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Nucleation of Silicon Dioxide Nanoparticles in the Film-Forming Tetraethoxysilane Solution

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Abstract: The nucleation process of silicon dioxide nanoparticles in tetraethoxysilane solutions is studied. For the investigation, infrared spectrometry, optical and transmission electron microscopy was used. Size distribution of nanoparticles was determined and corresponding histograms were plotted.

Keywords: Nucleation, silicon dioxide nanoparticles; Transmission electron microscopy, IR spectroscopy; tetraethoxysilane.

1 Introduction

Nucleation of nanoparticles in liquid media occurs in the metastable phase as a result of fluctuation formation of new phase nuclei. Modern theories of nucleation are based on Gibbs works developed further by Folmer, Frenkel, and others [1]. According to the Gibbs theory, nucleation takes place during the metastable- to-stable state transition. The examples of a metastable state are supercooled liquids and supersaturated solutions.

The supersaturated solution concentration is higher than that of the equilibrium one. The nucleation is associated with the free energy consumption to create a new interface. From this viewpoint, it is advantageous for the system to get rid of the excess component by “throwing it away” to form a separate phase. Initially, the new phase is formed as small nuclei. The nucleation process is a first-order phase transition.

The theoretical investigations have shown that during the phase transition two stages are observed: nucleation and nuclei growth [1]. According to the homogeneous nucleation theory, only the nuclei with sizes larger than some critical value can further grow in the supersaturated solution. Smaller nuclei either dissolve, or can form agglomerates of size larger than the critical one and grow further. Thus, the fluctuation formation of a new phase is a dynamic process that is rather sensitive and depends on many physicochemical factors. The process speed in both stages depends on the nature of the system reagents, its supersaturation degree, etc. The theoretical methods for the study of nucleation processes have a number of fundamental limitations. In this connection, experimental investigations become of great importance [2].

2 Materials and Methods

This work deals with the nucleation of silicon dioxide nanoparticles in tetraethoxysilane (TEOS) supersaturated solutions. For this purpose, two different TEOS solutions were prepared: one with ethanol, and the other with a mixture of butyl and isopropyl alcohols as a solvent. Hydrochloric acid was used as a catalyst. The obtained solutions were treated with a magnetic stirrer and filtered. The solution ripening time was 48 h. The pH value of the solutions was 6.2 and 6.3, respectively.
The silicon dioxide films were deposited onto hole-type polished silicon substrates of 60mm in diameter with crystallographic orientation <111>. The film deposition was performed by centrifuging. The centrifuge speed was determined experimentally and was 3000 – 3200rpm.
Before deposition, the silicon substrates were treated chemically in acetone and isopropyl alcohol for 20 min in each. The film annealing was performed stepwise in a thermostat at 130, 200 and 290°C, respectively. The final annealing was performed in the diffusion furnace KJ–

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1200–1001C in argon at 450 °C for an hour. The identification of the obtained films was performed by infrared spectrometry (spectrophotometer “Speccord”).

The relief of the deposited films was studied by using optical microscope LEITZ ERGOLUX with × 1250 magnification. The structure and size of the formed silicon dioxide nanoparticles were determined by transmission electron microscopy (JEM100–Sx).

To obtain micrographs, the solution was deposited onto a copper mesh and dried in the open air or was subject to thermal treatment in the thermostat up to 290 °C for 40 min.

3 Results

It was revealed that infrared transmission spectra of the deposited films had maximum absorption in the range of 1000 – 1150 cm^{-1} corresponding to Si–O oscillations (**Figure 1**). The experiments showed that when using the TEOS solution with ethanol, SiO_2 nanoparticles of essentially spheroid shape were formed (**Figure 2**). The size distribution of the nanoparticles is shown in the histogram (**Figure 3**).

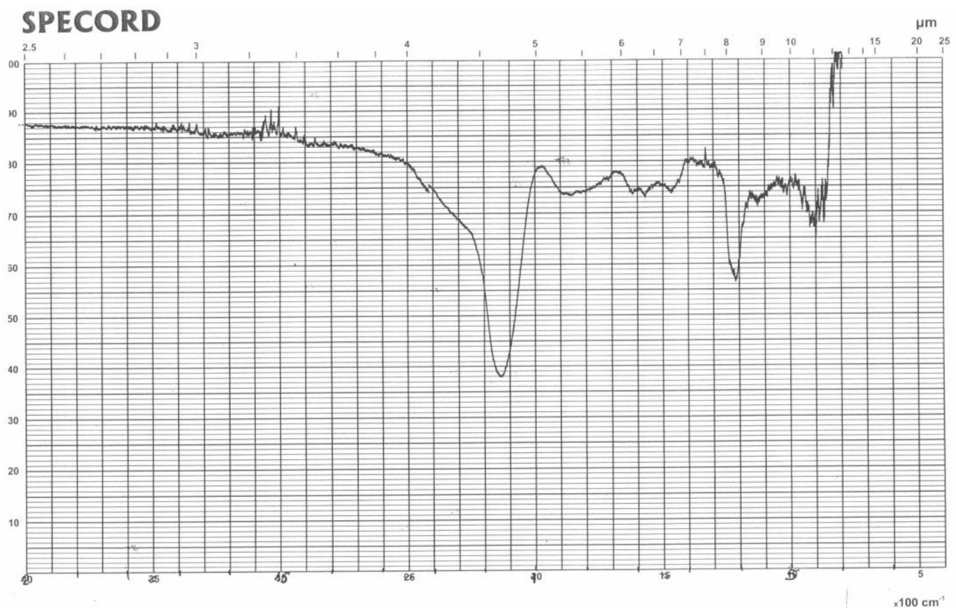

Figure 1. IR transmission spectra of SiO_2 films.

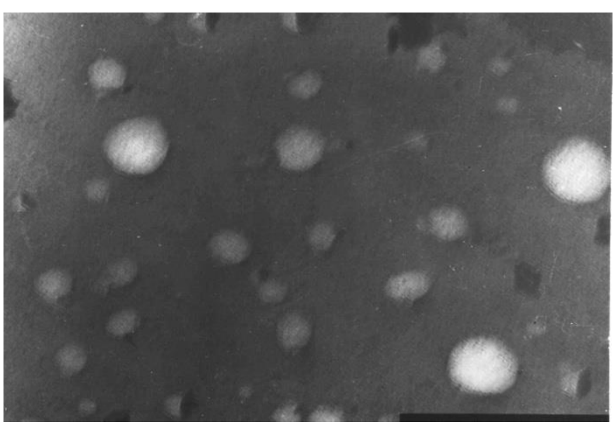

Figure 2. Micrograph of the synthesized nanoparticles of TEOS solutions with ethanol.

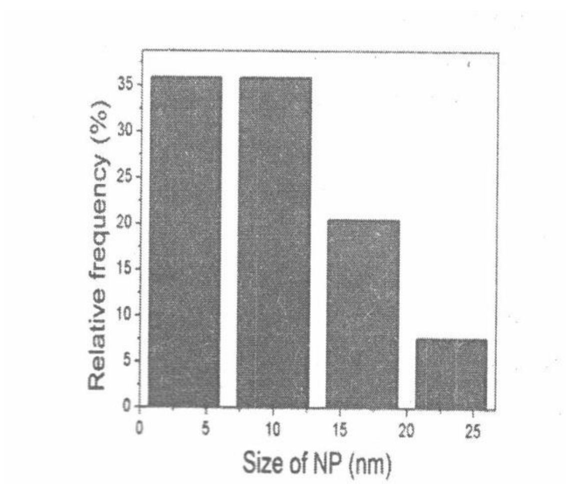

Figure 3. Size distribution of the nanoparticles of TEOS solutions with ethanol.

When using the TEOS solution with isopropyl and butyl alcohol, there appeared ellipsoidal, square and rhomboid nanoparticles (**Figure 4**). The size distribution of these nanoparticles is shown in the histogram (**Figure 5**).

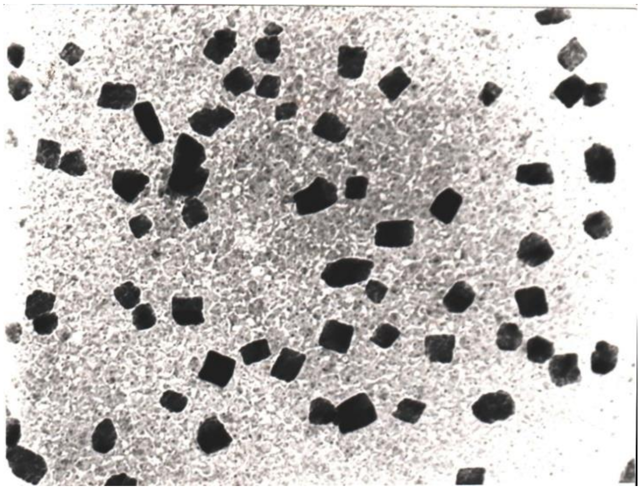

Figure 4. Micrograph of the synthesized nanoparticles of TEOS solutions with butyl and isopropyl alcohols (× 120000).

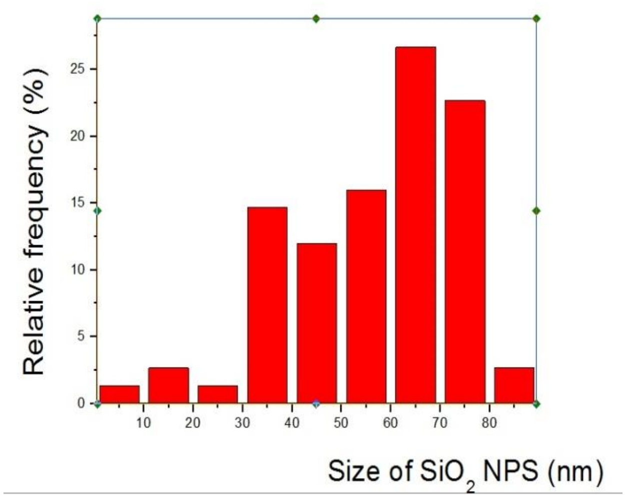

Figure 5. Size distribution of the nanoparticles of TEOS solutions with butyl and isopropyl alcohols.

It was established that the nucleation processes and the reproducible results depend substantially on factors such as the TEOS solution supersaturation degree, the pH value of the medium, the solution viscosity and the ambient temperature.

Identification of the nature of these parameters and their relation to the nucleation of nanoparticles requires additional studies.

4 Conclusion

The phenomenon of nucleation has already found practical application in many industrial processes, scientific research, medicine and biotechnology.

Mesoporous silicon dioxide nanoparticles have a high biocompatibility, high specific surface and are a promising material for containers for targeted drug delivery [3]. From this viewpoint, the obtained results are of interest to nanobiotechnology and medicine [4].

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References

[1] Yu.G.Frolov. The Course of Colloid Chemistry. Surface Phenomena and Disperse Systems. Moscow, Khimiya, 464 (1989).

[2] M.P.Anisimov. Nucleation: Theory and txperiment.Uspekhi-Chem.72(7), 699 (2009).

[3] V.Potapov, S.Muradov, V.Sivashenko, S.Rogatykh. Nanodisperse silicon dioxide: Application in medicine and veterinary science. *Nanoindustry***3**, 32-36 (2012),

[4] T.Pavliashvili, M.Janjalia, M.Gudavadze. Nucleation of silicon dioxide nanoparticles in the solution based on tetraethoxysilane. In: Abs. Int. Conf.“Innov. Technol. Metall.& Mater. Sci.” Tbilisi, GTU, 188-191 (2015).