Physicochemical regularities in highly filled polyaluminosilicate applied on aluminum base by 3D aerosol printing

A A Ivanov¹ and A S Chermoshentseva²

¹ Tomsk State University of Control Systems and Radioelectronics, Tomsk, 634050, Russia
² Bauman Moscow State Technical University, Moscow, 105005, Russia.

E-mail: alexchemtsu@rambler.ru

Abstract. A modified technique has been used to synthesize a highly filled polyaluminosilicate with a controlled supramolecular structure during its applying on an aluminium base by 3D aerosol printing. It has been found how the pH medium affects the polyaluminosilicate ability to form fractal supramolecular formations. Methods to control the highly filled polyaluminosilicate structure directly along the aluminium base surface have been found.

1. Introduction
In developed countries much attention is currently paid to the electronic industry development that leads to the need to create new materials and technologies to apply them on surfaces of different chemical nature. The materials should have not only the improved performance characteristics but also the controlled physicochemical properties during their application on various surfaces.

The current trend in technologies to apply the materials for microelectronic products and devices is reduced to the increasing use of 3D additive methods. 3D aerosol printing using a pneumatic aerosol generation principle is the most promising and developing method to apply materials on microelectronic products and devices. The pneumatic 3D aerosol printing method allows applying the materials with an accuracy of 50 nanometers that expands the scope of its application.

Therefore, the development of new approaches and scientific principles in the synthesis of new materials is basic to create fundamentally new microelectronic products. This is primarily due to the fact that when developing new materials one takes into account the technological features of their further use in production processes.

A sol-gel method is one of the methods to develop materials with specified properties that allows controlling their properties during their application by means of 3D aerosol printing. In our case, the aluminosilicates that form by hydrolytic polycondensation can produce macromolecules of different length, branching, and supramolecular formation. The gels with different supramolecular structures can form when the medium pH and number of unbound –OH groups in the aluminosilicates vary. By pH less than 3 the complete aluminosilicate hydrolysis leads to the formation of fractal supramolecular formations, the interdomain spaces of which are then closely packed with the particles of a dispersed filler. Consequently, a nonporous monolithic structure with new properties forms. At the system pH
more than 7 the structure becomes more porous. The gel formation does not occur due to the incomplete precipitation of silicon ions and aluminum hydroxide dissolution [1].

The study aim is to research the structure formation effect of a sol-gel system dendrimer morphology polyaluminosilicate - highly dispersed filler on the properties of the dielectric layers on an aluminum base applied by 3D aerosol printing.

The following basic objectives have been set to achieve this aim:

- to study the possibility to control the supramolecular structure during the highly filled polyaluminosilicate sol application for its close packing;
- to determine a kinetic parameter effect of the highly filled polyaluminosilicate on the surface properties of the dielectric layers on the aluminum base obtained by 3D aerosol printing.

2. Experiment
The modern methods to synthesize materials, first of all, should be considered as a key problem to create the materials with specified and controlled properties. Of many liquid-phase methods to create ceramic polymer nanomaterials, such as chemical precipitation, ion layering, and hydrothermal synthesis, the sol-gel method allows regular controlling the physicochemical processes at some stages, which in its turn allows using the sol-gel method to create defect-free ceramic nanostructures [2-5].

It is necessary to take into account the stages of sol destabilization and aggregation in case of the sol-gel method use to synthesize highly filled polyaluminosilicates with their subsequent use for 3D aerosol printing (figure 1). It is also necessary to take into account the oligoaluminosilicate solubility in water, because the pneumatic 3D aerosol printing method involves two stages of aerosol formation. The lack of –OH groups in the supramolecular oligoaluminosilicate structures promotes the macromolecule enlargement, thereby complicating further fractal structure formation.

![Figure 1. Pneumatic 3D aerosol printing unit in process of highly filled polyaluminosilicate topology applying on aluminum base.](image)

When the aluminosilicate monomer concentration in a solution exceeds the equilibrium solubility, the solid phase, on which the dissolved aluminosilicate is precipitated, is absent. It complicates the formation of a closely packed structure after its precipitation on the aluminum surface by 3D aerosol printing.

When the oligomer particle sizes approach the lower limit of colloidal dispersion (in our case, the process begins after the material hits the aluminum base surface), homogeneous nucleation occurs (figure 2) at the aluminosilicate polycondensation stage. The dispersed polyaluminosilicate phase particles begin to grow on the nuclei according to the condensation mechanism. As the particles grow on the aluminum base surface, the aggregation of individual particles begins that determines the final
polyaluminosilicate structure (figure 3). Larger particles grow by absorbing smaller particles, their solubility is increased. When the process proceeds above 63°C and at pH more than 6, anhydrous particles form inside the supramolecular aluminosilicate formations that is confirmed by the thermogravimetric studies (figure 4).

![Figure 2](image1.png)

**Figure 2.** Microphotograph (transmission electron microscopy) of nuclei formation of highly filled polyaluminosilicate of fractal morphology.

The particles with chemically bound –OH groups, which form at pH more than 6, are negatively charged and repel one another. Their growth occurs not due to their aggregation but by polycondensation with particles from a true solution. Particles with a close supramolecular structure packing form by the appropriate control of the medium pH, which does not exceed 8, and interaction with the highly dispersed filler particles after their joint mechanochemical activation.

Obtaining the highly filled polyaluminosilicates with close packing requires a special approach to their drying, namely the environment temperature and humidity control should be provided. The lack of such control inevitably leads to a change in the polyaluminosilicate structure.

![Figure 3](image2.png)

**Figure 3.** Microphotograph (transmission electron microscopy) of highly filled polyaluminosilicate of fractal morphology.
Figure 4. TG and DSC curves of dendrimer morphology polyaluminosilicate.

The thermogravimetric sample studies have been carried out by the NETZSCH STA 409 device and combined Q-600 TGA-DSC analyzer (TA Instruments, USA). The sample heating rate has been 10 gr./min in an argon atmosphere with a weighed analyzed sample from 8 to 10 mg. The gas medium composition has been controlled by mass spectrometry by means of the ProLab device (Thermo Scientific, USA).

The rate of chemically unbound water removal in interfactal and interdomain voids, which determines the final polyaluminosilicate macromolecular structure, is of great importance.

The first two peaks demonstrate water desorption in figure 4. The physically adsorbed water (moisture) desorption usually occurs at a temperature not lower than the adsorbate boiling point (in this case it is 100 °C). The fact that there is a desorption peak at 60 °C may indicate polycondensation processes occurring in the sample with water release. The chemically unbound water removal from the polyaluminosilicate matrix occurs due to capillary forces that transfer the liquid phase to the closely packed structure surface for evaporation. Therefore, it is important to select the optimal conditions to apply the highly filled polyaluminosilicate to the aluminum base surface by 3D aerosol printing.

The deep polycondensation of the highly filled polyaluminosilicate sol results in a target product formation with the closely packed supramolecular structure. It is carried out in an aluminosilicate sol phase directly on the aluminum base surface. Figures 4 and 5 illustrate the possibility to increase the polycondensation degree during heating. Water release occurs in two stages with maxima at 100 °C and 136 °C. At a temperature of 67-124 °C the sample loses six times more water than in the range of 129-147 °C, when all available OH-groups have already reacted (figure 4).
Figure 5. Distribution of highly filled polyaluminosilicate particle sizes (Mastersizer 2000 device).

3. Results and discussion

It is possible to control the supramolecular structure by the rate of its drying and polycondensation during the highly filled polyaluminosilicate sol applying. The chemically unbound water removal from the polyaluminosilicate matrix occurs due to capillary forces that transfer the liquid phase to the closely packed structure surface for evaporation.

The removal of chemically unbound –OH groups from the polymer polyaluminosilicate matrix occurs due to capillary forces that transfer the liquid phase to the supramolecular structure surface for evaporation.

Thus, one can control the failure stress, which directly affects the particle size and uniformity, by varying the drying temperature of the highly filled polyaluminosilicate. The high surface energy of the polyaluminosilicate is a driving force for this process.

The smaller is the size of the particles obtained by applying the highly filled polyaluminosilicate on the aluminum base by 3D aerosol printing, the larger is their specific surface area and the higher is their surface energy. Therefore, they should be dried at lower temperatures.

Thus, the study of a surface roughness degree of the highly filled polyaluminosilicate applied on the aluminum surface by 3D aerosol printing has shown that a sharp increase in temperature from room temperature to 70 °C at a heating rate of 5 degrees per second increases the surface roughness from 0.5 to 2.3 μm (Figure 6). This is primarily due to excessively rapid hydrolysis deepening and polycondensation that affects the entire material structuring.
Figure 6. Surface profilogram of highly filled polyaluminosilicate applied on aluminum base by 3D aerosol printing.

Since the film forming properties of polyaluminosilicate sols directly depend on their drying temperature and affect their self-organizing supramolecular structure, a necessary condition to obtain a defect-free closely packed structure is to select adequate conditions to apply it on the aluminum surface and to control gelation kinetics, which in its turn directly depends on the starting sol components.

4. Conclusion
As a result, the modified methods to obtain the highly filled polyaluminosilicate and control its physicochemical parameters have allowed studying the effect of polyaluminosilicate gel structure formation on the ability to form defect-free dielectric layers with a given degree of surface roughness. This, in turn, has made it possible to control the cohesive interaction between the applied layers and its adhesion behavior by the contact with the substrate when applying the highly filled polyaluminosilicate on the aluminum base by 3D aerosol printing.

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