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UDC 621.793; 621.382

*PRODUCTION OF SILICON NITRIDE LAYERS WITH STOICHIOMETRIC COMPOSITION AND SUPERSATURATION ON SILICON WITH THE HELP OF THE CHARACTERISTICS OF MAGNETRON DISCHARGE**

ABSTRACT. To develop an effective silicon-based light source, 30–100 nm thick layers of silicon nitride with a controlled composition and a low electrical resistivity have been obtained by the method of magnetron deposition. It has been found the conditions of magnetron discharge burning under which the samples of nitride films of SiN1.33 with stoichiometric composition, SiN samples with 7–10% silicon supersaturation and SiN1.2 samples with 2–3% silicon supersaturation have been produced.

The method of magnetron deposition of silicon nitride layers was chosen as it provides a more homogeneous distribution of elements over a layer thickness in comparison with the alternative method of chemical precipitation from the gas phase.

The control over the composition of the silicon nitride layers was carried out by measuring the characteristics of magnetron discharge. It is shown that the required degree of silicon supersaturation in a layer can be controlled by the discharge voltage value at a constant nitrogen pressure. The employed method of control is more accurate than the method of spectral analysis of optical radiation of magnetron discharge plasma. The second control method provides insufficient measuring accuracy due to the low intensity of nitrogen and silicon lines in the operating range of nitrogen pressure.

KEY WORDS. Magnetron spraying, a layer of silicon nitride, an efficient source of light.

The invention of an efficient silicon-based light source is of paramount importance for silicon optoelectronics. The development of high-performance silicon-based radiation structures will allow to combine electronic and optical equipment in one integrated circuit.

Inexpensive and powerful optoelectronic integrated circuits will be based on silicon devices with high-efficiency electroluminescence. In addition, microelectronic technologies make it possible to produce a new generation of flat-panel displays with silicon LEDs.

* The study was supported by the international grant of The Russian Foundation for Basic Research (Russia–Belarus), research project No. 12-08-90013-Bel_a

The relevance of the researches in this field is determined by the following factor. To get the system of *Si nanocrystals in a dielectric medium*, it is suggested to use a "weak" dielectric Si_3N_4 with a high dielectric constant ($\varepsilon = 6$) and a smaller band gap ($\approx$ 4–5 eV) instead of using SiO_2.

Nowadays the studies in this research area are in their initial stage. The number of articles devoted to this subject (*Si nanocrystals in a dielectric medium*) is limited. It has been demonstrated recently that structures with silicon nanocrystals (SN) embedded in a silicon oxide matrix (SiO_x) are characterized by intensive photoluminescence in the visible range [1, 2]. The disadvantages of the oxide version of the system of *Si nanocrystals in a dielectric medium* as an electroluminescence source are high ohmic resistance and low permittivity of SiO_2. Due to the difficulties of electron and hole tunnelling through wide-band-gap oxide and their radiative recombination in *Si* nanocrystals, there are few studies of the $Si/SN/SiO_2$ system electroluminescence [3, 4].

The ways of creating supersaturated silicon solutions in silicon nitride are developed in the research. This will allow to form structures of *Si nanocrystals in a dielectric medium* by means of equilibrium and quick heat treatment of supersaturated solutions of impurities in silicon-based dielectrics. The use of a 'weak' dielectric Si_3N_4 with low electrical resistance instead of SiO_2 will help to get the system of *Si nanocrystals in a dielectric medium* with enhanced electroluminescence efficiency.

The method of magnetron reactive deposition proposed in [5–7] was applied to obtain 30–100 nm thick layers of silicon nitride with a controlled composition. SiN_x layers are deposited on silicon substrates by means of sputtering of silicon cathode and supply of argon (a noble gas) and nitrogen (a reactive gas) into the active volume. The method of magnetron deposition of silicon nitride layers was chosen as it provides a homogeneous distribution of elements over a layer thickness in comparison with the alternative method of chemical precipitation from the gas phase. The changes in atomic concentration of the components in the second case are determined by the discontinuous feeding of reagents in the active volume.

Magnetron deposition modes of silicon nitride layers with stoichiometric composition and silicon supersaturation were performed on the magnetron module of the nanotechnology complex NanoFab-100.

The magnetron spraying module combines a number of technological processes in one vacuum cycle, including ion-beam cleaning and activation of a substrate surface and nanostructured monolayer and multilayer high-density coating with a predetermined composition.

Production of silicon nitride films by reactive magnetron sputtering was first suggested to be controlled by current-voltage characteristic (CVC) in [8, 9]. CVC also allows to control the composition of gas medium and regulate the argon and nitrogen flows in the process chamber. Si_3N_4 films with stoichiometric composition were produced at the voltage of 500–520 V and had a refractive index of 2.0–2.1 [9].

As the voltage was increased to 600 V, the films had excess *Si* and a refractive index of 2.6–2.8.

We have analysed a possibility of control over the production conditions of stoichiometric silicon nitride layers according to the voltage variation in pulsed magnetron discharge as the reactive gas partial pressure increases.

It has been demonstrated that as nitrogen partial pressure increases, the discharge voltage increases monotonically reaching its maximum $U = 455$ V at nitrogen pressure $P_{N2} = 0.1$ Pa and then decreases monotonically (see Fig. 1).

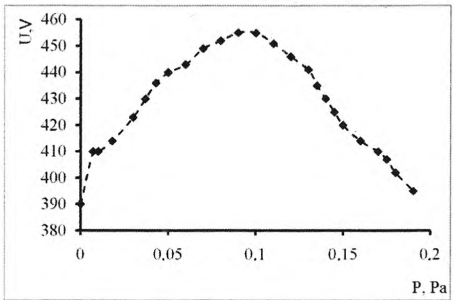

Fig. 1. Discharge voltage dependence on nitrogen partial pressure value

In the conditions of maximum discharge voltage when the cathode is partially covered with nitride, a silicon nitride layer with stoichiometric composition is sprayed on a substrate at a relatively high speed.

With an increase in power and discharge voltage ($U > 455$ V) at a constant reactive gas pressure ($P_{N2} = 0.1$ Pa), the silicon-to-nitrogen ratio increases in the film.

Therefore, the required degree of silicon supersaturation in a layer can be controlled by the discharge voltage value at a constant nitrogen pressure. Figure 2 shows the dependence of silicon-to-nitrogen ratio in a layer on the discharge voltage which allows to get the required silicon supersaturation.

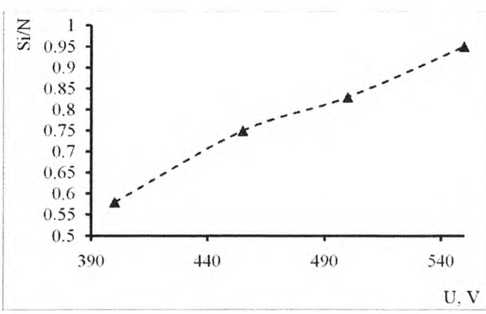

Fig. 2. The dependence of silicon-to-nitrogen ratio in a layer on the discharge voltage at a constant nitrogen pressure $P_{N2} = 0.1$ Pa

We have found the conditions of magnetron discharge burning under which the samples of silicon nitride films of $SiN_{1.33}$ with stoichiometric composition, *SiN* samples with 7–10% silicon supersaturation (U = 550 V) and $SiN_{1.2}$ samples with 2–3% silicon supersaturation (U = 480 V) have been produced.

A magnetron module with direct and pulsed current helps to maintain constant total gas pressure in the process chamber automatically and to change nitrogen and argon partial pressure controlling it by the leak rate. In these conditions the layer composition control according to the voltage and reactive gas pressure is more accurate than the method of spectral analysis of optical radiation of magnetron discharge plasma. The second control method [10] provides insufficient measuring accuracy due to the low intensity of nitrogen and silicon lines in the operating range of nitrogen pressure.

The qualitative composition analysis of the silicon nitride 60 nm thick layer was carried out in the focused ion beam (FIB) module by means of layer-by-layer gallium ion beam sputtering and the system of secondary ion mass spectrometry.

Thus, the modes of magnetron deposition of SiN_x layers with stoichiometric composition and a required silicon supersaturation on silicon substrates have been found. Samples of nitride films of $SiN_{1.33}$ with stoichiometric composition, *SiN* samples with 7–10% silicon supersaturation, and $SiN_{1.2}$ samples with 2–3% silicon supersaturation have been produced. The achieved precision of composition control over the produced layers by means of changing magnetron discharge characteristics exceeded the accuracy of the alternative method of spectral analysis of optical radiation of magnetron discharge plasma [10].

The produced nanomaterials will allow to form *Si nanocrystals in a dielectric medium* structures for LEDs.

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