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Collision Frequency of Adsorbed Particles*

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Abstract. The frequency of collision of adsorbed particles is of interest for two-dimensional nuclei formation in crystal growth and for growth of two-dimensional nano-particles. The interaction of two particles and their coalescence is impossible without collision. The density of particles (dimmers, trimmers etc.) is proportional to frequency of collisions. It has been assumed that the crystal surface is isotropic. The adsorbed particles, consisting of i-atoms, having radius r_i, migrate by velocity v_i and free path length L_i over the substrate. The probability for collision $\omega(x)$ between two kinds of particles a_i and a_k has been determined. An expression for the number of collisions per unit surface area per unit time has been derived. The number of collisions per unit length of a straight growth step per unit time has also been evaluated.

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1 Introduction

The particles migration on crystal surface has been investigated since long time by Field Ion Microscopy using the freeze-and-look technique [1-4]. At the moment two kinds of atoms migrations over the crystal surface have been observed – hopping motion and exchange motion. Exchange transport seems to be more active because fewer bonds are broken. This transport concerns only the homo diffusion (for example Pt on Pt). In case of hetero diffusion the hopping mechanism is more probable (for example Pd on Pt). In generally, which kind of mechanism takes place, depends on the interaction between ad-atoms and substrate.

One supposes that the jumps of the particles are not correlated – each jump is not influenced by the previous. Experiments are carried out in absence of any gradients (as well as temperature and concentration). In a sequence of observations, separated by short time intervals, during that the particle arrangement on the surface does not change substantially, the positions of particles on the surface has been identified and their trajectory – determined [4]. Observations

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show that the length of the jumps and their directions are quite arbitrary – the lengths are within the range (10-60 Å).

The determination of the frequency of collisions of adsorbed on the crystal surface atoms is the aim of the present work. The knowledge of the frequency is valuable for the two-dimensional nano-particles formation and as well as for the crystal growth nucleation.

2 Probability for Collision of Adsorbed Particles

The crystal surface is assumed to be isotropic – all directions of motion are equally probable. Two-dimensional particles a_i monatomic high, having circumference shape with radius r_i, mass m_i, velocity of motion v_i and free path length L_i are taken into consideration – i is the number of atoms in the particle. Two particles has been considered – A_k and B_i, where $A_k \in a_k$ and $B_i \in a_i$. Particle A_k is assumed to be immobile. B_i moves along the surface with velocity v_i. The collision of both particles occurs if the trajectory of B_i lies within the frame of angle α – the "angle of collision" (Figure 1). The probability for collision ω is provided by the ratio $\omega = \alpha/2\pi$ [5].

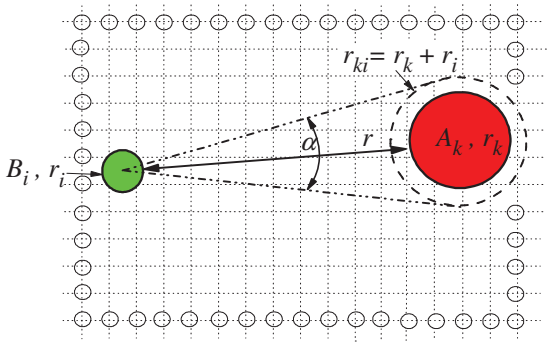

Figure 1: Angle of collision α.

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

where $r^* = \sqrt{L_i^2 + r_{ki}^2} - r_{ki}$. The probability for collision is a smooth and uninterrupted function of r [5], shown in Figure 2, where $x = r/r_{ki}$, $C = L_i/r_{ki}$, $x^* = r^*/r_{ki} = \sqrt{C^2 + 1} - 1$ and $x \in (0, C)$.

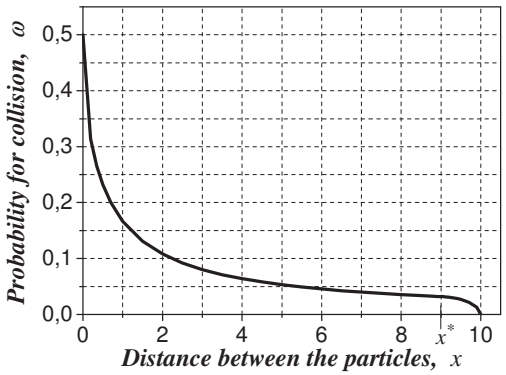

Figure 2: Probability for collision $\omega(x)$: $C = 10$, $x^* = 9.04988$.

3 Frequency of Collision

A ring around the particle A_k has been considered – it is situated between two circumferences with radii $(r + r_{ki})$ and $(r + r_{ki} + dr)$ respectively. The number dN_i of particles a_i within the ring is

$$dN_i = n_{i0}^s ds = 2\pi n_{i0}^s (r + r_{ki}) dr,$$

where n_{i0}^s is the density of particles a_i. All the particles dN_i have the same angle of collision α and probability for collision ω. That part of particles dN_i, which will collide with A_k within the time τ_i, is ωdN_i. The entire number N_i of these particles is

$$N_i = \int_0^{L_i} \omega dN_i = 2\pi n_{i0}^s \left[\int_0^{r^*} (r + r_{ki}) \omega_1 dr + \int_{r^*}^{L_i} (r + r_{ki}) \omega_2 dr \right] = 2 n_{i0}^s L_i r_{ki} \quad (2)$$

τ_i is the time for covering of the free pat length L_i: $\tau_i = L_i / \upsilon_i$. The frequency of collision is defined by number of collisions per unit time. How frequently particle A_k will be attacked per unit time by the particles a_i is given by the expression

$$\nu_{Ai} = \frac{\mathrm{N}_i}{\tau_i} = 2 n_{i0}^s r_{ki} \upsilon_i, \quad (3)$$

where A_k is an arbitrary particle of a_k: $A_k \in a_k$. Each particle a_k will get the same number of collisions per unit time by the particles a_i. The number of collisions per unit area of substrate surface per unit time is as follows:

$$\Re_{ki} = n_{k0}^s \nu_{Ai} = 2 n_{i0}^s n_{k0}^s r_{ki} \upsilon_i, \quad (4)$$

where n_{k0}^S is the density of particles a_k. All the collisions occurring per unit surface area per unit time is given by the sum over all possible collisions

$$\Re_0 = 2\sum_{i=1}^{m}\sum_{k=i+1}^{m} n_{i0}^s n_{k0}^s r_{ki} v_i, \tag{5}$$

where m is the number of atoms in the largest particle a_m of the system.

4 Frequency of Collisions with Straight Growth Step

Adsorbed single atoms have the greatest migration velocity with respect to all other clusters on the surface. One may suppose that the formation of clusters (dimmers, trimmers and etc.) occurs mainly by collisions with single atoms. Equation 4 allows determining the number of collisions with single atoms $(i = 1)$ of cluster a_k per unit length of its periphery per unit time. The length of the periphery of the cluster is as follows: $l_k = 2\pi r_k$. The frequency of collisions per unit length $\mathbb{R}_{Ai}^0$ of the particle A_k with the ad-atoms a_1 is

$$\mathbb{R}_{A1}^0 = \frac{\nu_{A1}}{l_k} = \frac{1}{\pi} n_{10}^s v_1 \frac{r_{k1}}{r_k}\,. \tag{6}$$

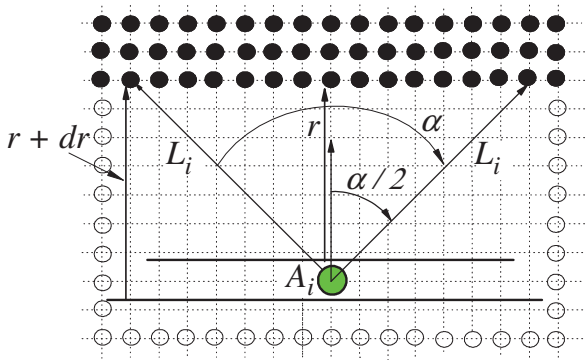

Figure 3: Frequency of collisions with a straight growth step – monatomic growth step is presented by the black particles.

In the case of a very large A_k particle ($r_k \to \infty$ and $k \to \infty$) the periphery becomes a straight line (Figure 3) and taking into account the equality $(r_{k1}/r_k) \to 1$, one obtains the number of collisions of the straight growth step with single ad-atoms per unit length per unit time – this quantity affects the growth rate of crystals and epitaxial layers

$$\mathbb{R}_{\infty 1}^0 = \frac{n_{10}^S v_1}{\pi}\,. \tag{7}$$

5 Discussion and Conclusions

The migration of single ad-atoms has been considered – at the moment how the motion of clusters (dimmers, trimmers etc.) occurs is not sufficiently studied. The density of adsorbed single atoms is in the range of $n_{10}^S \approx 2 \times 10^{12}$ cm^{-2} [6] – this is the number of single atoms, simultaneously sojourned on unit area of the surface. Their migration velocity is about $v_1 \approx 6 \times 10^3$ cm/s [6]. By Eq. 4 one obtains that the frequency of collisions between the ad-atoms is about $\nu_{11} \approx 3 \times 10^{21}$ cm^{-2}/s, where $r_{11} \approx 6 \times 10^{-8}$ cm. By coalescence of collided ad-atoms a dimmer may arise. If one assumes that the probability for coalescence of both collided atoms is about $\delta_{11}^+ \approx 0.1$ and the dimmers life time is about $\theta_d \approx 1$ ns, then the equilibrium density of the simultaneously sojourned on the surface dimmers will be about $n_{20}^S = \nu_{11}\theta_d\delta_{11}^+ \approx 3 \times 10^{11}$ cm^{-2}.

Following Eq. 7 the number of collisions of the ad-atoms with a straight growth step is in the range of $\mathbb{R}_{\infty 1}^0 \approx 4 \times 10^{15}$ (cm.s)$^{-1}$. By such a collision the ad-atom falls into a new situation – it becomes an atom in *step edge* position. In this position the binding energy with the substrate is greater than that in a dimmer or in an ad-atom position. The energy difference between the step-edge position and the dimmer one is: $\Delta E = E_{s.e.} - E_d = 2\phi_2$, where ϕ_2 is the binding energy with the next nearest neighbors. In case of Lenard-Jones interaction $\phi_2 \ll \phi_1$ – potential drops very abrupt. If the life time of an atom of dimmer is about $\theta_d \approx 1$ ns (as already assumed), then the life time in step edge position must be approximately the same $\theta_d \approx \theta_{s.e.}$. Then the number of atoms in step edge position, available simultaneously along a unit length is as follows: $\mathbb{N} = \theta_{s.e.}\mathbb{R}_{\infty 0}^0 \approx 4 \times 10^6$ cm^{-1}. The averaged distance between the atoms is about $\rho = \mathbb{N}^{-1} \approx 25$ $\mathring{A}$. As initially assumed, the surface migration is isotropic – all directions of motion are equally probable. It means that the flow of migrating atoms in all directions will be the same and all steps, available on the surface, will have the same frequency of collisions with the ad-atoms per unit length. The ad-atoms will be rarely supplied to the islands step, shorter than ρ. Its motion over the substrate will be hindered. Vice versa, steps longer than ρ will spread over the surface substantially faster.

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