Polycondensation processes occurring during 3D aerosol printing with new ceramic materials based on nanostructured highly dispersed fillers of polyaluminosilicates used in nano- and microelectronics and medicine

A A Ivanov¹, V A Polyushko² and A Yu Khomyakov¹
¹Tomsk State University of Control Systems and Radio Electronics, 40 Lenin Avenue, 634050, Tomsk, Russia
² Tomsk State University, 36 Lenin Avenue, 634050, Tomsk, Russia

E-mail: alexchemtsu@rambler.ru

Abstract. A new low temperature ceramic material for 3D printing based on polyaluminosilicate has been synthesized. Some of the synthesis stages are controlled by the parameters set for 3D aerosol printing. The processes of 3D aerosol printing of polyaluminosilicates filled with a highly dispersed filler have been studied. An optimal method for aerosol generation has been chosen that does not affect the supramolecular structure of a polyaluminosilicate binder. Ceramic dielectric topologies with high thermal conductivity and layer thickness in the nanometer range have been obtained by means of 3D aerosol printing of the synthesized material for the first time.

1. Introduction
3D printing is currently a rapidly developing modern technology to form various coatings and topologies in microelectronics products and devices that have related prospects for industrial application. The development of fundamental approaches to produce consumable products (the so-called “composite materials”) with the necessary functional and structural properties and careful physicochemical, morphological, rheological, and metrological analysis of the obtained stable suspensions and their components is one of the main problems related to the microprinting technology development. This problem is to a large extent limited to the synthesis and chemical modification of various functionalized nanoparticles with the set chemical and phase composition and morphology and also to the study of such particles behavior in the initial solution and in the process of solvent removing from a limited volume of a microdroplet. Nowadays, many high-tech companies all over the world switch to the technology of prototyping and commercial production of modern microelectronic, sensory, and photovoltaic devices using computer design and microprinting. It is not possible to obtain a specific dielectric layer or topology with the set thermophysical, physical, and chemical properties at the certain area of a device or product by means of traditional methods with the use of commonly applied materials.

Thus, metallic and nonmetallic materials commonly applied in various industries have to a great extent reached their functional and structural limits. However, the modern microelectronics industry requires new materials reliably operating in a complex combination of force and temperature fields
and being exposed to corrosive environment, radiation, extreme vacuum, and high pressure. One can solve this problem using modern nanostructured composite materials and processing techniques in combination with conventional materials.

The modern and available method to produce functional and structural materials with the necessary properties is currently a sol-gel technology that allows controlling the chemical nature of the material in the synthesis phase, thereby setting the required properties for the finished composites. The sol-gel technology is the primary method to obtain multipurpose nanodispersed materials. The actual tendency of sol-gel synthesis is to modify the siliceous compounds by both organic and inorganic substances. The sol-gel method peculiarity is the hydrolytic polycondensation reaction of alkaline silicates that occurs in the presence of inorganic substances (salt, acid) and low and high molecular organic modifiers. They give the specified physicochemical and technically essential properties to the formed materials. As a rule, the inorganic substances and modifiers are template agents contributing to the formation of silicate and hybrid nanocomposites with a specific structure [1-3].

The primary task is to apply the obtained material on different in their chemical nature bases and study the processes that occur when applying the obtained material. This task is to be solved along with the basic task to produce new ceramic composite materials with specified functional and structural properties used as consumable products for 3D printing of various coatings and topologies in microelectronic devices and products. Such process task as layers and topologies application generates current scientific challenges of surface physical chemistry, for example, the problem of material adhesive power and strength. Simultaneously, applying material on the product or device surface generates fundamental research of physicochemical processes.

Currently there are 2D and 3D printing of composite materials that relate to printing technology. The printing technology development is based on the achievements in the field of nanotechnology and nanomaterials. Consequently, the production of functional elements with the use of a printer relates to nanoelectronics. Research and development in this field of nanotechnology is a crucial task because it is dynamically developing now [1, 4-7].

The composite materials are promising because the structural elements with the phase composition peculiarities and unique properties can be formed in them. Such materials are used along with the 3D printing method to obtain a ceramic multilayered coating with high adhesive power, electric strength, and high thermal conductivity.

The study objective is to:

- research the polycondensation processes occurring during 3D aerosol printing with new ceramic materials based on polyaluminosilicates nanostructured with highly dispersed fillers;
- obtain multilayered ceramic layers and topologies of low temperature synthesis by 3D printing;
- study the test sample functional and structural properties;
- estimate their probable use as a dielectric ceramic coating with high adhesive power, electric strength, and high thermal conductivity in nano- and microelectronics, light engineering, and devices for special purposes.

2. Experiment

2.1. 3D printing. Ceramic layer printing on an aluminium base with a screw feeder.

A screw feeder is used in those cases when dose quality, accuracy, and frequency are important. One widely uses them to apply composite materials and glue. One can get the dose with a diameter of 200 microns and less with high frequency using a screw feeder. Ceramic layers on an aluminium base have been obtained by screw dosing with the help of the Spectrum II S2-920 dosing unit (one-track version) produced by Asymtek.

A screw or Archimedean screw is the main element that influences the quality of dose formation. The material is fed from a syringe into the channel with the screw by compressed air. Then the material is forced through a needle onto the substrate surface by the normalized screw rotation. The screw rotation angle and internal needle diameter determine the dose volume. Both heads are equipped
with motors with encoders and the feedback system that allows setting the rotation angle with an accuracy of 0.0095 degrees per one encoder value.

The cartridge of the screw feeder is removable. The screw rotates inside the cartridge. This allows fast replacing and cleaning of the screw and reducing the time for technological maintenance. The screw is made of tungsten carbide that has high strength, durability, and service life. It does not rust and is not exposed to oxidation.

The screw can have different screw pitches that allows using the composites of the third type and composite materials having smaller particle size. The smaller is the screw pitch, the smaller is the material dose that can be obtained. At the same time, the gap between the screw and the channel walls, through which the material is fed, is very important. It should be of such a size that the highly dispersed filler of the composite material is not pressed by bypassing the screw turns that may cause the leakage of the composite material applied on an aluminium base and the screw rotation blocking.

In addition, the cartridges differ in the type of a needle used. It is possible to use plastic, metal, and high-precision needles both with and without a stopper.

The advantages of a screw feeder:
- dosing of viscous materials such as highly filled composite materials;
- high stability and accuracy of doses;
- easy replacement and maintenance of a screw cartridge;
- the wide range of applied materials;
- a built-in encoder and the possibility of accurate control of the screw rotation angle.

The disadvantages:
- mechanical contact with a circuit board while dosing (for the needle with a stopper);
- the impossibility to apply layers and topologies with a layer thickness of less than 1 micron;
- the impossibility to apply the composite material with a wetting angle of 180°.

Figure 1 shows the profilogram of the topologies obtained as a result of the experiment.

![Figure 1](image)

**Figure 1.** Profile profilogram of three separate topologies obtained by method of screw dosing of polyaluminosilicate filled with highly dispersed filler on aluminium base.

The profilogram in Figure 1 shows that the wetting angle of all three lines applied on a smooth surface does not meet the requirements of printed electronics that exerts a great influence on this method applicability to obtain layers and topologies from synthesized polyaluminosilicate filled with highly dispersed fillers.

2.2. Ceramic layer printing on an aluminium base by means of 3D aerosol printing.
To obtain aerosol from dispersed liquids is one of the most crucial problems solved in some technological processes and definitely in 3D aerosol printing.

The dispersing can be carried out by various methods, the most widespread of which are hydraulic, mechanical, pneumatic, and electrostatic.

The hydraulic method is based on fluid passing through an aperture. Pressure differential, fluid viscosity, air density, and turbulence are the main factors that affect dispersing. In this method the agglomerate strength depends on the strength of individual particle contacts, coordination number, porosity, and the size of initial particles. The synthesized composite material based on the polyaluminosilicate filled with a highly dispersed filler forms an agglomerate in the form of a ball. The ball consists of many particles streamlined by a stream being exposed to the crushing effect of the pressure differential in a face part. The lateral efforts that arise in this process separate the particles of highly dispersed filler and the polyaluminosilicate macromolecules as a whole. Since the particles are connected by autohesion forces, the separation voltage is proportional to the pressure differential. When smaller particles streamline the agglomerate, the agglomerate body may be destroyed by erosion, or vice versa, the agglomerate may capture small particles. Therefore, the aerosol from partially destroyed polyaluminosilicate is obtained at the outlet. Even partially destroyed polyaluminosilicate is not capable of forming the supramolecular structure that binds the particles of the highly dispersed filler. Consequently, the opportunity to control and set the properties of the obtained layers and topologies based on the synthesized composite material fails.

The mechanical method uses crushing by a rotating disk. The initial pressure, degree of carrier medium compressibility, concentration, material dispersion, and polyaluminosilicate binder characteristics determine the disk movement parameters. The disk structural characteristics that affect the diffusion in the obtained aerosol stream and the carrier medium expansion are crucial. The effect of the carrier medium compressibility in case of sufficient pressure differentials results in a gas-dynamic mode of two-phase medium motion and the appearance of critical conditions for the outflow that differ from the critical conditions for the compressible homogeneous medium. Thus, the force action between the particles of the highly dispersed filler and polyaluminosilicate binder in their relative motion mainly occurs in the form of surface resistance forces and to some extent in the form of the Magnus forces during particle rotation. The decrease in the particle size of the highly dispersed filler corresponds to the increase in its resistance coefficient. At the same time, the particle surface area increases per the particle mass unit that leads to the increase in the surface forces of interaction with the carrier medium, i.e. with polyaluminosilicate. Simultaneously, higher movement uniformity of the composite material in the form of aerosol is achieved. The increase in the particle size leads to relative weakening of the surface forces that involve particles in pulsating motion. At the same time, the inertial resistance to this motion increases due to the mass increase. The feedback effect of impurities on the large-scale turbulence intensity that appears while crushing by a rotating disk reduces the turbulence intensity. It is due to the fact that the energy balance of the pulsating motion and required efficiency of turbulent stresses are determined according to an increase in the average mass density of the medium involved in the pulsating motion. The mass increases when the impurity concentration of the solid highly dispersed filler particles rises. During the research this method has shown that the interdomain space between polyaluminosilicate macromolecules changes. The entire internal structure of the polyaluminosilicate filled with the highly dispersed filler also changes when being applied (“printed”) with an aerosol. This fact is due to a mechanical influence that negatively affects the properties of the finished layer or topology.

The pneumatic method fragments liquid and droplets by the air flow using the droplet instability in motion. The criterion used to estimate the droplet instability determined by the ratio of the inertial liquid forces to the surface tension is called the Weber number.

If the inertial forces exceed the surface tension forces by six times, the droplets fragment into smaller ones.
The representations about the two-phase medium motion can be obtained in some limiting cases. A coarse material in limited concentrations less likely demonstrates the collisions of particles in the pneumatic method. The influence of turbulent pulsations on their motion is excluded due to the large mass of particles. As a result, it is possible to study in detail the motion of separate particles in the carrier stream by the action of forces from the stream with the simultaneous action of gravitational forces and the shock interaction of the filler particles with the container walls that occurs during motion. In this case, it is possible to obtain the data on the translational and angular velocity of the filler particles and conditions for their collision with the container wall. Moreover, it is also possible to estimate the energy costs taking place due to the loss by the wall collision or equivalent energy costs at the steady stream to restore the velocity of the filler particles after the shock that ultimately determines the additional hydraulic resistance by generating aerosol.

The distribution of particles in the container will be uniform for the highly dispersed filler particles at relatively high concentrations. In this case, the assumptions about the ideal properties of the carrier medium, i.e. polyaluminosilicate, devoid of viscosity are used to study the features of the dynamic stream modes of the compressible two-phase medium. The interaction of the carrier medium with impurity solid particles is supposed to be due to their resistance during their relative motion in the stream according to the experimentally obtained data. The additional friction resistance due to the interaction of impurities with the container wall is taken into account on the basis of the experimental data. Besides, the integral conditions for the continuity preservation, momentum, and energy in a closed form with respect to the unknown stream parameters can be determined for a compressible heterogeneous stream on this basis.

The ultrasound crushing of liquid occurs due to the energy of mechanical vibrations of the ultrasonic frequency of high intensity. R. L. Peskin determined a relationship between the film thickness $\delta$, the amplitude $\alpha$, and the frequency $\omega$ of the exciting force. The formed drop radius for large $\delta$ is defined as follows:

$$2a = \left(\frac{4\pi^3 \cdot \sigma}{\rho_1 \cdot \omega^3}\right)^{1/3}.$$

The electrostatic spraying of particles is possible when a charged liquid particle moves along the force lines of the electrostatic field under the impact of the Coulomb forces. The entire charge is distributed over the surface in a single drop of liquid. The interaction forces between the charged particle and field by the particle motion may lead to the drop crushing into smaller parts if the electrostatic field has the sufficiently high strength.

All these methods have a number of significant disadvantages. The pneumatic method is characterized by the low coefficient of transfer material being sprayed onto a product. The mechanical and hydraulic methods are characterized by high heterogeneity of the obtained aerosol. The electrostatic spraying of highly viscous liquids requires the use of an additional spraying agent. These disadvantages result in a decrease in the efficiency of technological processes, in which these spraying methods are used.

According to the research results, the most preferable method for us is the pneumatic method that allows working with highly viscous materials without destroying the supramolecular structure of a polymer binder.

We have used the synthesized polyaluminosilicate filled with a highly dispersed filler and the Aerosol Jet 15EX 3D printer of Neotech AMT company to obtain ceramic layers and topologies on aluminum bases by 3D aerosol printing with the help of the pneumatic method.

The technology to obtain and apply the aerosol is considered in the article. The applied material (polyaluminosilicate filled with a highly dispersed filler/ceramic ink) is injected into an aerosol generator. A pneumatic or ultrasonic generator can be used according to the ink type. A small amount of ink is enough to refill the ultrasonic generator, so it can be used to apply expensive materials.
Nevertheless, the range of ink viscosity and maximum diameter of solid particles are substantially limited. The pneumatic generator allows applying the materials with a wide range of viscosity and sequence larger diameter of solid particles, but a larger amount of ink is required to refill it. A working gas (nitrogen or air) is injected into the pneumatic generator through the narrow Venturi hole under pressure to produce the aerosol. The pressure increase causes the ink rise along the channel, and the aerosol is produced by the gas-ink contact. The exit pressure decreases, the gas velocity increases significantly. Consequently, fluid is sucked into the reduced pressure area through narrow channels from a chamber reservoir. When the liquid meets the air stream by the gas jet action, it is broken into small particles. These particles vary in size from 15 to 500 microns, it is the so-called "primary" aerosol. The particles then collide with a "flap" (plate, ball, etc.) that results in the "secondary" aerosol formation in the form of ultrafine particles ranging in size from 0.5 to 10 µm (about 0.5% of the initial aerosol). The secondary aerosol is then inhaled, and a large proportion of the primary aerosol particles (about 99%) is deposited on the inner walls of the chamber and is drawn back in the aerosol formation. The aerosol jet is focused at a distance of up to 5-15 mm from a nozzle that allows applying the ink on a three-dimensional base. It can be technically achieved by moving the printing head along three axes (x, y, z) and by inclining the base along two axes. The ultraviolet, infrared, or thermal drying is carried out after the ceramic ink is applied. The drying type depends on the number of layers and the base, which they are applied on.

The profilometric measurements of the topologies based on the polyaluminosilicate filled with a highly dispersed filler (ceramic ink) applied on a substrate have been carried out to estimate the uniformity of their application (Figure 2).

The profile measurements of the topologies printed on the substrate have been carried out with the Bruker DektakXT’s device. The device measures the roughness profile and parameters by a centre line system according to the range of values. The device feels the unevenness of the measured surface with a probe (a diamond needle) moving the inductive sensor along the measured surface. Then the mechanical oscillations of the probe convert into a digital signal.

![Figure 2. Profilogram photo of measured topologies of polyaluminosilicate filled with highly dispersed filler applied on substrate after thermal drying.](image)

Figure 2 shows that the wetting angle changes not more than 5% (taking into account the measuring device error) depending on the number of printed layers (topology thickness) that is permissible in microelectronics manufacturing.

One of the most important parameters of the applied layers and topologies is their adhesive strength to the substrate surface, which they are applied on. A research method to study their adhesive strength
has been chosen experimentally. The thin layers and small width of topologies printed with ceramic inks have been taken into account. The acoustic emission method has turned out to be the most suitable.

3. Conclusion
A new method of low-temperature ceramic material synthesis for 3D aerosol printing based on polyaluminosilicate has been developed. Some synthesis stages are controlled by the parameters set in 3D aerosol printing. The synthesized polyaluminosilicate matrix is able to locate up to 80% of highly dispersed filler in its inter-crown spaces and interdomain voids, thereby setting the necessary properties of the finished layers and topologies. The processes of 3D aerosol printing of polyaluminosilicates filled with highly dispersed filler have been studied. An optimal method of aerosol generation has been chosen that does not affect the supramolecular structure of the polyaluminosilicate binder. A study and comparative analysis of the 3D aerosol printing method and method of screw dosing have been carried out. The prospects of using the 3D aerosol printing method have been proved. The ceramic dielectric topologies with high thermal conductivity and thickness of layers in the nanometer range have been obtained by 3D aerosol printing of the synthesized material on the basis of the obtained results for the first time. Therefore, the use of the synthesized material based on polyaluminosilicate filled with a highly dispersed filler together with the 3D aerosol printing method allows obtaining the layers and topologies in the nano- and micrometer range that expands the nano- and microelectronics industry potential as a whole.

Acknowledgments
The reported study was funded by RFBR according to the research project № 18-29-11018.18.

References
[1] Ivanov A A, Tuev V I and Vilisov A A 2016 Key Engineering Materials 712 188–192
[2] Ivanov A A, Botvin V V and Filimoshkin A G 2014 Russian Journal of Applied Chemistry 87(2) 141–150
[3] Ivanov A A, Botvin V V and Filimoshkin A G 2014 Russian Journal of Applied Chemistry 87(2) 135–140
[4] Oth C and Kuhn T 2015 Kunststoffe International 76–80
[5] Khan S, Doh Y H, Khan A, Rahman A, Choi K H and Kim D S 2011 Current Applied Physics 11(1 SUPPL) 271–279
[6] Awais M N, Kim H C, Doh Y H and Choi K H 2013 Thin Solid Films 536 308–312
[7] Duraisamy N, Muhammad N M, Kim H and Choi K 2012 Thin Solid Films 520(15) 5070-5074