

Kinetic model of thin film growth by vapor deposition

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Abstract. A phenomenological kinetic model is proposed for describing the production of a thin film containing two components, A and B, by chemical and physical vapor deposition. The film was created by the “site-to-site” deposition of components A and B. The equations for the densities of components A and B in the surface layers were formed, and analytical and numerical solutions were obtained. The model includes the probabilities of different elementary processes for the interaction of gas phase components (molecules, radicals, atoms and ions) with those of A and B on the film surface. The deposition and erosion rates, the surface and volume densities of components A and B and the relative volume of microcavities inside the film were calculated as a function of the probabilities for the elementary processes of gas (plasma)-surface interactions. The experimental characteristics of *a*-Si:H thin films prepared by SiH₄ plasma deposition and those of carbon nitride thin films deposited from r.f. — magnetron sputtering and ion beam-assisted processes are compared with model calculations.

PACS. 81.15.Aa Theory and models of film growth – 81.15.Gh Chemical vapor deposition (including plasma-enhanced CVD, MOCVD, etc.) – 82.20.Wt Computational modeling; simulation

1 Introduction

Recently, a considerable amount of research has been focused on the use of chemical vapor deposition (CVD) and physical vapor deposition (PVD) for the production of thin films consisting of two chemical components (for example, Si–H, Si–N, C–H, C–N, Si–C, oxides, metals and others). Many of the characteristics of thin films have been identified experimentally, and their dependence on various parameters (gas composition, pressure, gas and substrate temperatures, discharge current, power, ion energy) has been established. Theoretical kinetic models have also been developed (see, for example, works [1–12]). These models are usually quite specific and describe particular experiments and situations mainly for growth of films containing one component. Most of them have been created for detailed investigation of diamond film growth [3–10]. The kinetic of growth of *a*-Si:H [1, 2] and SiO₂ [11, 12] thin films has also been studied. The investigations were carried out mainly by the Monte Carlo method [1, 2, 4–6, 8, 9]. The phenomenological model with using of balance equations for monolayers of C atoms was proposed in [7], for sputtering of C atoms under ion irradiation of a diamond film.

Here, we conduct a theoretical study of the production of a thin film containing two chemical components: A and

B. The proposed below model describes the deposition and film growth in a phenomenological manner, with simplifications and do not take into account the detailed effects of surface atomic structure and film morphology. Nevertheless, such kinetic model of binary deposition can, in our opinion, describe some important macro-characteristics of film growth, such as deposition rate and chemical composition of the film. The model includes the probabilities for the elementary processes of gas (plasma)-surface interactions and can provide qualitative and semi-quantitative interpretations of some experiments.

2 The main assumptions and peculiarities of model

We use the following simplifications and assumptions.

1. We suppose that the film is divided in atomic “layers”. The average interatomic distance within the film determines the average layer thickness.
2. Every layer consists of an array of sites. These sites can be empty or occupied by atom A or B.
3. In the layers of the growing film, the sites can be “opened” or “closed”, which means that they have or do not have contact with gas phase. The “opened” sites are the sites on film surface.
4. The chemically active site on film surface is the deposited atom with one or more dangling bonds.

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The deposition on such site of a new atom, arrived from gas phase, leads to “cover” the lower atom (that is, inserting this atom in film) and film growth (see Fig. 1).

5. The other (“lateral”) dangling bonds of chemically active sites can also create the chemical bonds but only between atoms in the same layer.
6. We will investigate the average density on film surface (per unit of surface square) of chemically active “opened” sites in the different layers. The model is one-dimensional and the position of sites-atoms in layer can be only determined by the deep location of this layer in the film.
7. Surface diffusion of chemically active adsorbed species (atoms, molecules, radical, ions) will be neglected.
8. The deposition will be described in terms of elementary surface chemical reactions, which determine the atomic densities on film surface. The time evolution of these densities will be described by the ordinary differential rate equations.

The last assumptions and approaches have been used in the one-dimensional model [2], which described the kinetic of diamond deposition. Some from above-mentioned assumptions have also been used in other works, mainly for modelling of kinetics of diamond film growth. For example, the absence of surface diffusion has been adopted in [8,9], where the growth of diamond film was investigated by Monte Carlo method.

3 The model for film growth with two types of atoms having dangling bonds

In the common case, every deposited component A and B potentially has the dangling bond. Here, we will investigate this case. We will calculate the densities N_n^A and N_n^B of components A and B respectively in the *open* site of layer with number “ n ” on the film surface. Numbering begins with the substrate, so that $n = 0$ and surface density N_0 . Here, the equations for the description of time evolution of N_0 , N_n^A and N_n^B can be formed as linear equations and written as:

$$\frac{dN_0}{dt} = -(P_0^A + P_0^B)N_0 \quad (1a)$$

$$\frac{dN_1^A}{dt} = -(P_1^{AA} + P_1^{AB})N_1^A + P_0^A N_0 \quad (1b)$$

$$\frac{dN_1^B}{dt} = -(P_1^{BB} + P_1^{BA})N_1^B + P_0^B N_0 \quad (1c)$$

$$\frac{dN_n^A}{dt} = -(P_n^{AA} + P_n^{AB})N_n^A + P_{n-1}^{AA}N_{n-1}^A + P_{n-1}^{BA}N_{n-1}^B \quad \text{for } n \geq 2 \quad (1d)$$

$$\frac{dN_n^B}{dt} = -(P_n^{BB} + P_n^{BA})N_n^B + P_{n-1}^{BB}N_{n-1}^B + P_{n-1}^{AB}N_{n-1}^A \quad \text{for } n \geq 2. \quad (1e)$$

Here, t is time; P_0^A and P_0^B are the probabilities per unit of time (in s^{-1}) for the chemical absorption of A and B

species by the substrate; P_n^{ij} are the probabilities (in s^{-1}) of chemical adsorption of gas component j ($j = A, B$) at the surface film site occupied by component i ($i = A, B$). As a result of this adsorption, the chemical bond $i-j$ is created and the deposited component j appears on the open site in layer $n+1$. Below, the probabilities P per unit of time are connected with often used dimensionless probabilities Γ in one collision by ratio $P = \Gamma \times Z$, where Z (in s^{-1}) is the collision frequency of gas phase component with surface chemical site. Note that equations (1a), (1b), (1c) are the simplest for describing the time evolution of chemically active sites on the substrate and the first layer. Here we will not investigate the peculiarities of this evolution (growth of areas, nucleation and coalescence of active sites [13]).

It is also important to note that the gas phase components A and B are not usually “pure” atoms of A and B. They might be gas phase molecular radicals or ions, which contain the A or B atom (ion) and are provided by plasma chemical gas phase reactions. The new surface chemical bond is usually created by the collision of these radicals with surface A or B atoms.

Thus, we have described deposition in a discrete form using the discrete equations (1). However, the continuous analogy of equations (1) will be used to obtain the analytical solution of our task. To obtain this solution, we decompose the values $P_{n+\Delta n}^{ij}/N_{n+\Delta n}^i$ in Taylor series:

$$P_{n+\Delta n}^{ij}N_{n+\Delta n}^i \approx P_n^{ij}N_n^i + \frac{\partial(P_n^{ij}N_n^i)}{\partial n}\Delta n + \dots; \quad \Delta n = \pm 1, \quad i = A, B; j = A, B. \quad (2)$$

Inserting (2) in (1), we obtain the equations in the partial derivatives:

$$\frac{\partial N_n^A}{\partial t} = -\frac{\partial(P_n^{AA}N_n^A)}{\partial n} - \frac{\partial(P_n^{BA}N_n^B)}{\partial n} - P_n^{AB}N_n^A + P_n^{BA}N_n^B, \quad (3a)$$

$$\frac{\partial N_n^B}{\partial t} = -\frac{\partial(P_n^{BB}N_n^B)}{\partial n} + \frac{\partial(P_n^{AB}N_n^A)}{\partial n} + P_n^{AB}N_n^A - P_n^{BA}N_n^B. \quad (3b)$$

We will adopt the assumption that $P_n^{ij} = P^{ij}$ ($i = A, B$; $j = A, B$) and will find the solution of equations (3) as

$$N_n^B = CN_n^A, \quad (4)$$

where C is a constant. After summing (3a), (3b) and using (4), we obtain

$$\frac{\partial N_n^A}{\partial t} = -P_{dep} \frac{\partial N_n^A}{\partial n}, \quad (5)$$

where

$$P_{dep} = \frac{1}{1+C} [P^{AA} + P^{AB} + C(P^{BB} + P^{BA})]. \quad (6)$$

The analytical solution of equation (5) gives the number n_b for the boundary layer of the film, which increases during deposition, as well as the deposition rate J_{dep} and

thickness L_{film} of the film

$$n_b = P_{dep} t, \quad J_{dep} = l P_{dep}, \quad L_{film} = l P_{dep} \tau_{dep}, \quad (7)$$

where τ_{dep} is the total deposition time; l is the thickness of one layer. This is the task parameter.

The coefficient C in (4), (6) can also be calculated from (3) for the quasi stationary conditions and with using the correlation $\sum_n (N_n^A + N_n^B) = \text{const.} = N_0^0$ (N_0^0 is the total density of active sites on film surface):

$$C = \frac{\Theta^B}{\Theta^A}, \quad \Theta^A = \frac{P^{BA}}{P^{BA} + P^{AB}}, \quad \Theta^A + \Theta^B = 1. \quad (8)$$

The values Θ^A and Θ^B are the relative densities of atoms A and B on film surface or the surface covering of species A and B, respectively. If we use (8), the deposition probability (6) can be written as

$$P_{dep} = P^{AA} \Theta^A + (P^{BB} + 2P^{BA}) \Theta^B. \quad (9)$$

Besides the deposition rate (9) and relative surface densities (8), the relative volume densities V^A and V^B of species A and B can also be obtained. We have:

$$V^A = \frac{P^{AA} \Theta^A + P^{BA} \Theta^B}{P_{dep}}; \quad V^B = \frac{(P^{BB} + P^{BA}) \Theta^B}{P_{dep}}. \quad (10)$$

It is interesting to note that the relative surface densities (8) differ from the volume densities V^A , V^B and are determined only by the probabilities P^{AB} , P^{BA} (unlike V^A , V^B , which also depend on P^{AA} , P^{BB}). The reason for this is that the surface densities are determined by the densities on *all open* sites while volume densities are determined by the densities inside the film (that is, the densities of the closed sites).

4 Description of film erosion

The simplest case of binary deposition and thin film production has been investigated in Section 3. However, the real situation can be more complex.

First, the growing film surface can be occupied by “passive” species M (molecules), which do not form chemical bonds with species A or B. Indeed, physical (but not chemical) absorption of species M can take place.

Second, the film surface can be bombarded by energetic particles (usually ions), which causes the desorption of M species (film-surface cleaning) and breaks the bonds A–A, A–B, B–B on the upper film layers (film erosion).

In this section, we examine the influence on film growth and erosion of bombarding by energetic ions.

In the framework of our model, the some parts $(dN_n^A/dt)_D$, $(dN_n^B/dt)_D$ must be added to the right side of equations (1d), (1e) to describe film erosion. To solve equations (1) with these additional parts we used the approximation (2) and obtained the coupled system of equations in the partial derivatives. The solution of these

equations gives the deposition rate J_{dep} , which can be calculated from (7) with new probability of deposition $P_{dep}^{(1)}$ (instead of P_{dep} , see (9)):

$$P_{dep}^{(1)} = (P^{AA} - D^{AA} + P^{AB} - D^{AB}) \Theta^A + (P^{BB} - D^{BB} + P^{BA} - D^{BA}) \Theta^B. \quad (11)$$

The surface coverings for species A, B here are the following

$$\Theta^B = \frac{P^{AB} + D^{AB}}{P^{BA} + D^{BA}} \Theta^A; \quad \Theta^A + \Theta^B = 1. \quad (12)$$

In (11), (12), the values D^{ij} are the probabilities (in s^{-1}) of breaking of the chemical bonds $i-j$ ($i = A, B$; $j = A, B$) by energetic particles (ions). They depend not only on the energy and flux of bombarding ions, but they also depend on the probabilities of R^{ij} to “open” the species j on the lower layer after breaking of $i-j$ bond and escaping of “ i ” atom. The values D^{ij} can be presented as

$$D^{ij} = D_0^{ij} R^{ij} \quad i = A, B; \quad j = A, B \quad (13)$$

where D_0^{ij} (in s^{-1}) depends on the energy and flux of bombarding ions and the type of chemical bond $i-j$. The dimensionless probabilities R^{ij} are

$$R^{AA} = \frac{(P^{AA} - D_0^{AA} R^{AA}) \Theta^A}{(P^{AA} - D_0^{AA} R^{AA}) \Theta^A + (P^{BA} - D_0^{BA} R^{BA}) \Theta^B}; \quad R^{AB} = 1 - R^{AA}, \quad (14a)$$

$$R^{BB} = \frac{(P^{BB} - D_0^{BB} R^{BB}) \Theta^B}{(P^{BB} - D_0^{BB} R^{BB}) \Theta^B + (P^{AB} - D_0^{AB} R^{AB}) \Theta^A}; \quad R^{BA} = 1 - R^{BB}. \quad (14b)$$

Thus, in the common case, we have 6 non-linear equations (12–14) to obtain 6 values Θ^A , Θ^B , R^{AA} , R^{AB} , R^{BA} , R^{BB} and calculate the deposition rate. The relative volume densities V^A and V^B are as follows:

$$V^A = \frac{(P^{AA} - D_0^{AA} R^{AA} - D_0^{AB} R^{AB}) \Theta^A + P^{BA} \Theta^B}{P_{dep}^{(1)}}, \quad (15a)$$

$$V^B = \frac{(P^{BB} - D_0^{BB} R^{BB} - D_0^{BA} R^{BA}) \Theta^B + P^{AB} \Theta^A}{P_{dep}^{(1)}}. \quad (15b)$$

Note that besides the calculation of the deposition rate, the sputter-erosion rate J_{eros} of the prepared film can also be determined when the film is bombarded by the energetic particles (ions). It can be calculated from equations (7), (11), (12) without probabilities P^{ij} :

$$J_{eros} = -l \left[(D_{eros}^{AA} + D_{eros}^{AB}) \Theta^A + (D_{eros}^{BB} + D_{eros}^{BA}) \Theta^B \right]. \quad (16)$$

The surface coverings for species A, B here are as follows:

$$\Theta^B = \frac{D_{eros}^{AB}}{D_{eros}^{BA}} \Theta^A; \quad \Theta^A + \Theta^B = 1; \quad D_{eros}^{ij} = D_{0eros}^{ij} R_{film}^{ij}. \quad (17)$$

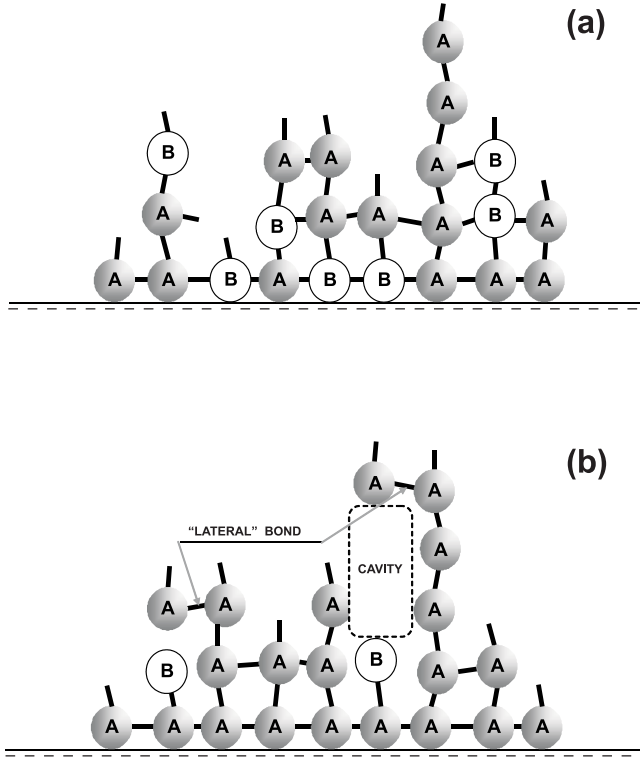


Fig. 1. Scheme showing site-by-site deposition and film growth with two components. (a) Both deposited atoms have dangling bonds; (b) the deposited component B (H atom) has not dangling bond.

The sign “–” on the right-hand side of (16) means that the film thickness decreases by erosion. The values D_{0eros}^{ij} in (16), (17) depend on the flux and energy of ions bombarding the film and causing erosion. However, the values R_{film}^{ij} depend on the history of film production, that is on each one of the probabilities P^{ij} , D_0^{ij} during deposition.

5 The model for film growth with H atoms

The modeling of this case is of particular interest because it is associated with the much-researched a -Si:H, a -C:H films. The absence of a dangling bond for the deposited surface H atoms gives rise to certain peculiarities in the subsequent deposition and film growth stages, which must be taken into consideration when modeling. Here, we will mark in B the H atom, which has not a dangling bond if it is deposited on film surface. Such B atom cannot be directly covered by another atom by creating a bond with B. It can occur only if the atom from the gas phase creates the chemical bond with the earlier deposited A atom from the *neighboring site of upper layer* $m > n$. Schematically, this is shown in Figure 1b. Beside this peculiarity, the deposited B atom on film surface can also be eliminated by chemical reaction (for example, such as $(B)_g + (BA)_s \rightarrow (B_2)_g + (A)_s$).

The above discussed peculiarities of the deposition must be taken into account in the balance equations for

surface densities N_n^A and N_n^B . As a result, the non-linear parts, describing the inserting of the B atom inside the film, appear in these equations. The simplest modified (compared with Eqs. (1)) equations for N_n^A and N_n^B in the open sites of layers $n \geq 2$ can be written as

$$\begin{aligned} \frac{dN_n^A}{dt} = & P^{AA}N_{n-1}^A - (P^{AA} + P^{AB})N_n^A \\ & + \frac{N_n^A}{N_0^0} \sum_{i=1}^{n-1} P_{in}^{iAA}N_i^B + P^{B-}N_{n+1}^B, \end{aligned} \quad (18a)$$

$$\frac{dN_n^B}{dt} = P^{AB}N_{n-1}^A - \frac{N_n^B}{N_0^0} \sum_{i=n+1}^{\infty} P_{ni}^{iAA}N_i^A - P^{B-}N_n^B. \quad (18b)$$

Here, P_{in}^{iAA} is the probability for the process of covering the B atom in site of layer “ n ” by the A atom in neighboring site of the upper layers “ i ”. In this case, the “lateral” chemical bond A–A is created, with previously deposited A atoms from the same layer “ i ”. Note, that the summary, provided in equation (18), takes into consideration the processes for covering the B atom by the A atom, with the creating of a chemical bond with the previously deposited A atoms in sites of all upper neighboring layers. It is assumed in (18), that the flux of B component to film surface is small as compare with flux of A component and that the probabilities P^{AA} , P^{AB} and P^{B-} are not dependent on the layer number “ n ”. To decrease the number of model parameters, it will also assumed that the probabilities P_{in}^{iAA} have only two values, namely those for layers $i, n = i+1$ and $i, n \neq i+1$. For example, $P_{i,i+1}^{iAA} = P^{AA}$ and $P_{in}^{iAA} = \beta P^{AA}$ for $n \neq i+1$, $\beta < 1$. The low value of β for $n \neq i+1$ is physically well grounded. In fact, in the case $n = i+1$ we have a direct collision of the bombarding gas phase atom A with the B atom in site of layer “ n ”. The energy that is released on the creation of the chemical bond between the bombarding atom and the previously deposited A atom from the site of neighboring layer “ $n+1$ ” is easily dissipated through interaction with this B atom. It promotes stabilization and the creation of a “lateral” chemical bond. However, in the case of $n \neq i+1$, the empty site (void) is found in layer “ n ”, and, as a result, the dissipation of energy, stabilization and the creation of a chemical bond is considerably hindered. The real β value is not known but can be determined by comparing kinetic calculations and experiments (see Sect. 6 below).

System (18) is, unlike equations (1), non-linear and numerical calculation is required for its solutions. However, an approximate analytical solution can be found if the relative volume density of B atoms is small. For this typical case, we can obtain the following simple expressions:

$$\begin{aligned} P_{dep} \approx & P^{AA}\Theta^A; \quad \Theta^A \approx \frac{P^{B-}}{P^{AB} + P^{B-}}; \\ \Theta^B \approx & \frac{P^{AB}}{P^{AB} + P^{B-}}. \end{aligned} \quad (19)$$

Note that non-linear equations (18) of our model can also describe the production of micro-cavities inside the film.

In fact, the non-linear parts $P_{in}^{lAA} N_n^A N_i^B / N_0^0$, are the rates describing the covering of the atom B in layer “ i ” by atom A in the upper layer “ n ”. In such cases, if $n \geq i + 2$, the empty sites (i.e. the space that is not occupied by any other A or B atom) is created over the B atom. The “length” of this cavity is $l \times (n - 1 - i)$ (see Fig. 1b). Note, that similar mechanism for incorporating of H atoms inside of film and creating of micro-cavities had been investigated in [2,8], where the Monte Carlo method had been used for simulation of chemical vapor deposition and production of a -Si-H film [2] and diamond [8].

The numerical solution of equations (18) (with additional non-linear parts describing the covering of A atoms) has been obtained for different values of probabilities and β parameter values. We typically solved 3001 equations, describing the time evolution for density N_0 of empty sites on the substrate and densities N_n^A, N_n^B , in 1500 opened layers. The thickness of a film with 1500 deposited layers ranges from 220 to 250 nm. Films with a thickness from 200 to 400 nm are those usually created and experimentally investigated in the laboratory of Barcelona University. Some of our results from the numerical calculations are discussed below in Section 6.

6 Application of the model to experimental results

Here we will compare some calculations, made in the framework of our model, with the experimental results [13–15].

In [14], the dependence on substrate temperature was obtained for the deposition rate. Note that we will compare the calculated and experimental results only for conditions of small discharge power ($W_{dis} = 1\text{--}5$ W) and gas pressure ($p \leq 30$ Pa). This enables us to avoid, in our opinion, the influence on the deposition rate and structural film properties of molecular clusters and dust nanoparticles, which are appeared with an increase in discharge power and gas pressure.

The probabilities P^{AA} , P^{AB} and P^{B-} in (18), (19) are determined by fluxes $\Phi(\text{SiH}_3)$ and $\Phi(\text{H})$ of radicals SiH_3 and H to film surface:

$$\begin{aligned} P^{AA} &\equiv P^{\text{SiSi}} = \sigma \delta_a \Phi(\text{SiH}_3); & P^{AB} &\equiv P^{\text{SiH}} = \sigma \delta_c \Phi(\text{H}); \\ P^{B-} &\equiv P^{\text{H-}} = \sigma \delta_d^{\text{Si}} \Phi(\text{SiH}_3) + \sigma \delta_d^{\text{H}} \Phi(\text{H}). \end{aligned} \quad (20)$$

Here, σ (in cm^2) is the cross-section of the chemically active site on film surface; δ_a , δ_c , δ_d^{Si} and δ_d^{H} are the “sticking” coefficients. According to [16], the sticking coefficient δ_a is independent on T_s . However, the other coefficients depend on T_s and this is, in our opinion, the main reason for the dependence on T_s of Θ^{Si} and, consequently, the deposition rate J_{dep} (see (7), (19)). We use the values 0.28 [16] or 0.15 [17] for δ_a and accept for δ_d^{Si} and δ_d^{H} the Arrhenius dependence on T_s :

$$\delta_d^{\text{Si}} = \exp(-E_d^{\text{Si}}/kT_s); \quad \delta_d^{\text{H}} = \exp(-E_d^{\text{H}}/kT_s). \quad (21)$$

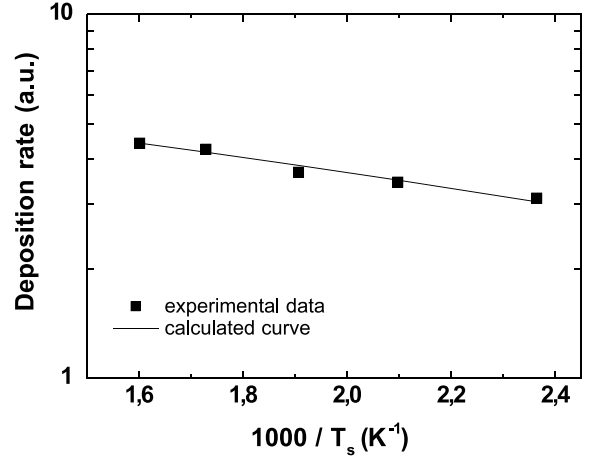


Fig. 2. Deposition rate of a -Si:H films (in arbitrary units) as a function of substrate temperature T_s at fixed pressure $p = 3$ Pa. Points: experiment in [14], line: model calculation.

The comparison of calculations and experimental data from [14] shows that for case $\delta_a = 0.28$ the best fitting corresponds to $\delta_c \approx 0.07$; $E_d^{\text{Si}}/k \approx 740$ K and $E_d^{\text{H}}/k \approx 1900$ K. For case $\delta_a = 0.15$, the fitting value $\delta_c \approx 0.16$. The experimental and calculated results are given in Figure 2. We have not calculated the gas density of radicals SiH_3 , which determine the absolute value of deposition rate (it is special separate task). That is why the values in Figure 2 are given in arbitrary units.

Besides the deposition rate, we have compared the theoretical and experimental absolute values of hydrogen content V^{H} and the micro-cavity fraction V^{cav} . These data were measured in [13] for fixed substrate temperature $T_s = 573$ K and different gas pressures and discharge powers. The experimental values V^{H} and V^{cav} for $p \leq 20$ Pa and low power $W_{dis} \leq 5$ W were $\sim 3\%$ and $\sim 1.2\%$ respectively for a film thickness of 390 nm (~ 2600 layers). Our numerical calculations for V^{H} and V^{cav} resulted 2.9% and 1.5% respectively when $\beta \approx 10^{-3}$. The calculated V^{H} value decreased smoothly while the V^{cav} value increased smoothly with thickness $\langle n \rangle$. Thus, we have obtained agreement between our calculations and absolute measurements [13] of V^{H} and V^{cav} if accept $\beta \approx 10^{-3}$. Of course, the calculated values V^{H} and V^{cav} depend on parameter β and grow with the increase of β .

In [15], the amorphous carbon nitride (a -CN) thin film was prepared in a hybrid plasma-based deposition process that allows nitrogen ion bombardment to be controlled independently, by combining r.f.-magnetron sputtering of a graphite target with simultaneous nitrogen-ion-beam assistance from a capacitively coupled r.f. ion source. The films were deposited on silicon substrates at 0.3 Pa of total pressure, using Ar and N₂ gas flows of 3 and 1 sccm, respectively. The energy of bombarding nitrogen ions was increased from 140 to 800 eV. The deposition rate and relative densities of C and N species on the surface and inside of the films were measured. In addition, the sputter-erosion rate of a -CN films due to bombardment by a 12 kV Ar⁺ ion beam was also measured. The experimental

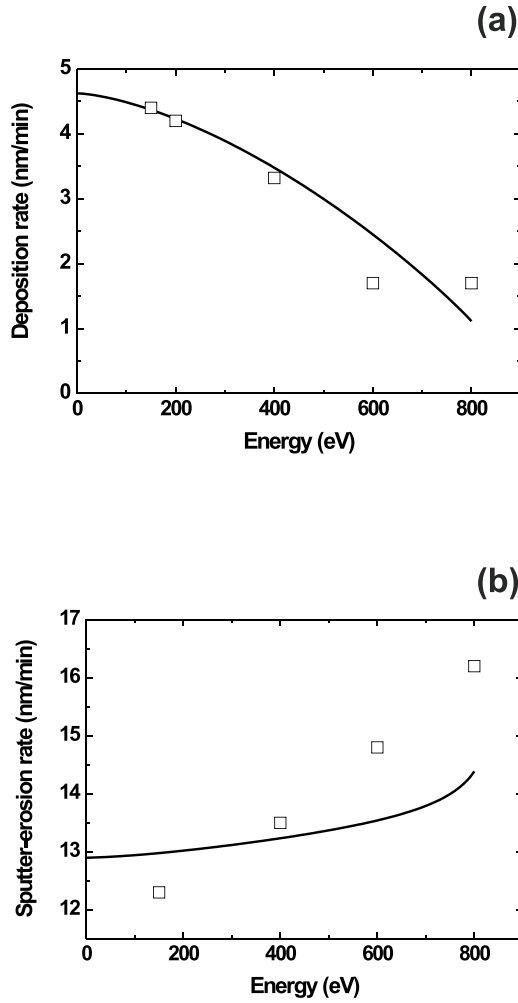


Fig. 3. Experimental values [15] (white squares) and model calculation (lines) of deposition rate (a) and sputter-erosion rate by 500 nA, 12 kV, Ar⁺ ion beam of CN film (b) as a function of nitrogen ion beam energy during deposition.

results and calculations of the model are given in Figures 3 and 4, which show satisfactory agreement. Of course, to obtain this agreement, the probabilities P^{ij} , D_0^{ij} , D_{0eros}^{ij} must be chosen by fitting. It was assumed that the film surface would be cleaned by energetic ions during the deposition and erosion. This assumption is justified because the cleaning of a film surface by energetic ions takes place during deposition and erosion.

We also assumed the thickness of one monolayer to be 0.15 nm. The ion energy E , here, is in eV. The dependencies on nitrogen ion energy E_{ion} for probabilities D_0^{ij} have been described by function $E_{ion}^{1.5}$. This function is proportional to ion energy flux at the film surface.

The obtained by fitting values $D_{0eros}^{NC} \approx 0.83 \text{ s}^{-1}$ and $D_{0eros}^{CC} \approx 2.28 D_{0eros}^{NC}$ permit to estimate the efficiency of sputtering $\delta_{Ar^+}^{NC}$ and $\delta_{Ar^+}^{CC}$ due to breaking of N–C and C–C chemical bonds by 12 keV argon ions. It can be done by

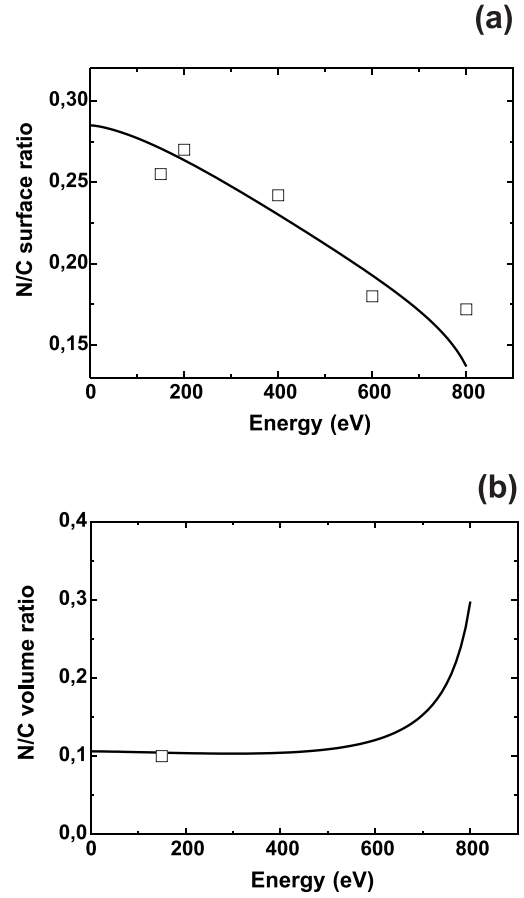


Fig. 4. Experimental values [15] (white squares) and model calculation (lines) of nitrogen to carbon surface atomic ratio (a) and nitrogen to carbon volume ratio (b) as a function of nitrogen ion beam energy during deposition.

using the relationships

$$D_{0eros}^{ij} = \sigma_{atom} \delta_{Ar^+}^{ij} \Phi(Ar^+); \quad \Phi(Ar^+) = \frac{1}{e} \frac{I(Ar^+)}{S}, \quad (22)$$

where σ_{atom} (in cm²) is the average cross-section of one atom (C or N) on film surface; $\Phi(Ar^+)$ (in cm⁻² s⁻¹) is the flux of Ar⁺ ions to film surface; $I(Ar^+)$ (in A) is the ion current; $e = 1.6 \times 10^{-19}$ C is the elementary charge; $S \approx 1.6 \times 10^{-3}$ cm² is the area of film surface, bombarded by Ar⁺ ions in the experiment [15]. Accepting $\sigma_{atom} \approx l^2 = 2.25 \times 10^{-16}$ cm² and use the obtained values D_{0eros}^{NC} , D_{0eros}^{CC} , we find from (22) $\delta_{Ar^+}^{NC} \approx 1.89$; $\delta_{Ar^+}^{CC} \approx 4.31$. For comparison, the literature data for $\delta_{Ar^+}^{CC}$ are 1.5; 2.0 and 3.75 for Ar⁺ ion energy 2; 4 and 10 keV respectively [18].

7 Conclusion

A phenomenological kinetic model has been proposed for description of thin film production by deposition of two components, A and B. Although the initial hypothesis of the model do not allow to determine the atomic location

or the crystalline order or bond type of the components A and B, it allows us to calculate the some measurable macro-characteristics of film: deposition and erosion rates, relative densities of components A and B on the surface and in the volume of the film and also the relative value of volume of micro-cavities. The model takes into consideration the various processes of gas (plasma)-surface interaction, and the probabilities for the elementary actions of these processes. The probabilities depend on the energies and fluxes of different gas phase components at the film surface, as well as on film (substrate) temperature, sticking coefficients and the probabilities of breaking the chemical or physical bonds on the film surface.

It is clear that every case of deposition and thin film production has its own peculiarities that determine the mechanism of deposition and the incorporation of components A and B into the film. Most commonly, it requires the detailed analysis of specific surface chemical reactions and the need to determine, first, the relationships between these reactions, second, the fluxes to the surface of the various atoms, ions, radicals and, third, the probabilities P^{ij} presented in our kinetic model.

Nevertheless, the model proposed here for the analysis of deposition and film growth, based on a study of the balance equations (non-linear in special cases) is, in our opinion, useful for interpretation of some experimental data. In the future, we plan to carry out the comparison with our new experiments.

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