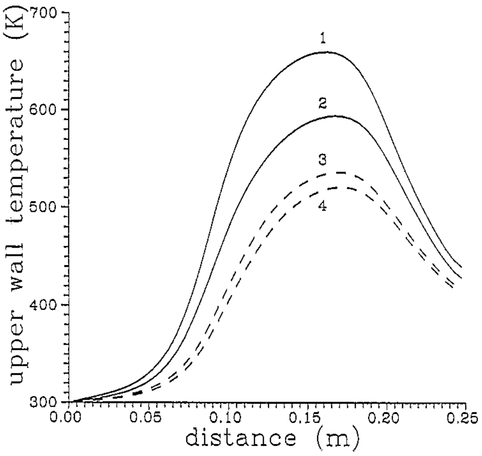

Fig. 7. Effect of the As film on the upper wall temperature distribution. (1), (3) Susceptor emissivity 0.9; (2), (4) 0.5. Solid line: pure quartz wall; dashed line: reactor wall covered by an As film.

5. Conclusions

A model for simulation of radiative heat transfer in CVD reactors, taking into account interference effects, has been presented. It is shown that interference phenomena in the semiconductor layer deposited on the reactor walls result in significant oscillations of the wall emittance and reflectance, and, consequently, in oscillatory variations of the wall temperature. The obtained decrease of wall temperature is found to be more significant in comparison with the results obtained by using the geometrical optics approximation. The essential slowdown of the deposition of a polycrystalline GaAs layer is predicted. Deposition of the As film results in a substantial decrease of the upper wall temperature, of about 130 K, due to the fact that arsenic is characterized by its metallic properties and has a high reflection coefficient.

Acknowledgements

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