

PARTICLE COLLISION FREQUENCY AND THE TWO-DIMENSIONAL PARTICLES NUCLEATION

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Abstract

The process of two-dimensional particles formation on the crystal surface, which takes place during layer deposition (epitaxial growth, evaporation, magnetron sputtering, etc.) is the subject of the present paper. These processes are the basis of the phase transition and responsible for the nuclei formation of the new phase creating growth steps on the substrate. The approach, presented here, may be useful for the study of the crystallization mechanisms and namely the mechanism of two-dimensional nuclei formation and the mechanism, assisted by screw dislocations.

Key words: two-dimensional particles, probability for collision, frequency of collisions

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Introduction. The crystal surface structure is a subject of many investigations till now [1–7] because all interactions between the two phases occur through the surface. The as-formed surface structure is a consequence of the surroundings and namely of the adsorption and desorption processes with the environment. The nano particles, generated on the crystal surface, are very topical – they are created by the same kinetic processes as the nuclei of the new phase during crystallization [8–22]. The solution of the problem is very complicated, because of the large amount of particles, adsorbed on the surface, because of the exceptional variety of possible particle structures, of possible particles interactions, affecting the process itself.

Experimental investigations of ad-atoms migration along the crystal surface are still not reliable. By field ion microscope the location of an ad-atom on the crystal surface was fixed and photographed at 77 K [6, 7]. For 30 s the sample was heated to 345 K and by cooling again to 77 K the next photograph was made. Putting together the pictures the mean square displacement of the ad-atoms was determined at different temperatures and the surface diffusion coefficient has been obtained. The great time difference between consecutive images does not

allow determining the character of particle motion along the surface. Usually, the character of motion is investigated theoretically using the molecular dynamic simulations [8–12]. These investigations show that the ad-atoms motion is torn in distances separated by temporary equilibrium states within the potential wells, available on the surface.

The problem of particles collisions and how frequently it occurs is the scope of the present paper. The interaction between two particles begins with their collision – without collision any particles interaction is impossible. The processes, collision and interaction, are separated in time – first collision occurs then comes interaction. Problems concerning particles interaction and the results in consequence of this interaction are coming after collision – they are treated in many works (for example [10–12]). These processes are not considered here because they are not the scope of the present paper. Whether in consequence of the collision particles they will coalesce or not, it depends on the potential of interaction, on the kind of collision, on the strength of collision. The rate of particles coalesce and the rate of new phase nuclei formation are proportional to the particles collision frequency. Because of that the knowledge of this frequency is very important.

The kinetics of the processes, considered here, may be useful for investigation of at least two mechanisms of crystal growth – the two-dimensional nuclei growth and the screw dislocations assisted growth.

Assumptions. Two-dimensional monatomic high nanoparticles, sited onto atomic smooth crystal surface are taken into consideration. These nanoparticles may take place at low intensity of the adsorption process and, consequently, at small density of ad-atoms on the surface. Such conditions are fulfilled in gas phase layer deposition processes at low pressures like low pressure chemical vapour deposition (LPCVD), molecular beam epitaxy (MBE), magnetron sputtering, vacuum evaporation, etc.

The crystal surface, being in contact with the mother phase (liquid or gas phase), is characterized by many atoms and clusters, available there and generated by the adsorbed particles. As a rule, the distances between them are so large that the particles interactions may be neglected. We assume that the particles do not interact with each other and their collisions are not a consequence of the interactions between them – the collisions are quite accidental. Particles are moving along the crystal surface continuously and incidentally are colliding with each other. The maximum interaction between them takes place just during collision and just then large particles arise, containing up to many hundreds of atoms. With other words, the rate of particles coalescence is proportional to the particles collision frequency.

The problem has been simplified assuming that the particles have a circumference shape. Particles with dimension of i are denoted by A_i : i is the number of atoms in the particle. The mass of particle is $m_i = im_0$ and its radius is, where m_0 is the mass of single atom. The velocity of the particle movement on the

crystal surface is v_i , L_i is the free path length and τ_i is the time for covering the distance of L_i . The free path length may be significant at high energy of ad-atoms – it means at high temperature and low pressure. This takes place in case of gas phase deposition processes – LPCVD, MBE, magnetron sputtering, etc. Then the substrate’s atoms are unable to affect the ad-atoms and their migration along the surface may be very long and almost rectilinear.

In case of liquid phase growth both phases are allied with respect to their density and particles’ energy. The free path length L_i and the velocity of movement v_i within both phases are relatively small. Both phases will strongly influence each other. Nevertheless, it is quite possible that the migration of particles along the crystal surface will meet the above mentioned assumptions.

Adsorbed particles are distributed uniformly on the crystal surface without concentration gradients – the deviations from this distribution are negligible so that no diffusion mass transport has been taken into account. Their motion on the surface is chaotic – it means all directions of motion are equally probable and there are no preferable directions of movement, i.e. the crystal surface is isotropic. The last assumption takes place in two cases: either the crystal structure itself is isotropic or the adsorbed on the surface atoms have high kinetic energy and the crystal surface atoms are unable to affect their behaviour.

Two particles are taken into consideration: particle A_k consisting of k -atoms and particle A_i , consisting of i -atoms (Fig. 1). The problem is further simplified by assuming that particle A_k is immobile and particle A_i moves with velocity of v_i , free path length L_i and time τ_i for covering the free path length. In case of collision, the coalescence between both particles is quite possible. In case of coalescence the process may be presented by the following reaction $A_k + A_i \leftrightarrow A_{k+i}$.

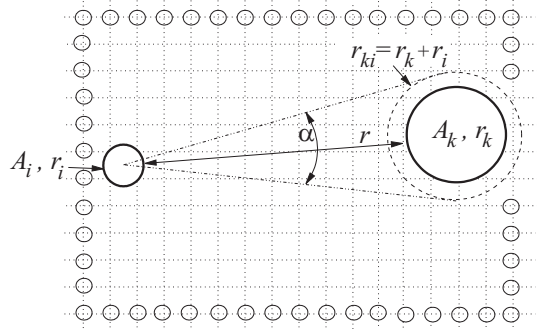


Fig. 1. Angle of collision α between two particles

The aim of the present paper is within the frame of these assumptions to determine the probability for collision of two particles A_k and A_i with dimensions r_k and r_i respectively, removed by a distance of r – this is the distance between their surfaces (Fig. 1). The position and trajectory of particles is defined by their centres. Similar approach is already used for the case of three-dimensional nanoparticles nucleation [23–26].

Probability for collision. The collision of both particles A_k and A_i occurs if the mobile particle A_i , during its migration along the surface, meets with the enlarged circumference with radius of $r_{ki} = r_i + r_k$ (Fig. 1) – the enlarged

circumference will be further called circumference of collision. It occurs, when its trajectory of the mobile particle A_i falls within the frame of angle α further called angle of collision. This is the angle at which the enlarged immobile particle A_k is to be observed, generally speaking, from the position of the mobile particle A_i . This angle is the measure for the probability for collision. The probability for collision is given by the ratio of the angle of collision α , divided by 2π , which is the angle of the entire circumference around particle A_i , consisting of all possible directions of motion – all directions are equally probable,

$$(1) \quad \omega = \frac{\alpha}{2\pi}.$$

In this way the following expressions for the probability for collision have been obtained:

$$(2) \quad \begin{aligned} \omega_1(r) &= \frac{1}{\pi} \arcsin \left(\frac{r_{ki}}{r + r_{ki}} \right) && \text{for } r \in (0, r^*), \\ \omega_2(r) &= \frac{1}{\pi} \arccos \left[\frac{(r + r_{ki})^2 + L_i^2 - r_{ki}^2}{2L_i(r + r_{ki})} \right] && \text{for } r \in (r^*, L_i), \end{aligned}$$

where by r^* is denoted the value $r^* = \sqrt{L_i^2 + r_{ki}^2} - r_{ki}$. One must point out that the obtained probability for collision is a smooth and uninterrupted function over all possible values of r : $r \in (0, L_i)$. At $r = r^*$ the following equalities are fulfilled: $\omega_1(r^*) = \omega_2(r^*)$ and $d\omega_1/dr = d\omega_2/dr$. The larger the distance r between both particles, the smaller the probability for collision ω is. For $r > r^*$ the probability decreases more sharply – a consequence of the limited value of the free path length L .

Frequency of collisions and discussion. Around the particle A_k two circumferences with radii $(r + r_{ki})$ and $(r + r_{ki} + dr)$ are considered respectively. The area, enclosed between both circumferences, is $ds = 2\pi(r + r_{ki})dr$ and the number of the particles A_i available within this area is $dn_i^s = n_i^s ds = 2\pi n_i^s (r + r_{ki})dr$, where n_i^s is the number of particles A_i per unit surface. All particles dn_i^s have the same angle of collision α and the same probability for collision ω . The number of particles collided with particle A_k , denoted by dN_i , is part of the quantity dn_i^s , defined by the probability ω : $dN_i = \omega dn_i^s$. All of the particles A_i , which will collide within time τ_i with the particle A_k , is given by the expression

$$(3) \quad \begin{aligned} N_i &= 2\pi n_i^s \int_0^{L_i} (r + r_{ki})\omega dr \\ &= 2\pi n_i^s \int_0^{r^*} (r + r_{ki})\omega_1 dr + 2\pi n_i^s \int_{r^*}^{L_i} (r + r_{ki})\omega_2 dr = 2n_i^s L_i r_{ki}. \end{aligned}$$

The frequency of collision of all particles A_i with the particle A_k is

$$(4) \quad \nu_{Ai} = \frac{N_i}{\tau_i} = 2n_i^s r_{ki} \frac{L_i}{\tau_i} = 2n_i^s r_{ki} v_i.$$

Equation 4 provides the number of collisions per unit time of particle A_k with all A_i particles – in other words, this is the frequency of collisions of particle A_k with all the A_i particles. The number of A_k particles per unit area is n_k^s and each of them will have the same frequency of collisions ν_{Ai} with the particles A_i . The total number of collisions ν_{ki} per unit time per unit area between all the particles A_i and A_k is

$$(5) \quad \nu_{ki} = n_k^s \nu_{Ai} = 2n_i^s n_k^s r_{ki} v_i.$$

Equation 5 shows that the frequency of collisions between both types of particles A_k and A_i is determined by the product of their densities, of their size and of the velocity of movement. One must point out that equation 5, by its essence, is very similar to the mass interaction law, well known from the chemical kinetics. The rate C_S of a reaction of the synthesis of compound AB : $A + B \rightarrow AB$, is given by the product of densities of both reagents A and B : $C_S \sim c_A c_B$. The rate C_D of the reverse reaction of decay $AB \rightarrow A + B$ is defined by the density of the compound AB : $C_D \sim c_{AB}$. In equilibrium both rates must be equal: $C_S = C_D$.

With the aid of equation 5 one may obtain the number ν_0 of all collisions per unit time per unit area between all the particles in the system

$$(6) \quad \nu_0 = 2 \sum_{i=1}^M \sum_{k=i}^M n_i^s n_k^s r_{ki} v_i,$$

where M is the size of the largest particle in the system.

Conclusion. Within the framework of given assumptions the probability for collisions ω of two particles with different size has been determined. It is defined as ratio between the angle for collisions α and the angle 2π of the entire circumference, consisting of all possible directions of movement. The angle for collision α is the angle at which the immobile particle is observed (generally speaking) from the position of the mobile one. The obtained expression for the probability for collision is a smooth and uninterrupted function of the coordinate. With the help of the probability for collision ω , the frequency of collisions per unit time per unit area ν between the particles, adsorbed onto the crystal surface,

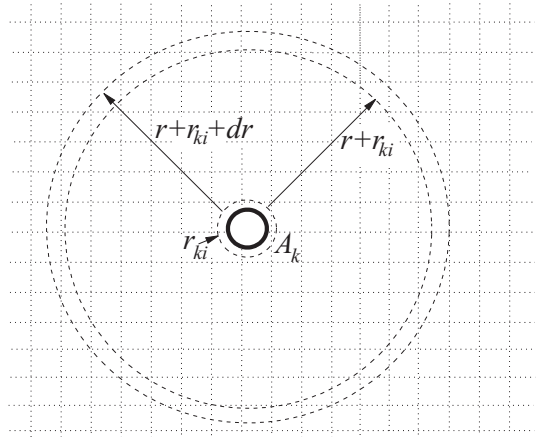


Fig. 2. Determination of the frequency of collision

has been obtained. The frequency is proportional to the product of the particle's density, of the particle's size and of its velocity. This expression, by its essence, is very similar to the mass interaction law, well known from the chemical kinetics.

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