INTRODUCTION

Silicon carbonitride \( \text{SiC}_x\text{N}_y \) films offer a promising functional material for the preparation of dielectric layers in structures metal–dielectric–semiconductor. Their characteristic features are high resistance and thermal conductivity along with low thermal expansion, which provides rich opportunities for the creation of functional composites with high dielectric and thermo conductive properties. The variation of the main composition of films ensures adjustment of their physicochemical properties, such as specific conductance, dielectric strength, mechanical strength, and chemical resistance within wide ranges [1].

Silicon carbonitride films are usually analyzed by X-ray spectrometry techniques: X-ray fluorescence analysis and X-ray electron probe microanalysis as well as secondary ion mass spectrometry (SIMS) [2]. The data delivered by these methods are normally just qualitative or in the best semiquantitative, which is because of the lack of reference samples of appropriate composition. Note that generally X-ray fluorescence and SIMS may not register light elements and hydrogen in the film composition. The authors of [3–5] have proposed a method for determining traces of gas-forming elements, including hydrogen in high-purity materials on a tandem mass reflectron with a double-pulse laser emitter. The method implemented a special procedure of clearing sample surface by a double laser impulse. The method implements a special procedure of clearing sample surface by a double laser impulse. The method is designated for the determination of low, i.e., trace, concentrations of gas-forming impurities in the range \( 10^{-6} \)–\( 10^{-2} \) wt %. In this work we describe a method of laser mass-spectrometry analysis (LMS) for the quantitative determination of the major composition of \( \text{SiC}_x\text{N}_y \) films with instrument calibration by of neat stoichiometric compounds of silicon, i.e., silicon carbide, silicon nitride, and silicon oxide. To reduce the error of quantitative analysis, we revealed and eliminated instrumental discriminations of ions by mass, adjusted an EMAL-2 mass spectrometer, chose the conditions of laser sampling, and found the coefficients of relative sensitivity.

EXPERIMENTAL

The work was carried out on an EMAL-2 laser mass spectrometer with double focusing (Elektron, Russia) arranged in the Mattauch–Herzog geometry. Laser irradiation from a \( \text{Nd} : \text{YAG} \) laser in the giant pulse mode was used. The mass spectra were recorded on Ilford Q2 photoplates and RENEX photofilms.

Silicon carbonitride films. The objects of investigation were silicon carbonitride films prepared by the method of plasma-enhanced chemical vapor deposition of organosilicon species, such as hexamethyldisilazane, methyl tris(diethylamino)silane, etc. and the introduction of activator gases, helium, nitrogen, oxygen, etc. into the reactive medium [1]. Samples of films were prepared in the Laboratory of Epitaxial Layers of the Nikolaev Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences.

Parameters of laser sampling. The conditions for laser sampling should provide an effective and non-selective sputtering of a \( \text{SiC}_x\text{N}_y \) film with the minimum contribution of the support material to the analytical signal. To achieve this aim we examined the relation between the diameters of craters forming on the sample surface and the specific power of laser irradiation and pulse frequency. A \( \text{Nd} : \text{YAG} \) laser with the
wavelength 1.064 μm and pulse duration 15 ns was used. The energy of the laser pulse was varied by changing voltage on the main block of the laser. The data on size and relief of craters were obtained using a Hitachi-3400 scanning electron microscope and a Solver Pro (NT-MDT) atomic force microscope. At the minimal energy of the pulse 50 mJ, the depth of the crater was ~0.2–0.4 μm and its diameter, ~30–40 μm. If the energy of the pulse was increased to 1000 mJ, the crater depth increased to ~0.8–1.0 μm and the diameter of the destruction zone, to ~90–100 μm. The microphotographs of the craters (Figs. 1, 2) show that the walls of the craters are fire-finished and fragments of solidified liquid phase are observed around the craters.

To prevent the overlapping of craters, we screened the frequency of laser pulses and the rate of sample scan. As was found, at sample scanning at the rate of 50 mm/min and pulse frequency of 25 Hz, the craters on surface do not overlap (Fig. 2), which helps stabilizing ablation by film materials and reducing the contribution from the support material. Based on the study performed, we decided on the following optimal conditions of sampling for the LMS analysis of thin films: pulse frequency 25 Hz, scanning rate 50 mm/min, and specific power of laser radiation \( (1–2) \times 10^9 \text{ W/cm}^2 \). Under the selected conditions, the craters formed have the width ~0.4–0.5 μm and did not overlap; meanwhile the input of the support material did not exceed 5–10%.

### Determination of relative sensitivity coefficients (RSC)

To determine RSC for light elements, i.e., C, N, O, we analyzed reference samples, namely, compounds of the known stoichiometric composition: single crystal forms of silicon carbide (SiC) and nitride (Si₃N₄), and quartz (SiO₂). As the determination of RSC for nitrogen may be affected by the overlapping of the lines of nitrogen ions \(^{14}\text{N}^+\) and \(^{15}\text{N}^+\) with doubly charged silicon ions \(^{28}\text{Si}^{2+}\) and \(^{30}\text{Si}^{2+}\), the intensity of the doubly charged silicon ions was measured before. As was found, at the chosen power of laser radiation \((1–2) \times 10^9 \text{ W/cm}^2\), the contribution of the doubly charged silicon ions is no higher than 1%; therefore, in the evaluation of RSC for nitrogen against silicon using a Si₃N₄ sample it is quite negligible.

The value RSC for element X against silicon was calculated in accordance to [6, 7] using Eq. (1):

\[
\text{RSC}_X = \frac{c_X I_X A_X}{c_S i_S i_A_S},
\]

where \(I_X\) is the intensity of isotope atoms of an element in question, \(c_X\) is element concentration in the reference sample, and \(A_X\) is the abundance of the isotope.

To determine concentrations we used Eq. (2):

\[
c_X = \frac{I_X M_X}{A_X \text{RSC}_X} \left( \sum_{\gamma=1}^{4} \frac{I_i M_i}{A_i \text{RSC}_i} \right)^{-1} \times 100\%.
\]

where \(I_X, I_i\) are the intensities of the analytical line; \(I_X, I_i\) are the abundance of the element; \(M_X, M_i\) are the average atomic weights of the element; the sum was calculated for the main component C, N, O, and Si.

Using samples of stoichiometric composition we found the average RSC values for carbon, nitrogen,

<table>
<thead>
<tr>
<th>Reference sample</th>
<th>Element</th>
<th>RSC (average value)</th>
<th>RSD ((P = 95, \ n = 4)), %</th>
<th>(U_{\text{ion}})</th>
<th>Bond energy Si–X, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon carbide</td>
<td>C</td>
<td>0.22</td>
<td>24</td>
<td>11.26</td>
<td>194</td>
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<tr>
<td>Silicon nitride</td>
<td>N</td>
<td>0.064</td>
<td>19</td>
<td>14.53</td>
<td>187</td>
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<tr>
<td>Silicon oxide</td>
<td>O</td>
<td>0.63</td>
<td>9</td>
<td>13.62</td>
<td>183</td>
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<tr>
<td>Silicon single crystal</td>
<td>Si</td>
<td>1.0</td>
<td>–</td>
<td>8.15</td>
<td>234</td>
</tr>
</tbody>
</table>