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# *THE STUDY OF THE COMPOSITION OF SILICON-SUPERSATURATED LAYERS OF SILICON NITRIDE WITH THE HELP OF SECONDARY ION MASS SPECTROMETRY**

*ABSTRACT. The elemental composition of supersaturated solutions of silicon in silicon nitride has been investigated. The supersaturated solutions were obtained using two following methods: the method of magnetron sputtering of a silicon cathode in the presence of the reactive gas of nitrogen and the method of silicon ions implantation into the obtained 60 nm thick stoichiometric samples of SiN1.33 at irradiation doses of the order of (2–5) 1016 см-2. In the future, these technologies will provide a formation of 'Si nanocrystals in a dielectric' structures intended for creation of highly efficient electro-luminescent light source for optoelectronics by using the method of equilibrium and fast thermal treatments.*

*Preliminary research of the composition homogeneity of the produced silicon nitride films have been carried out by means of the layer-by-layer sputtering of these films with a beam of gallium ions. The distribution of elements through the thickness of the silicon-supersaturated layer of silicon nitride and the distribution of implanted silicon ions through the thickness of silicon nitride layer of stoichiometric composition have been obtained with the help of secondary ion mass spectrometry. Measurement accuracy is higher than the accuracy of the method of Rutherford backscattering. The investigations of the composition of the obtained nanomaterials allow an optimization of modes of mature plasma beam technologies for creation of silicon-based light-emitting materials with the required parameters.*

*KEY WORDS. An efficient source of light, the layer of silicon nitride, ion implantation, secondary-ion mass-spectrometry.*

The development of methods for obtaining supersaturated solutions of silicon in silicon nitride and the formation of the 'nanocrystals in a dielectric' systems by the method of heat treatment of supersaturated solutions of impurities in silicon-based dielectrics are essential for silicon optoelectronics. Such an approach to the modification of optoelectronic properties of silicon is novel and has a great practical potential to create efficient silicon-based light sources.

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Previously the authors have developed the modes of magnetron deposition of 30–100 nm thick layers of *SiNx* on silicon substrates when silicon cathode sputtering and supplying an inert gas of argon and a reactive gas of nitrogen in the working volume. The stoichiometric samples of nitride films of $SiN_{1.33}$; the samples of *SiN* with silicon supersaturation of about 7–10%, and the samples of $SiN_{1.2}$ with silicon supersaturation of 2–3% have been obtained. To create silicon nitride layers with a controlled composition and low electrical resistance for efficient electroluminescence the method of reactive magnetron sputter deposition proposed in [1–5] has been used. When magnetron sputtering silicon nitride is deposited with a more uniform distribution of elements through the thickness of the layer in comparison with the alternative chemical vapor deposition method.

Further the silicon ions implantation in the obtained stoichiometric 60 nm thick samples of $SiN_{1.33}$ at irradiation doses of the order of (2–5) $10^{16}$ $cm^{-2}$ has been carried out. The implantation module of nanotechnological complex *NanoFab-100* has been used to introduce silicon in silicon nitride layers of stoichiometric composition.

The implantation module of focused ion beams is used to modify the surface of substrates, combining the quality of FIB technology with an ion doping method. It allows creating nanostructures with specified properties of order of tens of nanometers in size.

For a preliminary assessment of the degree of silicon supersaturation of silicon nitride layers one can apply an express nondestructive optical method—the method of ellipsometry used in microelectronics to control dielectric layers. By the refractive index, determined by this method, it is possible to judge about the degree of silicon supersaturation of non-stoichiometric nitride silicon layers [6]. However, this method turns out ineffective as the optical properties of $SiN_x$ films depend not only on the total amount of excess silicon, but also on the form of the excess silicon in the film—in clusters or randomly distributed in the atomic grid [7].

The distribution of the elemental composition through the thickness of the layer can be investigated by the method of Rutherford backscattering (RBS). The sources of errors when using this method are: the energy scatter of the incident ion beam, the detector resolution, the sub-optimal geometric conditions of the experiment, the use of software products for the energy spectrum treatment, and instrumental errors. The measurement error of the film thickness and the profile of depth distribution of elements by RBS do not exceed 7.2% [8].

An alternative method to RBS is the method of secondary ion mass spectrometry, the error of which does not exceed 3%. Higher accuracy of this method is stipulated by the presence of only instrumental errors in the calibration of the mass analyzer.

The analysis of the quantitative composition of the 60 nm thick layer of silicon nitride supersaturated with silicon and silicon ions-implanted layer of stoichiometric silicon nitride has been carried out in the module of focused ion beams (FIB) with the help of layer-by-layer sputtering of gallium and the system of secondary ion mass spectrometry.

The module of focused ion beam with a scanning electron microscope and with the system of secondary ion mass spectroscopy is used to modify the surface by cutting and ion beam etching, and to investigate the structure and the composition of nanomaterials.

First, under the conditions of layer-by-layer sputtering of silicon nitride film by ion beam with the 1 nm step the composition of the silicon nitride layer of $SiN_{1.33}$ and the layers supersaturated with silicon with the help of the system of secondary ion mass spectrometry have been investigated. As it can be seen from Fig. 1, the ratio of the number of silicon atoms to the number of nitrogen atoms through the thickness of $SiN_{1.33}$ layer is practically unchanged. The same uniformity of the distribution of elements through the thickness of the layer is observed in silicon-supersaturated samples.

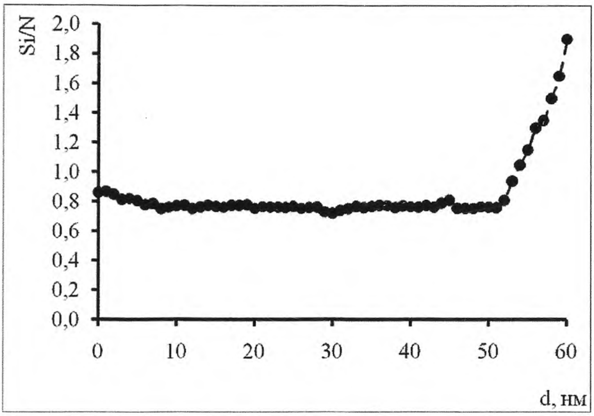

*Fig. 1.* Change of the ratio of the number of silicon atoms to the number of nitrogen atoms through the thickness of the layer.

Then, using the same system the distribution of implanted ions of silicon through the thickness of the composite material of $SiN_{1.33}/Si$ has been investigated. In Fig. 2 the points reflect the experimental distribution of implanted silicon ions and the solid curve is the distribution obtained from the calculation by the Monte Carlo method with the help of a software product [9, 10].

We have obtained 2 nm resolution of the discrete method of layer-by-layer sputtering and 3% measurement accuracy of quantitative composition of the 30–100 nm thick material with the help of the system of secondary ion mass spectrometry, which exceeds the accuracy of the method of Rutherford backscattering.

Thus, the method of creating silicon solutions with a required supersaturation in silicon nitride layers has been developed. Preliminary studies of the composition of the obtained nanomaterials have been carried out to optimize the modes of mature technologies for creation of silicon-based light-emitting materials with the required parameters (of multilayer structures comprising the layers supersaturated with silicon and thin barrier layers for the localization of recombination processes of charge carriers in quantum wells).

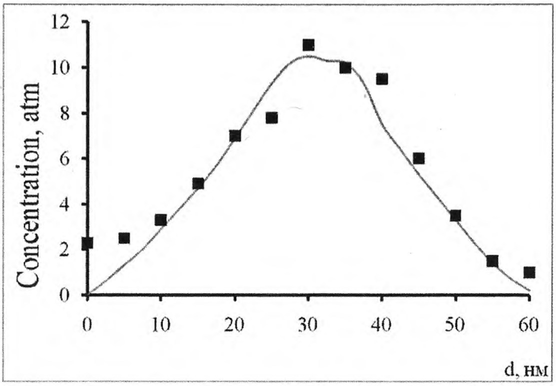

*Fig. 2.* Distribution of implanted silicon ions through the thickness of stoichiometric silicon nitride layer: the curve in the form of points is the experimental distribution, the solid line is the calculated distribution

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