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Atmospheric pressure PECVD nanoparticles: Mechanism of nanoparticle self-organisation into micron sized fractal clusters on a solid surface

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This paper covers the results from a study of the formation mechanism of fractal clusters from nanoparticles synthesised in atmospheric pressure radio frequency discharge. Two-dimensional structures with random configuration and self-similarity properties are formed by nanoparticles on the solid substrate surface. Typical linear dimensions of such structures have been in the micron range. On the basis of the previously demonstrated experimental results, the physico-mathematical model of the nanoparticle self-organisation is developed. The physical model includes the electrical charge effect of the deposit surface, spatial distribution of the surface electrical potential and the topography rearrangement phenomenon under the arising electrostatic forces. The threshold character of the agglomeration process initiation is found. Dependence of the formed structure topography on the character of the electrical potential change is demonstrated. The requisite conditions of classical fractal formation are revealed. The results from the computational simulation, which is conducted with the use of fractal analysis, indicate a high level of coincidence with the experimental results.

1. Introduction

Nanoparticles as such are the most intriguing object of nanotechnology world. Nanoparticles and nanopowders have been widely used as materials with unique properties [1-4] as components of composites [5-8], ceramics [9-11], catalysts [12-15], sensor functional materials [2,5,12,16-18] and potentially can be utilized for biomedical applications [4,5,17-21]. In the case of gas sensor, biosensor or catalyst design, the surface plays a crucial role as a functional element with a contact of environment. Control and determination of such surface characteristics as surface area, density, structure, order, organisation and bifurcation are challenging issues. Desired pattern can be created by means of electron-beam lithography [22,23], for instance, which is costly and complicated method having resolution limitations [24]. However, the alternative approach is to design self-assembly structures [25], which are widespread in the nature [26,27], on the substrate surface, where nanoparticles are construction materials.

Various kinds of agglomerates from nanoparticles can be obtained in vapor phase [28-34], liquid [35-40] or on the solid surface [41-47] by different ways. It should be noted that among deposition methods, atmospheric pressure plasma enchased chemical vapor deposition (AP-PECVD) is of high interest due to several advantages, for example, (i) the convenience of use and the simplicity of hardware design; (ii) high concentrations of precursors in the vapor phase and, as consequence, high product yield; (iii) low thermal input to the substrate due to intrinsic low-temperature nature; (iv) high controllability and repeatability; (v) compatibility with CMOS design. A particular feature of atmospheric pressure plasma-assisted processes is that homogeneous reactions promote the nanoparticle formation [52,53], which then can build self-assembled structures. Understanding of mechanisms of nanoparticles self-organisation process is a key point for making the ordered structure on the substrate surface.

This work gives a brief extract from our previously obtained experimental results [46-47,54,55] with the assistance of the computational simulation; reveals the mechanisms and proposes the physico-mathematical model of the formation process of micron-sized fractal clusters from nanoparticles on the solid substrate surface during AP-PECVD.

2. Experimental details

Silicon dioxide nanoparticles were synthesized during an AP-PECVD process. Figure 1 represents the reaction chamber scheme. A vertical cold-wall reaction chamber 1 was used. The body of the chamber 1 was made from optical quartz, enabling the observation of the discharge morphology and to register the optical emission spectra. A remote capacitively-coupled plasma (CCP) was generated and sustained in the gap 4 between the two plane-parallel mesh electrodes 3 at atmospheric pressure. The diameter of the electrodes made of stainless steel was 24

mm. The electrode bodies 2 were water-cooled by means of the system 5. The mixture of the precursor and carrier gas was introduced into the synthesis (plasma) zone 4 from the top region of the reaction chamber. The mesh electrodes 3, separated by 2 mm, were placed perpendicular to the gas flow direction in such a way that gas went through mesh electrodes 3. Helium was used as a plasma-forming and carrier gas. Tetraethoxysilane (TEOS) was utilized as a precursor. The flow rate of helium, which formed plasma, varied within the range of 100-850 sccm, that of the gas-carrier through the evaporator was 100 sccm. The gas flow velocity, which corresponded to the total He gas flow, was in the range 0.47-1.94 cm/s. The evaporator temperature varied from 20 to 40°C, which related to TEOS concentration from $4.7 \cdot 10^{-5}$ to $8.4 \cdot 10^{-5}$ g/cm³ in the reaction chamber. Atmospheric pressure was used. Deposition time was from 10 to 30 min. Nanoparticles synthesized in zone 4 were then transferred by gas flow through the plasma downstream area 6 to the substrate 7, which is placed perpendicular to the gas flow direction. The distance between the bottom electrode and the substrate was 40 mm. The formed products were deposited on the substrate, which were pieces of silicon wafer (111) with specific electrical resistivity of 4.5 Ω ·cm. The substrate was situated on the susceptor 8 cooled with liquid nitrogen when it was necessary to provide room temperature of the surface.

RF power (operation frequency 13.56 MHz) was applied to the top electrode; the bottom electrode was grounded. The RF circuit included a variometer, which was installed between the RF power source and the discharge gap for RF matching. The discharge current and the voltage were acquired by means of a current transformer and a voltage divider, respectively, and then were multiplied with a measured power factor to get a true discharge driving power. In all the experiments, the power value was kept at 15 W.

The precursor conversion rate in plasma was evaluated by FTIR-spectroscopy of the gas phase in the reactor outlet. It was found out that the TEOS conversion rate was in the range of 85–98% under studied conditions. Gas phase changes were accompanied by white powder deposition on the substrate surface. According to X-Ray photoelectron spectroscopy, the chemical composition results were consistent with silicon dioxide. Then the synthesis product, which is silicon dioxide nanoparticles, was analyzed by means of scanning electron microscopy (SEM).

3. Experimental results

We give brief overview of our previous results in this section. The main claim [46,47,55] was that various spontaneous self-assembly processes of silicon dioxide nanoparticles take place on the substrate surface. Based on the morphological differences of the experimentally obtained deposit, we distinguished several typical agglomerate kinds, which could be formed by nanoparticles with a size in the range of 10–60 nm. All agglomerates always appeared



Figure 1. Scheme of a reactor: 1 – chamber walls, 2 – electrode bodies, 3 – electrode meshes, 4 – plasma zone, 5 – water cooling system of electrode bodies, 6 – discharge downstream area, 7 – substrate, 8 – substrate holder.

simultaneously. Their characteristics such as morphology and number kept changing with deposition conditions change.

The first agglomeration type was described as the formation of tangled chains, which consisted of individual nanoparticles (Figure 2d), with different lengths. The deposit volume always filled with tangled chains. The formation mechanism and dynamics of this agglomeration type will be considered in our paper [45] with the assistance of the computational simulation.

The second agglomeration type was expressed as the formation of two-dimensional structures, which were composed of tangled chains made of nanoparticles, with a random configuration and with a typical size in the micron range (Figure 2a,b,c). It should be mentioned that those areas are characterised by the depletion of the synthesised products (nanoparticles), which is observed with the use of scanning electron microscopy in many cases near the obtained structures. Those structures displayed properties of affine self-similarity in a certain range of scales, *i.e.* the piece of the self-similar object was similar to the whole object after scaling (which stands for invariance with respect to scaling). It allowed the consideration of those objects as fractals (fractal clusters). In addition, the experimentally observed decrease of obtained structures density was a typical feature of all fractals. Experimental dependences of the fractional metric dimension of Hausdorff-Besicovitch of formed fractal clusters on such deposition parameters as TEOS concentration, gas flow velocity and deposition time were considered previously in [46].

The following facts that (i) the formed deposits had an inhomogeneous character (Figure 2a,b,c), (ii) the deposit was

capable of changing [46], (iii) the classical fractal clusters were observed (Figure 2b,c), indicated the intensive migration processes of the synthesised product along the substrate surface. The surface nanoparticle migration is highly likely caused by potential difference (potential barrier in order to overcome the activation energy) separating one equilibrium surface state from another [56-58], therefore even continuous movement could be conceived as the sequence of several single steps (shocks). The mathematical model for such movement was described in details [59-62]. Different ways of energy acquisition by a nanoparticle for passing the potential barrier existed, for instance, heat exchange in the system "plasma – gas flow – a nanoparticle – the substrate" [63-65].

The formed deposit consisted of tangled chains made of nanoparticles. The nanoparticle interaction can be described with the use of the Lennard-Jones (LJ) potential [45,66,67]. We estimated [45] that the nanoparticle interaction energy was approximately 10^2 kJ/mol, whereas the kinetic energy of the nanoparticles as defined by deposit temperature was 0.9 kJ/mol. The potential energy was two orders of magnitude more than the kinetic energy. Thus, it was supposed that strong interactions of nanoparticles in chains, which formed the deposit volume, prevented their migration along the substrate due to diffusion. This supposition was confirmed by our experiment described in [46]. It was demonstrated that surface

rearrangement also happened under the conditions when the substrate was cooled down to liquid nitrogen temperature.

Previously observed experimental data [46,47] demonstrated a significant role of other mechanisms. We propose a hypothesis that the migration character of the deposit substance resulting in the deposit inhomogeneity appearance (in the micron range) was caused by electrical interaction.

It was experimentally demonstrated in our previous paper [65] that positive ions with concentrations up to $10^{6}-10^{7}$ cm⁻¹ were found at 10–80 mm distance behind plasma zone, *i.e.* in the area where the substrate was situated. A distance of 40 mm was used for nanoparticle deposition. These ions transferred electrical charge to the surface of the formed deposit. Thereupon, a certain electrical potential appeared in each point of the deposit. This potential was defined by deposit geometry, amount of charges brought by ions, and amount of charges flowed down to the substrate through the deposit.

On the basis of the observed phenomena, we presented a model visualisation [46] of the agglomeration mechanisms (for the second agglomeration type). According to it inhomogeneity of the electrical potential on the deposit surface appeared to be due to (i) the electrical breakdown resulting from the movement of charged nanoparticles along the surface and (ii) the rearrangement of morphology under the arising electrostatic forces.



Figure 2. Typical SEM images of the deposit surface formed by silicon dioxide nanoparticles on monocrystalline Si (a, b, d) and amorphous alloy AMAG (c).

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4. Qualitative discussion of the fractal cluster formation model

On the basis of the computational simulation, we have demonstrated [45] that nanoparticles can agglomerate on the substrate surface with the formation of the deposit volume with tangled chains. Van der Waals, Coulomb and dipole interactions between nanoparticles are taken into account. According to the simulation, the deposit profile is not uniform, however typical prominent sizes are varied from no more than several tenths of a nanoparticle radius. On the other hand, the experimental results have shown that characteristic dimensions of the second agglomeration kind (fractal clusters) are in the micron range, indicating that the mentioned interactions wouldn't afford a description of their formation.

The shift from the tangled chain formation to fractal clusters shaping is highly likely connected with the electrical potential φ increase on the deposit surface due to a significant extension of time for the charge flowing down to the substrate through the deposit with the thickness H. Figure 3a shows that distributions of the electrical potential φ are not uniform and changing in time. The potential φ is above the obtained deposit surface at the distance equaled the critical radius r_c of the LJ potential, *i.e.* at 2.5 nanoparticle radiuses. A variance of the electrical potential $\left|\partial \varphi / \partial H\right|$ expressing the electric field intensity between the substrate and the deposit surface tends to increase in time, as shown in Figure 3b. The presented dependence illustrates the nonmonotonic abrupt growth of the electrical potential vs. time. Observed shocks of the dependence indicate a stochastic character of the deposit profile changing process and the charge flowing down to the substrate.

We would assume that there is a point in time for any arbitrary chosen electric field intensity, when the electric potential gradient *vs*. the deposit thickness exceeds this value E_c for a certain local surface area.

$$\forall \left| \vec{E}_{c} \right| \quad \exists t : \quad \left| -\nabla \varphi \right|_{t} > \left| \vec{E}_{c} \right| \tag{1}$$

This state can be expressed formally as (1). This supposition represents a basis for the suggested physical model of the second agglomeration type formation (*i.e.* the ramified system of the micron-range surface inhomogeneities of the formed deposit).

The model includes several consecutive processes, which can happen during the deposition, illustrated in Figure 4. The deposit 2-3 consisting of tangled chains is forming at the substrate 1. We assume that the deposit has low conductivity, so that the charge state vs. the thickness is not uniform. To put it in simpler words, the deposit surface 3 is charged and separated from the substrate by the layer of nonconductive material 2. During the first step, the electrical breakdown occurs in the certain local area 4 of the surface of the deposit, which continues forming from nanoparticles. The electrical breakdown should be read as the infinitely fast, in relation to any considered processes, creation of a conducting channel 5 between the charged deposit surface 3 and the substrate 1.

The criterion of the electrical breakdown is an event occurrence, when the $|\partial \varphi / \partial H|$ value has reached a certain critical value in the concerned local area of the deposit surface in the point of time t_c :

$$\left\|-\frac{\partial\varphi}{\partial H}\right\|_{t_c} > E_c \tag{2}$$

Due to high conductivity of the channel 5, its potential is close to the substrate I potential. As a result, the potential difference between the highly-conductive channel and the lowconductive charged surface layer of the deposit leads to the arising of the electrical field directed along the substrate on the deposit surface area 6 near the channel. The electrical breakdown in this area enhances the growth of the highlyconductive channel 7 along the surface, which progresses over time with an increase of size and branching. This process stops when the surface electrical field intensity falls to less than the critical value due to the potential drop along the channel during its length growth.



Figure 3. (a) Distributions of the electrical potential φ above the deposit surface for two moments of time $t_1 < t_2$ and (b) Dependence of the maximum value of the electrical potential variance $|\partial \varphi / \partial H|$ over time.

The next step is expressed as the rearrangement of the deposit surface. We suppose that even if the electric field intensity is insufficient for the breakdown development, but this value causes the electrostatic forces which lead to the tangled chains breaking and to the deposit volume reformation. The surface rearrangement is considered as a transfer of charged chain components from the nearby areas 8 to the conductive channel. Thus, the deposit relief with both "ridge" systems and the material depletion around them has been formed.

The typical time of breakdown development is approximately equal to 10^{-7} – 10^{-9} s [68], which is significantly less than the duration of any transport processes. This fact allows us to present the formation process of the second type agglomerate (fractal clusters) as two consecutive steps:

I. The first step is the generation of the non-uniform electrical potential on the deposit surface due to the charge transfer by nanoparticles synthesised in the RF discharge (breakdown channel development);

II. The second step includes changes of the formed deposit surface (surface rearrangement) owing to the substance transfer under the electrostatic forces arising due to the uneven electrical potential

5. Modeling of the fractal cluster formation: breakdown channel configuration (step I)

5.1. Problem definition and solution pattern

The modeling of the breakdown phenomenon is widely described in the papers [59-62,69-71] for different mediums and for various types of field geometry. In spite of the absence of a general breakdown model, which can explain all experimentally observed data, the conventional approach [63] is based on the Laplace equation solution for the potential in isotropic dielectric without free charge carriers (3). The model suggested [64] is the most frequently used.

 $\Delta \varphi = 0 \qquad (3) \mbox{In regard to optimisation of the computational simulation process, several drawbacks of this method have been emphasised. First of all, there is no effective algorithm of the cluster generation in the lattice. Secondly, this method seems unreasonably resource-intensive because of the necessary cyclic recalculation of the Laplace equation solution for all computational regions.$

The modeling of the breakdown phenomenon was widely described in the papers [69–71] for different media and for various types of field geometry. The conventional approach to the simulation of breakdown processes [72] was based on the



Figure 4. Steps of the deposit relief formation on the substrate surface. Notations: 1 - the substrate; 2 - 3 - the volume of the synthesised material; 3 - the charged deposit surface; 4 - the local surface area, where the electrical breakdown takes place; 5 - the volume conducting channel; 6 - the area close to the channel 5, where the surface electrical force appeared; 7 - the surface conductive channel; 8 - a charged unit of the deposit volume being transferred to the channel area; 9 - the formed surface structure called "ridges"; U - the potential in the local area of the deposit surface; H - the deposit thickness; E_1 and $E_2 -$ the electrical force intensities ($E_1 < E_2$).

Laplace equation solution for the potential in an isotropic dielectric without free charge carriers. The most frequently used model, which was based on such an approach, was suggested by Niemeyer *et. al.* [73].

Niemeyer's model is built on the proposal that the pattern of breakdown channels grows in a random manner in the space divided into finite elements. The channel is lengthened because of the joining of certain elements. The probability P of element joining depends only on the character of the local electrical field near the channel pattern. Breakdown probability increases dramatically with increase of electrical field; therefore, a power law was used for the definition of element joining to the channel:

$$P_k \sim E_k^\eta \tag{4}$$

where E_k is the electric field in the k^{th} element, which is one of the closest to channel pattern, and η is the growth criterion.

Using Niemeyer's model, several patterns related to different growth criteria were obtained for $N=10^4$ elements. The dependence of the fractal dimension on growth criteria is presented in Table 1. Examples of obtained patterns are displayed in Figure 5.

Table 1. The dependence of the fractal dimension on growth criteria.						
* In the case $\eta = 0$, the probability of element joining does not depend on electrical field. Therefore, all space will be completely filled.						
п	0	1	2	3	4	5

1.45

1.35

1.09

1.05

2.00*

1.75

The most frequent case in our experiments related to fractals with fractal dimension around 1.7. Such a value is correlated to growth criteria $\eta = 1$, according to Table 1. In this case, the probability of element joining is expressed as $P \sim \nabla \varphi$, which is equivalent to that of the diffusion-limited aggregation (DLA) model proposed by Witten and Sander [74].

In that context, describing the breakdown development process, we used the model of diffusion-limited aggregation (DLA) proposed by Witten and Sander [74]. It allows the expression of the geometry of the formed surface channel as a fractal cluster [75] initiated from the centre, which can be the deposit surface area, where the breakdown occurred.

In the model case, the fractal cluster is a superposition of infinitely thin surface conductive channels (the channel width is much less than the length) built randomly and beginning from the initiating centre. Such a two-dimensional channel system seems disordered, however it is not devoid of order. The criterion characterising this order is the fractal dimension of the cluster. Those clusters have fractal properties because, firstly, their density decreases with their growth and, secondly, the formed structures are affine self-similar [26].

Let us describe the process of the fractal cluster growth. We consider the surface channels growth as the increase of their length in a random direction due to the addition of elements with finite size. The value of surface occupation density Z(r) by the channels has been chosen as the cluster characteristic. The cluster growth is a stationary process and can be described with the use of the continuity equation (5):

$$\frac{\partial Z}{\partial t} + divj = 0 \tag{5}$$

where j is flux to a cluster with finite size elements. In the case, when flux is defined by a random character of the added elements with finite size, it can be expressed as (6). Then the equation for surface occupation density is rewritten as a standard diffusion equation (7).

$$j = -D\nabla \overline{Z} \tag{6}$$

$$\frac{\partial Z}{\partial t} = D\Delta Z \tag{7}$$

where D is constant.

In a stationary case, the value of the occupation density gradient is negligibly small, so the cluster growth occurs with practically a constant rate. The expression for channel density takes the form of the Laplace equation:

$$\Delta Z = 0 \tag{8}$$

Next, this equation is supplemented by the boundary condition describing the cluster growth character. As Z(r) is a continuous function, it is possible to build an uninterrupted cluster border (edge), which has a ramified structure. As far as



Figure 5. Typical shapes of breakdown patterns for different growth criteria.

the cluster growth begins from prominences, the boundary condition is presented as the growth rate of the cluster border (9).

$$\upsilon = an\nabla Z \tag{9}$$

where a is number coefficient, n is unit vector directed normally to the border.

We assume that the unevenness appears at the cluster border in the initial moments and is enhanced during the cluster growth. This process leads to instability, which increases the occupation density gradient on the border prominences, which scale decreases during the fractal cluster growth. In order to provide applicability of the Witten–Sander model, the minimal size scale of a border element has been added to the Laplace equation and the border growth rate. This border scale defines the necessary element of size of the fractal cluster. In these conditions, the characteristics and the structure of the cluster, which is obtained by solving the Laplace equation with the choice of border element size, are similar to the cluster fabricated by addition of separate elements having the border scale [72].

It is possible to use the DLA model for getting the fractal structures of the breakdown channels for the problem of the dielectric electrical breakdown ($\Delta \varphi = 0$) with the usage of the minimal scale of the conductive channel equaled to the particle size, of which the deposit consists.

5.2. Results and discussion

As we have suggested the possibility of the electrical breakdown of the formed deposit (1) and applied the DLA method, then we obtain a conductive channel configuration. In other words, we have a geometric projection of the conductive channel system, whose electrical potential is very different from the average on the deposit surface. The solution has two cases depending on the breakdown type satisfying the criterion (2):

1. The complete breakdown. This case relates to the situation when a highly-conductive channel towards the grounded substrate is formed in the local area of the deposit surface. Electrical charges flowing down this channel do not change the substrate and the channel potentials. Formally, it can be expressed that an electrical potential well with depth equaled to zero appears in the breakdown area. It makes sense, because the fractal growth is the stationary process in our model. This representation has regard to the physical process of bridging (cutting off) any possible ways of the charge leakage from the deposit surface by the highly-conductive channel.

The simulation results (Figure 6a) showed the feature of a classical fractal with the fractal dimension equal to 1.6. These results correlate very closely with the experimental results displayed in Figure 6b, presenting an SEM image of the formed deposit from SiO_2 nanoparticles. The fractal dimension of this second-type agglomerate is 1.6 as well.



Figure 6. (a) The simulation results from the complete breakdown development obtained with the use of the DLA method; (b) An example of SEM image of the deposit surface formed from the SiO2 nanoparticles.

2. The partial breakdown. This case corresponds to the situation when a highly-conductive channel forms in the local deposit surface area and develops till the endpoint in the deposit depth, which is connected with the substrate by a capacitor with finite capacity. The capacitor is charging as the charge flows down. Gradual charging of the capacitor limits the entrance of new charges. Formally, it can be described as an electrical potential well with finite initial potential, which is more or equal to the substrate potential, that is formed in the breakdown area. As charges flow down to the potential well, its depth decreases to zero. It means that the conductive channel potential is equalised to the potential of the surrounding surface areas. This formed drain does not bridge other paths for charge leakage from the deposit surface, that leads to realisation of several breakdowns simultaneously.

In order to simulate the case of the partial breakdown development, the simplified model used for the case of the complete breakdown should be modified. This situation can be illustrated with the use of the model of the cluster-cluster aggregation [46]. The main difference is absence of a single initial centre. Multiple fractal clusters are forming, developing and creating bigger clusters all the time. In a limited case, the system can transform to the sole giant fractal cluster.

The results from the partial breakdown development of the formed deposit are shown in Figure 7. It should be noted that the iteration number in the cell model is not connected to the real time conductive channel development. Typical channel formation time, in the case of the dielectric breakdown, is $t_{bd} \approx 10^{-7}-10^{-9}$ s, which is much less than the characteristic time of the deposit formation. The fractal dimension slightly drops from 1.42 to 1.36 and 1.34 at the initial and following moments (Figure 7a,b,c), respectively. Figure 7d presents an example of a real SEM image of the deposit surface formed from SiO₂ nanoparticles and shows fractal clusters with the dimension of 1.36.



Figure 7. (a-c) The simulation results from the partial breakdown development obtained with the use of the method of cell cluster-cluster aggregation; (d) An example of SEM image of the deposit surface formed from the SiO_2 nanoparticles.

Thus, according to the assumption that the breakdown of the formed deposit is possibly due to the surface charging, the twodimensional projection of the conductive channels is revealed. The potential of those ramified structures sharply differs from the average surface potential.

Comparison of the simulation results (Figure 6a and Figure 7a-c) and the experimentally observed fractal clusters topography (Figure 6b and Figure 7d) indicates good conformity. Depending on the different breakdown types, various kinds of channel geometry and deposit topography are realised.

6. Modeling of the fractal cluster formation: surface rearrangement (step II)

6.1. Problem definition and solution pattern

At any instant of time before the breakdown, the electrical potential of the chosen point of the deposit profile (Figure 8, curve 1) can be expressed as a random variable φ_{ky}^i with known mathematical expectation $M(\varphi_i)$ and dispersion $D(\varphi_i)$. Index y is a coordinate defining a position of the *i*th point along the deposit height from the substrate level y=0, to Δr , $2\Delta r$,..., $n\Delta r$, h; where Δr is nanoparticle size and h is the deposit height (thickness). The index x is a coordinate of the *i*th point along the surface from x=0 to Δr , $2\Delta r$,..., $m\Delta r$.

Let us chose any random moment of time when the breakdown process starts. The breakdown criterion, which is equation (10), between the i^{th} point on the deposit surface and the j^{th} point in the deposit depth is presented below.

$$\frac{\varphi_{xh^{i}}^{i} - \varphi_{xy}^{j}}{n\Delta r} > E_{c}, \qquad (10)$$

where E_c is a critical value of electric field.

Coordinates (x,y) corresponde to surface points where breakdown takes place, and the potential value φ_{xy}^{i} can be found from equation (8) for each value of E_{c} .

In the case of complete breakdown that takes place through the entire deposit thickness, there is a simplified version of equation (10):

$$\left|\frac{\varphi_{xh}^{i}}{h}\right| > E_{c} \tag{11}$$

The value of electrical potential in the local area of the surface will be equal to the substrate potential, *i.e.* zero.

In the case of partial breakdowns, these happen in the local deposit surface area and develop until the endpoint j in the deposit depth with potential φ_{xy}^{j} , when the inequality is valid. Electrical potential in the breakdown area will be greater than or equal to zero. The potential value depends on several parameters such as deposit thickness, packing density for nanoparticles, electronic structure, *etc*.

A consideration these processes can be simply illustrated by an equivalent electric circuit (Figure 9). Ions incoming from the reaction chamber are expressed as current source CS. Chains consisting of nanoparticles and formed deposit volume can be described as series capacitors C_1-C_n in parallel with resistors R_1-R_n , which define charge flowing down to the grounded substrate. In the case of the partial breakdown, not all capacitors break down (Figure 9b). The resulting capacitance will be larger than the original capacitance of the chains. The process of charge transfer to the breakdown area is limited by the charging time of capacitor C_n . In the case of complete breakdown, all capacitances that form the chain break down. The process of charge transfer to the breakdown area is limited by the resistance of the formed conductive channel R_j .



Figure 8. The original (curve 1) and the smoothed (curve 2) electrical potential profile in the breakdown surroundings.

We assume that the breakdown electrical voltage (the potential well depth) is known. We introduce the hypothesis that the electrical charge enters the area of the formed channel by transference of the charged part of the nanoparticle chains, which formed according to the model of the first-type agglomeration [45] in the δ surroundings of the channel.

This process can develop in various ways depending on the breakdown type. In the case of the partial breakdown, the potential well depth decreases in the process of electrical charge acquiring till the moment when the potential gradient at the well border is less than the breakdown electrical field intensity. In the case of the complete breakdown, the infinite depth of the potential well appears, the charge transfer process to this well is not limited. In either case, the charge transfer is accompanied by a deposit topography change.

In the context of the hypothesis of the first-type agglomeration [45] and using those results, chains consisting of partly charged nanoparticles are considered. An array of such tangled chains with different lengths fills any volume of the formed deposit. Let us evaluate the δ surroundings of the breakdown channel. The electrical force, which is defined by the electrical field intensity, acts upon a charge q_i of each chain in those surroundings. The chain breaks and the detached parts





Figure 9. (a) Equivalent electric circuit of deposit breakdown. The moment when critical potential is achieved in the local point of the surface of formed deposit in the case of (b) partial breakdown and (c) complete breakdown.

which are transfered to the breakdown area take their places according to this force. As result, the electrical potential well begins to be occupied partly or fully in the breakdown area. Simultaneously, the electrostatic potential decreases in the δ surroundings due to the flowing down of electrical charges transferred by the chain parts. A combination of the mentioned changes in the electrical potentials can be described as a process of smoothing the deposit potential profile. Schematically, the chain transfer is shown in Figure 10c.

The problem of the charge flowing down and the potential profile smoothing because of chains movement have been solved by means of the linear-regression method [76] or the least square method in the δ channel surroundings.

The solution was based on minimization of the sum of squares of potential-values deviation from a chosen third-order polynomial approximation. Choice of such an approximation was motivated by the condition that electrical potential and field should be smooth functions. Coefficients of polynomial approximation were found from the condition of minimization of the j^{th} point with coordinates $(x_j; y_j)$:

$$\sum_{i=j-\delta}^{j+\delta} (\varphi_i - P(x_i; y_i)) \to \min$$
 (12)

Figure 8 presents the original (curve 1) and the smoothing profile (curve 2) of the deposit electrical potential for δ =5.

6.2. Results and discussion

The simulation results of the geometrical profile rearrangement of the formed deposit are demonstrated in Figure 10a,b. Those results are presented as a two-dimensional crosssection of the deposit in the unrestricted area of the surface channel. A similar change in the geometrical profile takes place along the full length of the breakdown channels. It is illustrated



Figure 10. (a) The original and (b) the modified geometrical profile across the deposit volume. (c) The chain transfer scheme.

that the geometrical profile of the formed profile is modified. Increase of the deposit height is observed in the area of the breakdown channel. Simultaneously with the vertical growth, the depletion of the surroundings by the synthesised product occurs.

Thus, the formed deposit can be rearranged along the full length of the breakdown channels in this way, when the vertical structures and the depletion areas are formed.

7. Conclusions

The physical model of the micron fractal structures formation, which consists of nanoparticles synthesised in an RF atmospheric pressure discharge, on the substrate surface is proposed. The suggested model includes three main steps in the formed deposit rearrangement:

- Acquiring of charges transferred by ions from the discharge area on the deposit surface;
- An electrical breakdown of the deposit volume and the formation of the ramified surface area with a non-uniform electrical potential, *i.e.* the conductive channels;
- The rearrangement of the deposit surface under the electrostatic forces arising near the conductive channels.

Those phenomena have been simulated with the use of fractal analysis. The simulation results agree well with experimental observation. This fact proves the adequacy of the suggested mechanism of the deposit relief formation from nanoparticles.

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