

PLASMA METHODS FOR NANOSTRUCTURING THE POLYMER MATRIX OF PIEZOELECTRIC NANOCOMPOSITES

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The actual problems of developing nanocomposites using gas discharge plasma in a dielectric system - dielectric - air gap - dielectric cylinder with a polymer solution are considered. In the conditions of simultaneous action of electric discharge plasma, temperature and nanoparticle ejection into the polymer solution, immobilization of nanoparticles was carried out.

Keywords: polymer composites, nanocomposites, electric discharge plasma, plasma assisted crystallization.

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1. INTRODUCTION

It is well-known that composites on the basis of rhombohedra, tetragonal, heterogeneous structure as well as polar and nonpolar polymers possess higher piezoelectric characteristics and can be employed as the converters of various purposes. These composites possess a higher sensitivity in the regime of receiving the acoustic waves. Main reason of this effect is sufficient higher piezo-modulus (d_{ij}) and lower dielectric permittivity so that the piezosensitivity is defined as $g_{ij} = d_{ij}/\epsilon\epsilon_0$. However the above described piezoelectric composites have a small efficiency in the regime of generation of acoustic waves because of relatively small value of Young's modulus (Y^E), coefficient of electro-mechanical binding and mechanical quality. The main reason of the lesser piezomodulus is an existence of subsurface polymeric phase formed as a result of thermal compressing on the surface of piezoelement. Numerous experimental results showed that the sub-electrode region always is the region enriched with polymer regardless of the obtaining technology of matrix composites. Existence of sub-polymeric layer is accompanied by decrease in mechanical and thermal properties of composite entirely. We may assume that, an achievement in the field of nanotechnology enables to obtain piezoelectric elements, energetic capacitive and low-power piezoelectric materials. [1-4,13]. It is well-known that the nanostructured polymer composites of various assignments have been recently developed. The scientific investigations are mainly doing in two directions:

1. Performance of nano-structuring in the process of polymers' synthesis;

2. Development of new piezoelectric materials on the base of the hybrid nano- and micro-sized piezoelectric composite materials like $Pb(ZrTi)O_3$.

Nanosized piezoelectric materials are synthesized by using SiO_2 , TiO_2 and $BaTiO_3$ [5, 6]. It is worthy to note that, fabrication of nanoparticles on the basis of multicomponent $Pb(ZrTi)O_3$ ceramics is of particular interest, since they are good piezoelectric materials with

high values of d_{ij} , K_{ij} , Q_m (d_{ij} is a piezo-modulus, K_{ij} are refers to electromechanical coupling coefficient, and Q_m indicates mechanical quality factor). However, nowadays the reliable experimental results are absent in the literature on the synthesis of nanosized particles from the family of $Pb(ZrTi)O_3$.

The aim of our activities in this work is a development of plasma methods for immobilization of nanoparticles in the polymeric matrix of piezoelectric composites.

To achieve this aim following tasks were performed:

– Immobilization of nanoparticles and their uniform distribution in the polymer matrix (PVDF and LDPE) by simultaneous influence of the electrical discharge plasma and temperature;

– Development of a deposition technology for nanostructured polymeric solution on the surface of the piezoelectric substrate by simultaneous electrical discharge plasma exposure and temperature.

2. MATERIAL AND METHODS

We consider the matrix composites (0-3 type) on the basis of PKR-7M (tetragonal) type piezoelectric ceramics from family of lead zirconate titanate, thermoplastic polymer polyethylene of high density PEHD with a melt fluidity index of 1.3 g / 10 min (load- 2.0 kg, temperature 190°C) and silicon dioxide SiO_2 dielectric. Selection of carbon-chain polymer- polyethylene is related to the fact that it is characterized with high reproducibility due to its composition, structure and physical and chemical properties. A PKR-7M (PZT-5H) piezoceramic was selected due to its high piezoelectric modulus $d_{33} = 760 \cdot 10^{-12}$ C/N), Young's modulus ($Y_{11}^E = 0.57 \cdot 10^{11}$ Pa) and dielectric permittivity ($\epsilon_{33}/\epsilon_0 = 5000$). The silicon dioxide SiO_2 particles were used in spherical shape with density of 22 g/m³, specific surface area of 200 m²/g, and the electrical conductivity of $10^{-12} \cdot (m)^{-1}$. The plasma crystallization of composite promotes arising the active centers with physical and chemical nature in the polymeric phase [12-15]. Duration of discharge exposure

was varied from 15 to 30 min. depending on the properties and volumetric content of polymer and piezoelectric ceramic in composite. A thickness of the gas gap, where micro-discharges were initiated was 0.5 - 4 mm. The voltage applied to the gas-insulator-composite system was (3 – 20) kV [6-12]. Selected SiO₂ nanoparticles possess significant surface activity and enough high activity. The high surface energy of nanoparticles leads to unusual surficial properties and reactions. Therefore, one of the problems in the development of polymeric nanocomposites is effective dispersing, stabilizing the nanoparticles and preventing their mobilization in the polymer matrix of composite. Specified tasks were solved by employment the technology suggested by us for modification of polymeric phase; this consists of the crystallization starting at the melting temperature under effect of electric discharge plasma in electronegative gas electro-thermo-plasmonic crystallization of [1-7]. The stabilizing effect is explained by the formation of active centers of oxidation and submicro-size regions of stapling of macromolecules for localization of the dielectric nanoparticles owing to the effect of plasma of electric discharge in the polymeric phase of composite. This leads to the formation of a strong structure composed of SiO₂ particles as well as oxidized and cross-linked local regions of the polymer macromolecules. Wherein nanoparticles of dielectric occupy active sites in the polymer matrix without destroying the macrostructure of the piezoelectric composite. It should be pointed out that a strengthening of the polymer with dispersed nano fillers is a fundamental issue for the creation of polymer materials with various purposes [13-15]. Two main factors for strengthening are assumed to be the particle size or specific surface area of the filler and the polymer-filler binder [13]. Note that among all broad class of polymeric composites a new types of filled materials are polymeric nanocomposite in which one of the sizes (length, width and height) of dispersed phase does not exceed 100 nm at least [13]. Due to ultra-dispersive property of inorganic dispersant (filler), such systems may exhibit unusual electrical [11-15], mechanical [13], and thermo-physical [1-6,13] properties which do not possess microcomposites. The functional components of polymeric HC may be metals, dielectrics, semiconductors, and organic as well as inorganic substances [13]. For our studies it is necessary to use the dielectric ultra-dispersed particle as nano dispersant since electret, piezo – and pyro electric composites gain the mentioned properties after their electro-thermal polarization [1-15], which requires a high dielectric resistance and electrical strength. The above specified composites are obtained from a homogeneous powder mixture of components. The temperature and pressure for compressing of composites were selected within 437-463 K and 30 MPa respectively. The thickness and diameter of the piezo- composite were chosen as $250 \cdot 10^{-6}$ m, and $(160-200) \cdot 10^{-6}$ m respectively. Piezoelectric modulus of composites was determined in quasi-static mode, with an accuracy of 10%. Note that the thermal compressing process results in an additional purification of the composite from the solvent molecules and elimination of microphase separation of nano- and microcomposites at their

intersection. Thus, a quasi-monolite structure is produced on the base of which the piezo electric converters of various purposes with high electromechanical and piezoelectric characteristics are prepared. The volume content of nanophase was varied in the range from 0.1 to 1%.

3. RESULTS AND DISCUSSION

The polymeric matrix materials proposed by us consist of a layer enriched by polymer phase dispersed by ferroelectric particles. Hybrid piezoelectric materials in turn, consist of the subsurface layer and the polymeric piezoelectric substrate. Nanostructured polymeric solutions are deposited on the surface of the piezoelectric substrate by employing chemical method. Thus, the polymer layer deposited on the surface of the piezoelectric substrate in the hybrid composite is a nanostructured composite. The dissolved polymeric layer deposited on the surface serves as a subsurface layer with high mechanical properties. The polymer- piezoceramic substrate in the hybrid composite serves as micro piezoceramics while the composite of polymer - BaTiO₃ as well as polymer - of SiO₂ corresponds to nanocomposite. Currently the microstructured polymer composites are well studied. It has been found that, a formation of the piezoelectric effect in the microstructured composites is mainly due to formation of a quasi-neutral system of polymer - ferroelectric ceramics. With the variation in size of piezo-phase particles, structure, volume, content and physico - chemical properties of components, as well as polarization conditions one can optimize the technological regimes for obtaining the piezoelectric composites. The effects of electron-ion and polarization processes on the piezoelectric properties are not studied enough. Therefore a piezoelectric, mechanical and electromechanical property of composites, as well as a production of a piezoelectric substrate is not sufficiently studied. The main reason of appearance of this effect is the presence of electrical and mechanical losses in the subsurface region of the composite element. It should be pointed out that the mentioned losses almost always occur in the piezoelectric elements independently on the fabrication technology of the elements. The main objective of the development of technology of hybrid piezoelectric materials fabrication of a piezoelectric substrate dispersed by of microsize particles of PZT. This is mainly due to the fact that the interfacial losses are noticeably reduced due to lack of a polymer-rich layer in the composite. In order to solve this problem, the modification of the surface layer by the electric discharge plasma is required.

The dielectric substrate modifications were carried out by effect of barrier discharge existed in the system of polymer - gas - polymer. These technological operations are performed as follows:

- The possibility of a uniform modification of the discharge of the composite;
- The possibility of varying the surface of the piezoelectric substrate with energy entering from the discharge channel up to the surface of the piezoelectric substrate;

- It is also necessary to develop the technology for uniform erosion of the polymer phase surface.

In Fig.1, the optical picture of the development of a barrier discharge channels is demonstrated. Fig. 1b shows the electric barrier discharge pattern. It is seen that the barrier discharge is discrete in time and space. As can be seen, micro-discharges arise in different sections of the surface of the dielectric substrate.

That is, the mentioned characteristics allow us to treat uniformly the surface of the dielectric substrate. In our experiments the voltage applied to the test cell was $20 \cdot 10^3$ V, while the length of the plasma channel varied between 0.5-6 mm dependently on the experiment conditions.

It should be pointed out that, in the conditions of electric discharge plasma the modification piezo-substrate surface develops as follows:

- The substrate is subjected to the action of electrons and ions, ionizing radiation, and local discharge surface.

- The chemical factors in the process of etching of piezoelectric element surface are a thermal destruction, cut off the polymer's main chain and the photo-destruction.

- The degree of etching under the influence micro-discharge is mainly determined by the energy transferred from the channel to piezo-substrate surface.

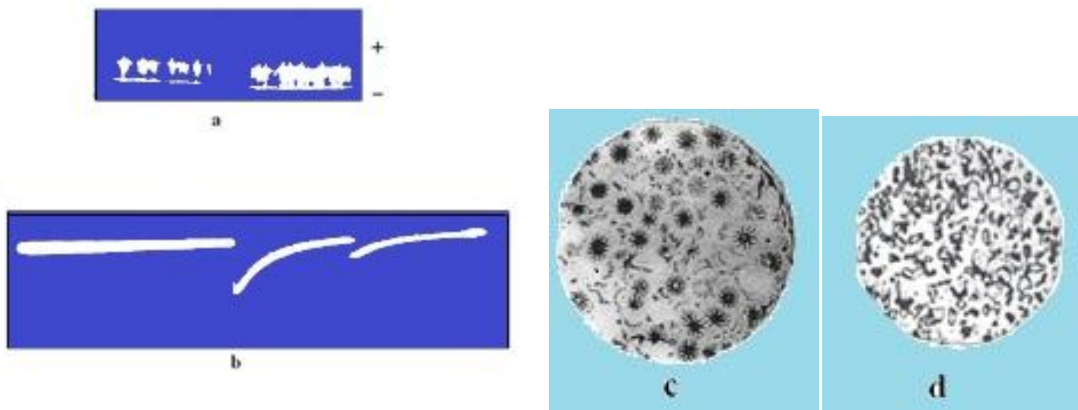


Fig.1. The test cell consists of a dielectric, gas layer and a dielectric. The micro-discharges appear under the influence of high voltages, which lead to erosion of the subsurface layer of composite.

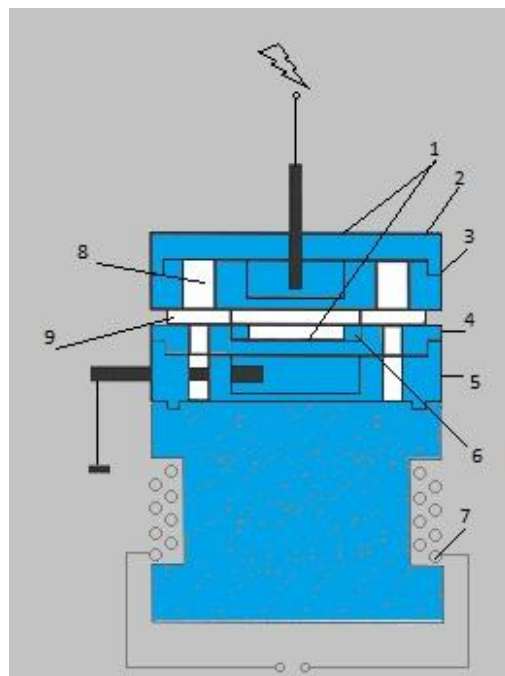


Fig. 2. A core proposed for nanostructuring of polymer solution .The core consists of a metal - dielectric - gas - polymer solution - piezoelectric substrate - metal structure:
 1 - electrodes, 2 – dielectric safety washer, 3 - dielectric anode, 4 - dielectric cathode, 5 - insulator, 6 - metallic cylinder, 7 - heating element, 8 - leading, 9 – limiters of dielectric distance: $T_p = 383$ K; $t_p = 0.5$ hours.

One can assume that etching of piezo-substrate surface occurs as a result of transfer of energy entering from the channel in the fields of contact between plasma and composite surface. Due to the local energy transfer, a heating of piezo substrate surface with subsequent erosion takes place.

It is known that, the electrons and ions of high energy, low molecular oxygen containing groups, atomic oxygen, ozone and ionizing radiation are synthesized in the plasma channel of barrier discharge. As a result, these physico-chemical processes including erosion provide uniform etching of the piezoelectric substrate. The next technological operation is a chemical deposition of previously nanostructured polymer solution on the substrate surface.

For this purpose a special dielectric core was constructed, which allows us to perform a plasma barrier discharge in it. The core consists of a metal electrode, dielectric substrate, an air layer, a polymeric solution and dielectric cathode.

Firstly, note that the immobilization of nanoparticles in polymeric phase is carried out by several methods:

1) Chemical method – inclusion of inorganic nanoparticles into the polymer or obtaining and distribution of nanoparticles upon polycondensation, polymerization and copolymerization reactions.;

2) immobilization of nanoparticles in polymeric solution due to effect of acoustic waves.

3) immobilization of nanoparticles in polymeric solution by mechanical effects, e.g. under vibration.

4) immobilization of nanoparticles in polymeric solution due to the gas discharge (crown discharge).

Analysing of the above mentioned methods shows that the immobilization of nanoparticles in the polymer phase may be carried out by applying of these methods. However, the first method seems to be complicated in comparison with other mentioned methods. The second method is employed under realizing of the acoustic converters, which is constructively more complex and it is related to covitation effect. That is why immobilization implementation depends on the distribution of covitation centers. An energy released in the covitation process is not sufficient for immobilization and therefore it is impossible to increase and to regulate of energy in this process. It is difficult to provide the intensification of immobilization process by crown discharge, since one can not smoothly change the energy by increasing the voltage applied to channels of the crown discharge. An effective performance of the immobilization process under the mechanical vibrations is impossible, e.g. in the centrifuges.

In this work, a technology for effective performance of immobilization by using the barrier type electric gas discharge is developed. For this purpose, the following dielectric structure have been used : metal - dielectric - gas gap - polymer solution - dielectric - metal. The main aim in the selection of this system is the opportunity of regulation of the released energy in the plasma channels upon gas discharge in the wide interval. Indeed, in the dielectric structure offered by us one can change parameters of gas discharge in the wide range by varying electrophysical parameters and geometrical sizes of

dielectric, air gap, solution, and composite. One of the basic step of manufacturing of new type piezo-electrics on the base of hybrids of composites with polymeric matrix and nano and microsize phase is the obtaining of nanostructured polymeric solution, its deposition on the piezo electric substrate and prediction of physical characteristics.

Primarily, a polymer solution is obtained in a solvent and then it is nanostructured under conditions of electrical gas discharge plasma with BaTiO₃ and SiO₂ nanoparticles of 70 nm sizes. As a solvent were taken toluene and kselol with boiling point >100⁰ S. The solution process was carried out under combined effects of temperature and electric gas discharge plasma created by the sinusoidal voltage with 25·10³ V voltage and 50Hz frequency. In order to accelerate the solution process of polymer in a solvent its macromolecules are divided into smaller segments under electric gas discharge and hence we provide the reasonable variant of polymer's solution in toluene. Destruction of the macromolecules is carried out by the combined effect of high energy electrons, ions; ionizing radiations synthesized in plasma channel as well as small molecule active compounds with oxygen origin. For this purpose a special experimental core was developed. Experimental core consists of metal - dielectric - gas - polymer solution - piezoelectric substrate - dielectric - metal system. The electric discharge is formed under influence of high voltage in the air gap between polymeric solution and dielectric anode. Thus, the polymer solution is continuously exposed to electric and gas discharge. The melting process of polymer in toluene and its next nanostructuring is carried out at the boiling temperature (20-40K) of solvent. One of the main next stages is an immobilization of pre-encapsulated BaTiO₃ and SiO₂ nanoparticles of of 60 - 70 nm sizes. In addition, it should be pointed out that the active gas products, ionizing radiations, high energy electrons, ions and mechanical waves are generated in the dielectric structure in the gap of dielectric-gas-polymeric solution due to electric discharge in the gas phase. As a result, the immobilization process of nanoparticles breaks down and, nevertheless, the new immobilization centers can be created. One of the positive aspects of the use of dielectric structure is that there is an advantage of uniform distribution of plasma channels over its surface instead of their stabilization at certain point. The main reason of such distribution is the formation of electric charge spots on the dielectric surface whilst creation of every discharge channel. Stabilization of electric charges is observed at the contact region between channel and dielectric when each local discharge is created. Therefore, the second plasma channel is formed apart the first channel as soon as possible. Since this principle is valid also for the further micro discharges, this ultimately leads to uniform distribution of micro discharges over the dielectric's surface. (Figure 2). This means that the identical probability distribution of immobilization process is provided in the whole volume of polymer solution. In this case the volume of polymer solution undergoes the influence of electric gas discharge and possibility of mobilization of nanoparticles in this volume is destructed. To predict the nanostructuring of composites the TSD spectrum is used in this work. Our

activity can be summarized as follow: if an immobilization does not occur then the TSD spectrum obtained for microcomposites should not differ from that obtained for the element with the nanocomposite. This demonstrates that the nanoparticles added to polymer are mobilized as large clusters, i.e. they behave as a microparticle and therefore one can assume that the obtained TSD spectrum is similar to that obtained for the microcomposites. If a nanostructuring of composite was already realized, then the TSC should be different and tempreature corresponding to the maximum of spectrum shifts toward its higher values. Therefore, in order to perform nanostructuring of the composites under

investigation it should be found a certain relationship between this process and electric gas discharge obtained due to effect of higher voltage in the metal-dielectric-gas-solution-composite-metal structure used in producing of composite based hybrid systems.

A great significance has a prediction of influence of electric gas discharge formation in the dielectric structure, effect of liquid phase on the gas discharging parameters and influence of the electric gas discharging in the evaporation of liquid phase to the parameters of the plasma channels. For this purpose we use a Volt-Coulomb characteristic (Fig.3).

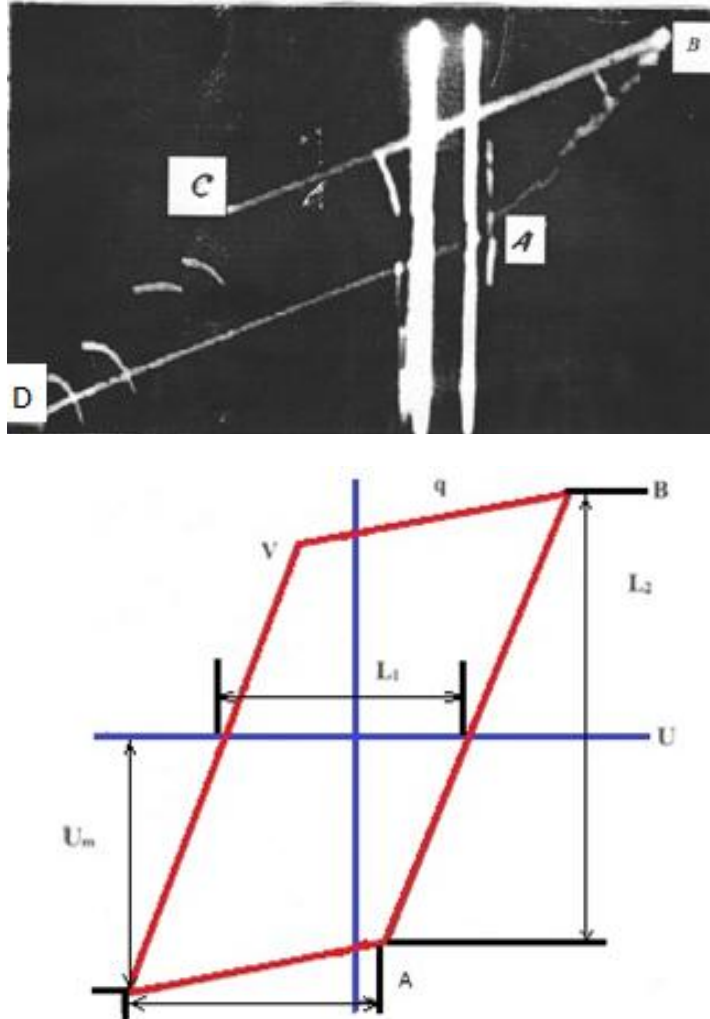


Fig. 3. Volt-Coulomb characteristic of the dielectric – air - polymer solution - piezo substrate - dielectric system corresponding to the core with a dielectric structure.

As it is seen from the Volt-Coulomb characteristic, the electric discharges in the dielectric structures under investigation have a discrete character (Fig.1, a and b). The liquid phase(solvent) evaporates under the combined influence of temperature and plasma, and it is deposited on the nanostructured polymer solution-composite system. During this process a variation in the thickness of liquid phase results in the following effects:

- A decrease in thickness with evaporation of liquid phase causes increase in its capacity and therefore a distributed voltage decreases gradually.

- The situation is oppositely for an air layer. A thickness of air gap increases with evaporation of liquid phase and hence a voltage increases due to decrease of capacity.

The ignition voltage increases with increase of thickness of air gap. This causes the change of width of volt-coulomb characteristic. Therefore the volt-coulomb characteristic is used for diagnosis. Indeed, an increase in the width of Volt-Coulomb characteristic, a change in its height corresponding to the energy of further discharges and transferred charge quantity occurs. Therefore,

analysing Volt-Coulomb characteristics one can diagnose the electro-physical, electro-mechanical and electro-chemical processes occurring in the core under investigation.

If we accept that the volt - coulomb characteristic is simple and its parameters are valuable as a source of information, then the process of chemical deposition can be controlled by this method. In our experiments the time instant of a great significance is the accurate recording of the moment completion of the deposition process. Otherwise, an erosion processes will occur at the contact surfaces between electric gas discharge plasma channels and composite. To determine exact time instant of perfect vaporization of liquid phase as well as end of the deposition process following tasks were carried out:

- we determine ignition voltage of electric gas discharge in the metal - dielectric – air layer-liquid phase- composite-metal system;
- we determine ignition voltage of electric gas discharge in the system of metal-dielectric-air layer-composite-metal ;
- The greatest value of ignition voltage of the system studied is the voltage corresponding to the end of nanostructuring process.

The voltage circuit is automatically cutted off at this limit of width of volt-coulomb characteristic. As we noted earlier the ignition voltage increases linearly (it

is seen from figure) since the air layer thickness increases as the electrochemical deposition process is developed. Apart from the volt-coulomb characteristics a controlling scheme can be performed by the quantity of charge transferred in individual channels of electric gas discharge plasma , i.e. registration of current pulses.

Studies show that the nanostructuring of polymer phase that will be deposited on the composite can be provided through precisely regulation the vaporization temperature of nanostructuring polymer solution as well as concentration of nanoparticles in solution in the investigated dielectric structure.

CONCLUSIONS

Thus, the immobilization of nanoparticles in a polymeric matrix is carried out by plasma method in the following sequence:

4. A diagnosis of immobilization process of nanoparticles in solution is carried out by volt-coulomb characteristic.
5. Time instance corresponding to the maximum values of width (which corresponds to the ignition voltage of electric discharge in a gas gap of core) and height of volt coulomb characteristic indicates a completion of both immobilization and nanostructuring.

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