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2D Model DC Discharge Reactor for Diamond Deposition

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Abstract: Two-dimensional model of the reactive gas flow, heat transfer and electrodynamical phenomena in dc discharge reactor for diamond film deposition was developed. Contrary to early proposed models we calculate electron-molecule reaction rate coefficients by solving the Boltzmann equation for electron energy distribution function. These coefficients are used for chemical gas composition calculations. The effective numerical method for the chemical kinetics equations solving was developed. Electric field strength was determined from the total current conservation condition and the electron balance equation. Spatial distributions and fluxes of the chemical species and the gas flow parameters were obtained as a result of the self-consistent calculations. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

The present report is devoted to simulation of physical and chemical phenomena proceeding in reactor using for chemical vapour deposition (CVD) of diamond films. Great difficulties arising in construction and realisation of complex self-consistent models for detailed description of numerous CVD systems give rise to various simplifications of these models. Indeed, the majority of models being present in literature are one-dimensional or reduce to it[1,2] in spite of two-dimensional spatial modelling required as minimum. Recently 2-D models mainly for hot-filament and plasma-jet CVD reactors have occurred. However they contain simplified description of chemical kinetics[3] or do not take into account the correlation of heat transfer and chemical kinetics.[4]

2 MODEL

We have developed 2-D model for self-consistent calculation of fluid flow, heat transfer and gas-phase chemistry. For concrete reactor (HFCVD, plasma activated CVD) this model is complemented by the submodel for simulation of the reactor activation processes. As an example we describe the model of dc discharge reactor. Such a reactor is realised in our laboratory. The modelled reactor consists of a chamber with 5.6 cm diameter, two electrodes with 2.6 cm diameter and 2 cm gap between its. Working gas (H2/CH4 mixture) issuing from the hole system in the cathode produces an axisymmetric flow when it impinges upon the substrate.

Program CheR realising the dc discharge reactor model includes the gas dynamics block, the chemical kinetics block, the non- equilibrium electron kinetics and electrodynamics block. The equations of conservation of mass, momentum, energy and chemical species were solved numerically for cylindrical geometry (z,r):

$$\nabla_t \rho = -\nabla(\rho \mathbf{v}) \tag{1}$$

$$\nabla_t \rho u = -\nabla(\rho u \mathbf{v}) - \nabla_z P + \nabla W_z + \rho g \tag{2}$$

$$\nabla_t \rho v = -\nabla(\rho v \mathbf{v}) - \nabla_r P + \nabla W_r - 2\mu v / r^2 \tag{3}$$

$$\begin{aligned} \nabla_t \rho \varepsilon = &- \nabla(\rho \varepsilon \mathbf{v}) - P \nabla_z u - P/r \nabla_r (r v) \\ &- \nabla Q_\lambda - \nabla\left(\sum_{i=1}^{k} h_i j_i^D\right) + Q_J \end{aligned} \tag{4}$$

$$\begin{aligned} \nabla_t n_i &= -\nabla(n_i \mathbf{v} + j_i^D/m_i) + S_i - L_i n_i \quad i = 1, k-1 \\ n_K \equiv n_{H2} &= \left(\rho - \sum_{i=1}^{k-1} m_i n_i\right)/m_k \end{aligned} \tag{5}$$

where $\nabla_x = \partial/\partial x, x = t, z, r$; $\nabla(\rho v) = \partial(\rho u)/\partial z + (\partial(r\rho v)/\partial r)/r\rho$ is the gas density, $\mathbf{v} = (u, v)^T$, u and v are the axial and radial velocity components, P is a scalar pressure; $W_z = (2\mu\nabla_z u, \mu \cdot (\nabla_r u + \nabla_z v))^T$, $W_r = (\mu \cdot (\nabla_r u + \nabla_z v), 2\mu\nabla_r v)^T$, $\mu = \mu(T)$ is the gas viscosity, ε, h and c are specific energy, enthalpy and heat, $Q_\lambda = (-\lambda\nabla_z T, -\lambda\nabla_r T)^T$, $\lambda^P = \lambda(T)$ is a thermal conductivity, T is the gas temperature, Q_J is Joule heating, n_i and m_i are *i*th component concentration and mass, S_i and $L_i n_i$ are the chemical production and loss rates; the mass diffusion flux of *i*th component $j_i = -N^2 m_k m_i D_{ik}/\rho\nabla x_i - D_i^T/m_i \nabla \ln T$, $X_i = n_i/N$ D_{ik} and D_i^T are the binary molecular diffusivity and thermal diffusion coefficients,[3] N is gas concentration.

The gas-phase reaction mechanism (35 reactions, 16 species) is similar to that of the work.[1] Formulation of the boundary conditions involves difficulties only for chemical species on the substrate, where the surface reactions should be taken into account. For H and CH_3 the boundary conditions were derived from Goodwin's surface-reaction mechanism.[5] For other species zeroth diffusional flux on the substrate is used as the boundary condition.

Equations (1)–(5) with the initial and boundary conditions, thermal and caloric equations of state are solved for a 30×25 grid, using "large particle" method.[6] For the conservation equations of chemical species a special method was developed. The main ideas of this method can be formulated as follows. At each time step and each space grid point the implicit Euler scheme is used. The obtained nonlinear equation system for the species concentrations is solved by the combined method with the Zaidel, Newton and simple iterations being involved. At first some Zaidel iterations are performed. Then Newton iteration is carried out only for the components for which the convergence has not been achieved. In such cases the Jacobian is calculated analytically and the Jacobi matrix inversion is done by the Gauss method. The simple iteration for all components is the last to be made and provides for the method conservatism. In addition at each step the contributions of the diffusion and convection processes are taken into account using explicit scheme. It is also necessary to emphasise that the built-in chemical reaction translator makes possible to calculate analytically the Jacobian for an arbitrary set of components and ensures the economic organisation of the Zaidel iteration calculations. Furthermore the method provides the opportunity to carry out the calculation with a large time step.

Non-stationary eqns (1)–(5) are integrated until steady state regime is reached. Simultaneously stationary electron balance equation is solved on each level z of the spatial grid:

$$k_i^{H2} n_{H2} n_e + \frac{1}{r}\frac{\partial}{\partial r}\left(D_{ea} r \frac{\partial n_e}{\partial r}\right) - \beta n_e^2 = 0 \tag{6}$$

Electric field strength was determined from total current conservation condition:

$$\int_o^R 2\pi r j_e \mathrm{d}r = I \tag{7}$$

We neglected the sheet effects and assumed the plasma electroneutrality. The value of total current I and current column radius R were taken from the experiment, the current density $j \simeq j_e$. In eqn (6) D_{ea} is the ambipolar diffusion coefficient,[7] β is the dissociative electron and ion H_3^+ recombination coefficient. The ionization rate coefficient $k_i{}^{H2}$, the dissociation rate coefficients and other electron kinetic coefficients were determined by solving in two-term approach the Boltzmann equation for electron energy distribution function. The functional dependencies of these coefficients from parameter E/N were constructed and used in program CheR. Under our conditions ($P = 100$–200 Torr) the cathode layer is sufficiently thin, we took it into account only in boundary conditions for T. In bulk discharge we assumed that $E_r \ll E_z$ and consequently $\partial E_z/\partial r = 0$. At these assumptions the value $E_z(z)$ in each layer z of the grid was determined from nonlinear eqns (6) and (7) which were solved with help from the Newton iterative procedure. The positive column voltage in calculations was about 410 V, that with account of cathode fall $\simeq 250$ V was in good agreement with the experimentally measured total discharge voltage $U = 650$ V.

3 RESULTS

All plasmachemical component and gas flow parameter spatial distributions and flows were calculated as a result of self-consistent solution of eqns (1)–(7). For typical regime ($P = 150$ Torr, $u_{\mathrm{inlet}} = 80$ cm/s, $I = 1$ A) the gas temperature and flow fields are presented on Fig. 1. As is seen chemical species transfer on substrate mainly occurred by diffusion processes. However it is necessary to

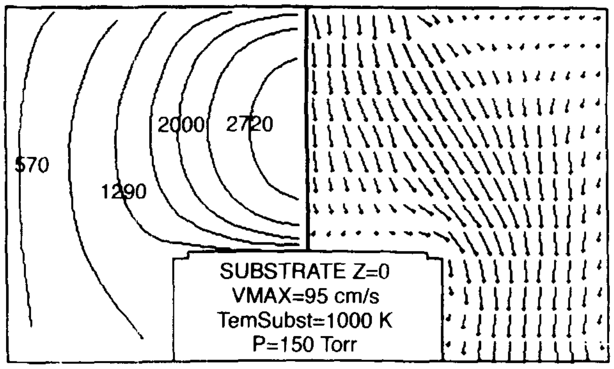

Fig. 1. Gas temperature and flow field.

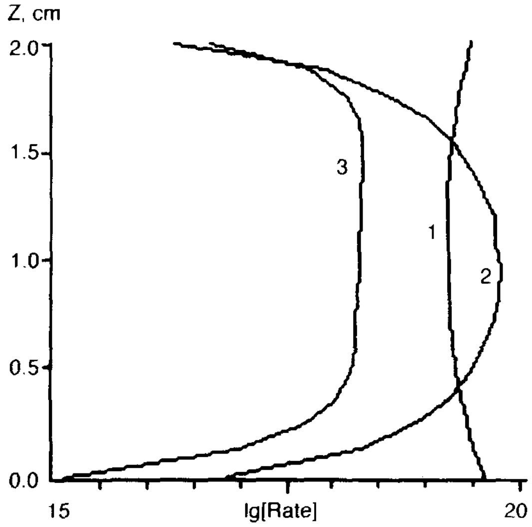

Fig. 2. Production rate of H ($cm^{-3}s^{-1}$), (z = 0—substrate, z = 2—cathode).

take into account convective mass transport in reactor volume. The gas temperature distribution is critical for gas-phase reaction mechanism. As is seen from Fig. 1 the temperature maximum $T \simeq 3000$ K is reached in discharge centre smoothly dropped in radial and electrode direction. Such temperature profiles are determined by Joule heating distribution and conductive heat transfer, including reactive conductivity, i.e. heat transfer by diffusion of the radicals. With increase of the inlet velocity the role of convective heat flow is increased and the temperature maximum is shifted to the substrate.

For optimisation of PACVD reactor it is important to know the relationship between the equilibrium thermal and nonequilibrium electron mechanisms of the radical production, in particular the relationship between molecular dissociation rates.by electron impact and by collisions with neutrals. Notice that the electron temperature is significantly higher than gas temperature in nonequilibrium plasma. In Fig. 2 we have presented the rate distributions along the axis of atomic hydrogen production by electron impact with molecules H_2 (1), thermal dissociation of H_2 (2) and CH_4 (3). As it is to be seen the electron impact dissociation is of fundamental importance in our reactor. Thus for efficient utility of input power the electron impact dissociation rate should be increased. It is possible to attain this aim by dilution of working gas with noble gas, for example, argon.

4 CONCLUSION

The developed 2-D model provided with graphical envelope and built-in chemical reaction translator permits to carry out the simulation and optimisation of various CVD diamond film reactors.

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