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# The coating a liquid glass of the optical element substrates and its molecular composition

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The article presents the results obtained by coating a liquid glass solution to the substrates of optical elements, followed by their etching with an ion beam. Particular attention is turned on the surface roughness of the optical element both after the deposition of liquid glass and after etching. A film of the applied glass composition was studied using secondary ion mass spectrometry (SIMS).

**Keywords:** liquid glass, films, surface roughness, polishing, ion etching, secondary ion mass spectrometry.

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## Introduction

Currently, there is an urgent need for searching new materials that can act as substrates of optical elements, in particular, for space-based X-ray telescopes. A number of requirements are imposed on these materials, first of all — low mass, as well as strength and the possibility of precision surface treatment, since a small wavelength imposes strict requirements on the accuracy of the shape and surface roughness [1]. For vacuum (VUV) and extreme (EUV) ultraviolet ranges of electromagnetic radiation ($\lambda = 10 - 200\,\text{nm}$), the value of the effective surface roughness should be less than 1 nm, and the shape accuracy — is better than $\lambda/14$, where $\lambda$ — working wavelength. The most promising material for the substrates of mirrors of space telescopes of the visible and infrared (IR) ranges is beryllium, however, when switching to the short-wave range, it is impossible to achieve the required roughness values by either mechanical or ion polishing [2]. Acceptable roughness parameters at the level of 1.5 nm were obtained by coating beryllium with amorphous nickel with subsequent polishing. Thus, at the moment, a beryllium base coated with amorphous nickel [3] is considered for space telescopes.

In addition, the requirements for the quality of the surface shape, as a rule, imply carrying out a finishing correction of the shape and / or its aspherization. The main technique that ensures the achievement of the requirements of the VUV and EUV wavelength ranges is ion etching. However, the paper [3] shows that the ion treatment of nickel also does not provide the required roughness values.

This paper presents studies on applying a technological coating from the so-called „liquid glass“ to the substrate in order to correct the initial roughness of the substrate, followed by ion beam etching.

The complex of compounds encompassed by the concept of „liquid glass“ is quite extensive. In general, it is understood as solutions of silicates, most often alkali metals (potassium, sodium or lithium), but modified glasses are also found, which are silicates of strong organic bases, such as, for example, quaternary ammonium bases. As a material, liquid glasses are quite common in production. They are used in construction as an additive in concrete or in finishing coatings, in steelmaking, in the paper industry, as adhesives, as an additive in paint and varnish products for fire resistance, etc. [4]. Particularly interesting, in our opinion, is the use of liquid glasses as part of polishing coatings. Moreover, liquid glass is an affordable and low-toxic material.

In our in the previous paper [5], devoted to liquid glass, we studied the prospects for smoothing the surface of chrome films of three different compositions of liquid glass: 45% aqueous solution of sodium silicate ($Na_2SiO_3$), 45% aqueous solution of quaternary ammonium base silicate ($((N(CH_3)_4)_2O{\cdot}nSiO_2$) and a urea-modified aqueous solution of sodium metasilicate with a percentage of silicate and urea of 34.0 and 4.5%, respectively ($Na_2SiO_3{+}(NH_2)_2CO$). The solution containing urea turned out to be the most successful composition providing acceptable roughness values for the EUV wavelength range of electromagnetic radiation, even after ion etching, as it was revealed in experiments with chrome films. The possibility of smoothing the surface roughness of optical elements that are not amenable to finishing polishing was demonstrated in the spatial frequency range $0.049{-}63.5\,\mu\text{m}^{-1}$ by applying

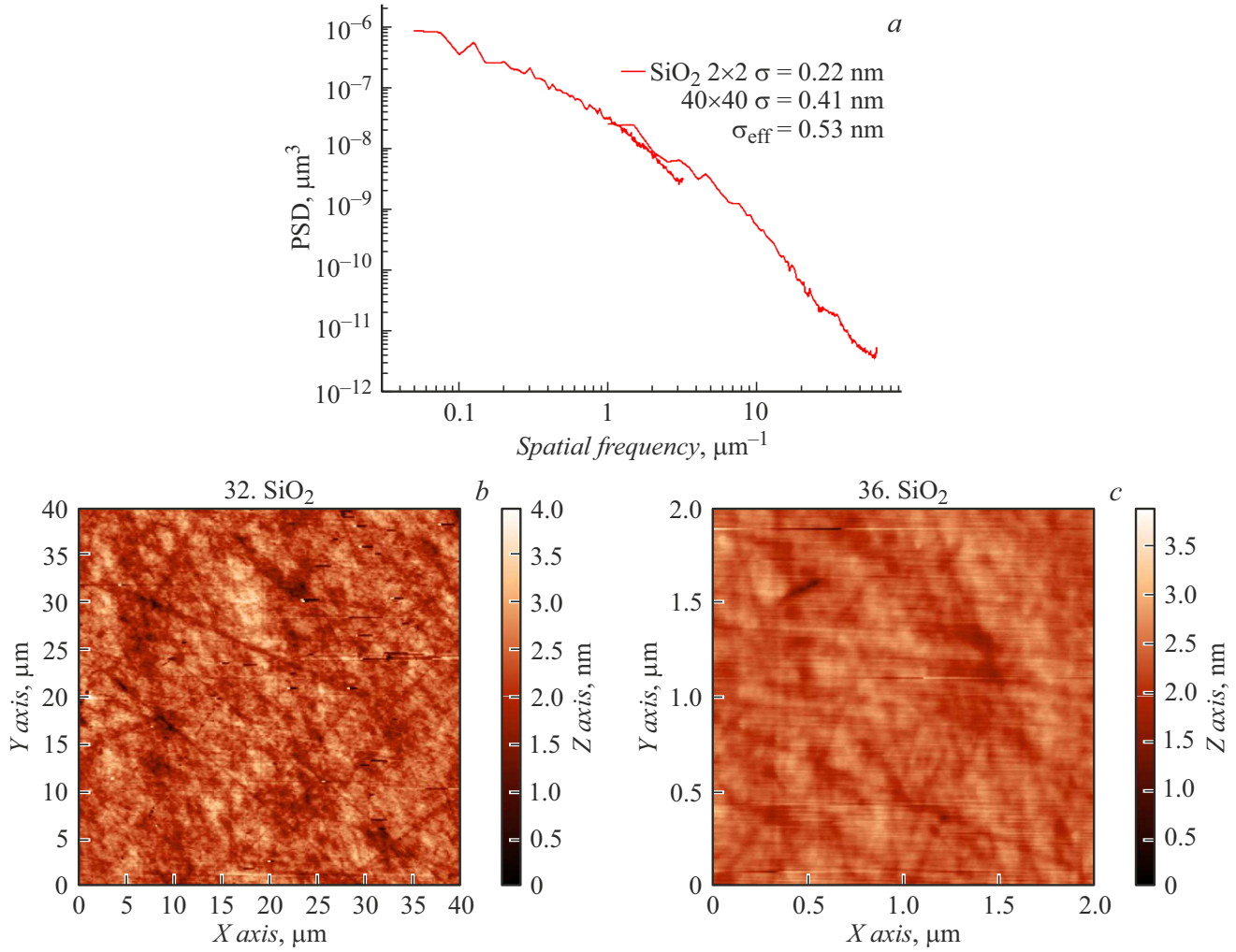



**Figure 1.** *a* — PSD is the surface function of the original quartz, *b, c* — AFM frames 40×40 and 2×2 $\mu$m respectively.

„liquid glass“ composition ($Na_2SiO_3+(NH_2)_2CO$), followed by polishing with accelerated argon ions with an energy of 800 eV and a current density of 0.7 mA/cm$^2$, directed normal to the surface. It was possible to obtain an effective roughness of 0.86 nm over the entire range of spatial frequencies on chromium films with a thickness of 500 nm with an initial roughness at the level of 3.9 nm, after applying a layer of „liquid glass“ and ion polishing [5].

Thus, after obtaining the composition of liquid glass that is optimal in its smoothing characteristics, it is necessary to investigate the possibility of its application to the surface of nickel, which is directly used for space tasks. In parallel, it was proposed to investigate the possibility of using liquid glass as a technological coating on quartz substrates. The presence of a technological coating allows for conducting the restoration procedure — in case of errors or failures of the technological process (ion polishing), it will be possible to remove it without any consequences for the original substrate.

## 1. Description of experiments

Ion etching was performed using an ion beam etching unit described in detail in [6]. The sample was placed on a slide table normal to the ion beam to conduct the experiment. A „witness“ was used to control the etching depth, part of the surface of which was covered with a mask. Next, an argon operating pressure of $1.3\cdot10^{-2}$ Pa, was created in the chamber, the ion current density ($j = 0.5$ mA/cm$^2$) and the accelerating voltage ($U_{acc} = 800$ V) was set, the value of which determines the ion energy. The sample was subjected to ion bombardment. After that, the etching depth and surface roughness were measured. The etching depth was measured using a Talysurf CCI 2000 white light interference microscope (the height of the step formed at the mask boundary was measured).

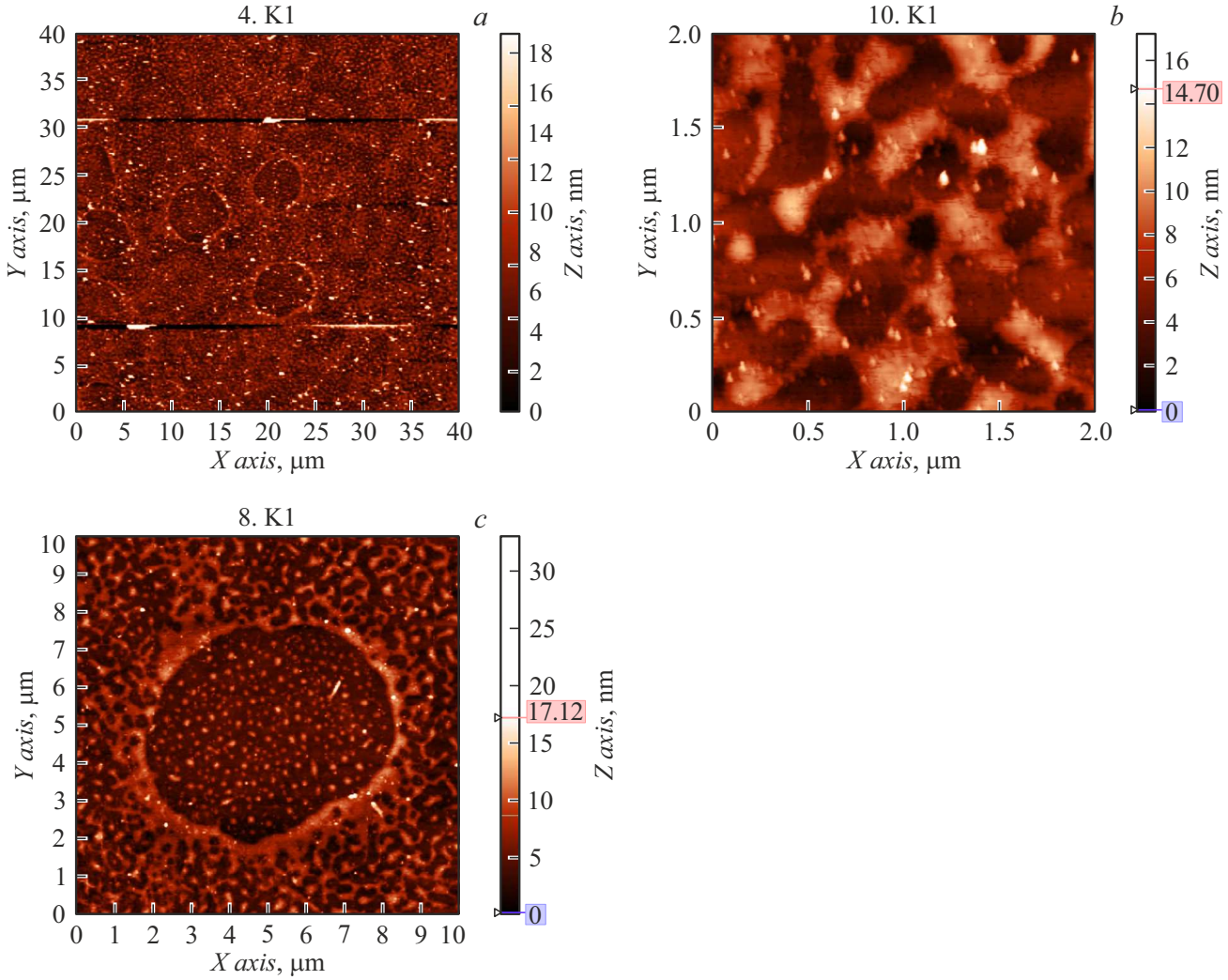



**Figure 2.** AFM frames of quartz surface after liquid glass application: *a* — 40×40, *b* — 2×2, *c* — 10×10 $\mu$m.

The roughness of all surfaces was measured using an atomic-force microscope (AFM) NTegra before and after applying the structures. The roughness was calculated using the power spectral density function (PSD function) [7] calculated from two frames 40×40 and 2×2 $\mu$m.

The thickness of the liquid glass films was measured gravimetrically [8,9], it ranged from 450 to 490 nm.

The study of films using secondary ion mass spectrometry (SIMS) was carried out using a secondary ion mass spectrometer TOF SIMS 5 for elemental analysis by depth and by sample area (manufacturer IONTOF, Germany, 2008). A low-energy atomizing ion gun with Cs ions with a beam energy from 250 eV to 2 keV was used as a sputtering beam. A liquid metal ion gun with Bi ions with a very low current value (1 pA, 25 keV) and short pulses (< 1 ns, up to 50 kHz) was used as the analyzing beam.

## 2. Results of liquid glass application followed by ion beam etching

The studied liquid glass solution was applied to quartz plates with an initial roughness of $\sigma_{eff} = 0.53$ nm (Fig. 1). During this experiment, for the first time, the roughness of the quartz surface changed significantly for the worse $\sigma_{eff} = 6.8$ nm, as shown in Fig. 2. Uneven drop-shaped structures were observed on quartz, which may be associated with the features of solidification of liquid glass, in particular, with the coagulation of silicon oxide and silicic acid particles during cooling and the formation of polysilicate structures. It is noteworthy that with further ion etching, all these structures were smoothed, and the final roughness of the quartz sample was $\sigma_{eff} = 1.2$ nm (Fig. 3). Better results were achieved with repeated independent experience of applying liquid glass to quartz: $\sigma_{eff} = 0.9$ nm (Fig. 4), in this case there were no teardrop-shaped defects on the surface, however, the application of liquid glass to

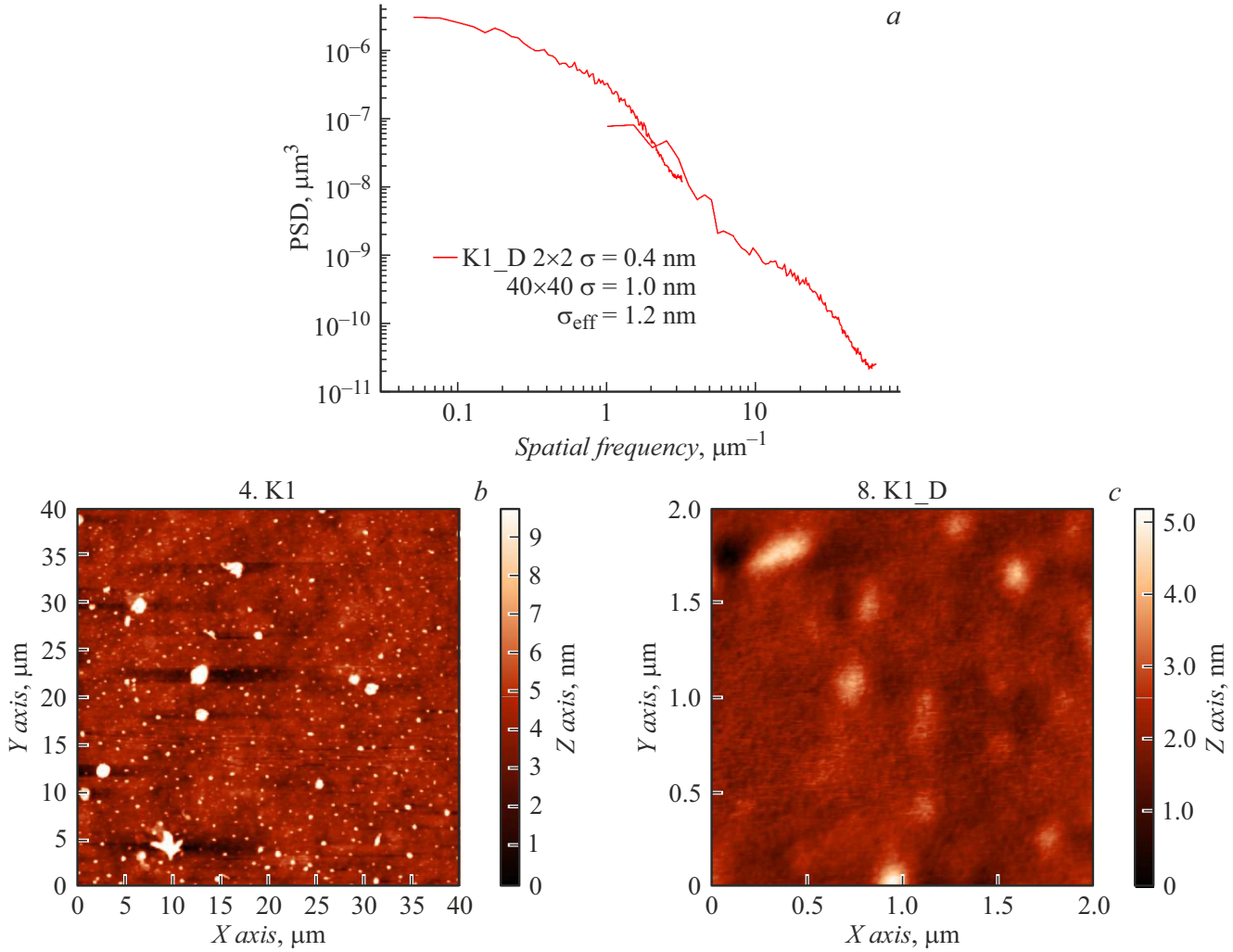



**Figure 3.** *a* — PSD function of the surface of liquid glass after etching. AFM surface frames: *b* — 40×40, *c* —2×2 $\mu$m.

quartz led to a deterioration in the roughness of the sample relative to the initial one in any case. Repeated experience of etching the surface of liquid glass with an ion beam also did not lead to results satisfactory for X-ray optical elements.

Thick (700nm) films with the roughness of $\sigma_{eff} = 2.8$ nm (Fig. 5) were made on silicon substrates by magnetron sputtering for experiments with nickel. Unfortunately, there was no improvement in roughness on nickel films, similar to what happened on chromium films. After applying the liquid glass, the roughness deteriorated to the value $\sigma_{eff} = 5$ nm (Fig. 6), and ion etching only slightly improved the situation: $\sigma_{eff} = 4.8$ nm (fig. 7). At the same time, as on chromium films, fine-grained structures are formed on nickel films when liquid glass is applied to them, as mentioned earlier [5], associated with the features of the surface effects of glass solidification. Unsuccessful attempts to repeat the success of smoothing the surface obtained on chromium films allows concluding that it is necessary to individually select the compositions of liquid glass for each type of substrate.

## 3. SIMS results

A thick layer of liquid glass deposited on a chrome film was studied using SIMS. Both negative and positive ions were registered.

First of all, we were interested in the composition of liquid glass during solidification, in addition, the question of whether the liquid glass interacts directly with the metal film itself remained open.

According to the patent [10], when urea 2 is introduced into a liquid glass solution, the pH of the entire mixture increases, which, in turn, leads to hydrolysis of soluble glass with the formation of free sodium hydroxide and silicic acid gel $H_2Si_2O_5$ 1. In turn, urea can bind both with alkali to the formation of neutral

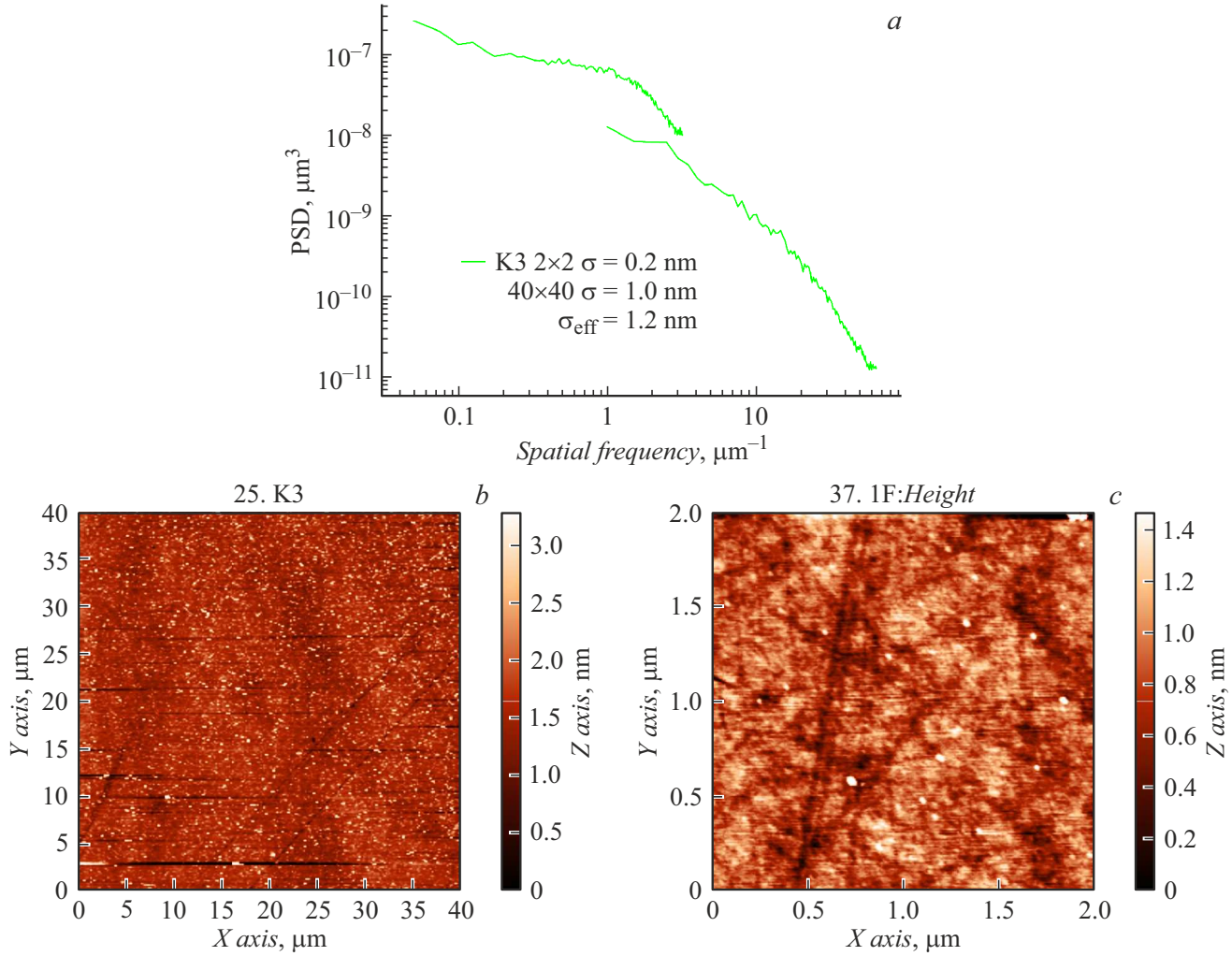



**Figure 4.** *a* — PSD is the surface function of liquid glass on quartz. AFM frames of liquid glass surface on quartz: *b* — 40×40, *c* —2×2 $\mu$m.

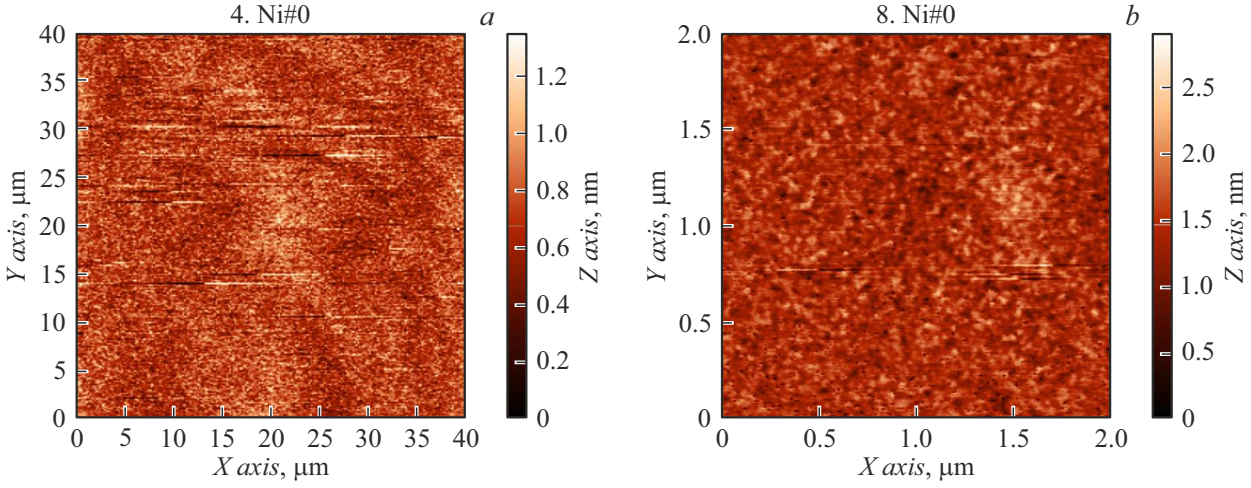
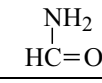
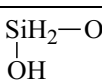
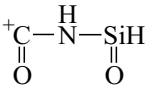
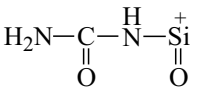
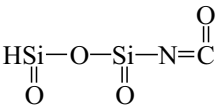
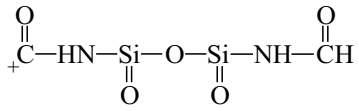


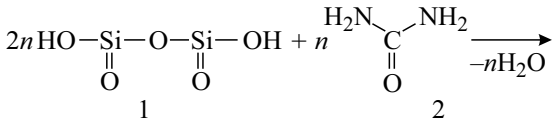

**Figure 5.** AFM frames of the initial nickel surface: *a* — 40×40, *b* — 2×2 $\mu$m.

Results of liquid glass study using SIMS

| The mass of the found ion, m/z | Assumed structure of the charged particle* | Calculated mass |
|---|---|---|
| 22.64 | $Na^+$ | 22.99 |
| 45.96; 46.44 |  | 45.02, 46.02 |
| 61.93; 63.01 |  | 63.11 |
| 64.98 |  | 64.12 |
| 77.78; 77.96 | $H_2SiO_3$ | 78.10 |
| 84.96 | $NaHCO_3$ | 84.00 |
| 88.03 |  | 88.12 |
| 101.09; 102.94 |  | 103.13 |
| 128.86 | $NaHSi_2O_3$ | 128.16 |
| 146.85 |  | 146.94 |
| 190.76 |  | 191.22 |

*Note:* ∗ it is important to understand that all the particles listed in the table, even those that are presented as neutral for ease of understanding, actually have a charge.

salts, and with silicic acid gel to the formation of water-insoluble polysilicatamides of the following structure 3:



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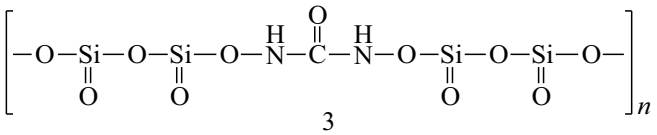
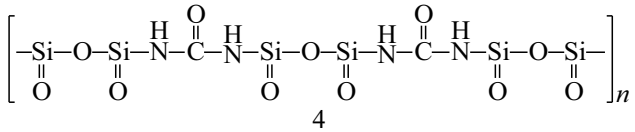


3

Thus, one of the tasks set during the study was to make sure whether the frozen liquid glass film is really a polymer layer. The table summarizes the masses of the most intense peaks of ions and the estimated structure of these particles, in accordance with their calculated mass.

The most intense peaks in the mass spectra are the peaks of sodium ions, soda ($NaHCO_3$), nitric oxide (Fig. 8). Peaks with a higher molecular weight, but with a lower intensity, in our opinion, belong to ions fragmented during the analysis of the polymer structure. We assume that its structure differs from that presented in the literature and is a chain in which fragments of hydrated silicate oxide are combined with fragments of urea 4. In addition to the fragments of this polymer itself, there are fragments of silanol groups ($Si(OH)_2$) and silicic acid itself $H_2SiO_3$:



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The presence of soda in the mass spectrum is explained by the processes of hydration-dehydration in combination with the sorption of $CO_2$ from the air, which in the presence of free alkali lead to the formation of sodium bicarbonate: $NaOH+CO_2 = NaHCO_3$. Thus, it was found using SIMS that the proposed composition of liquid glass

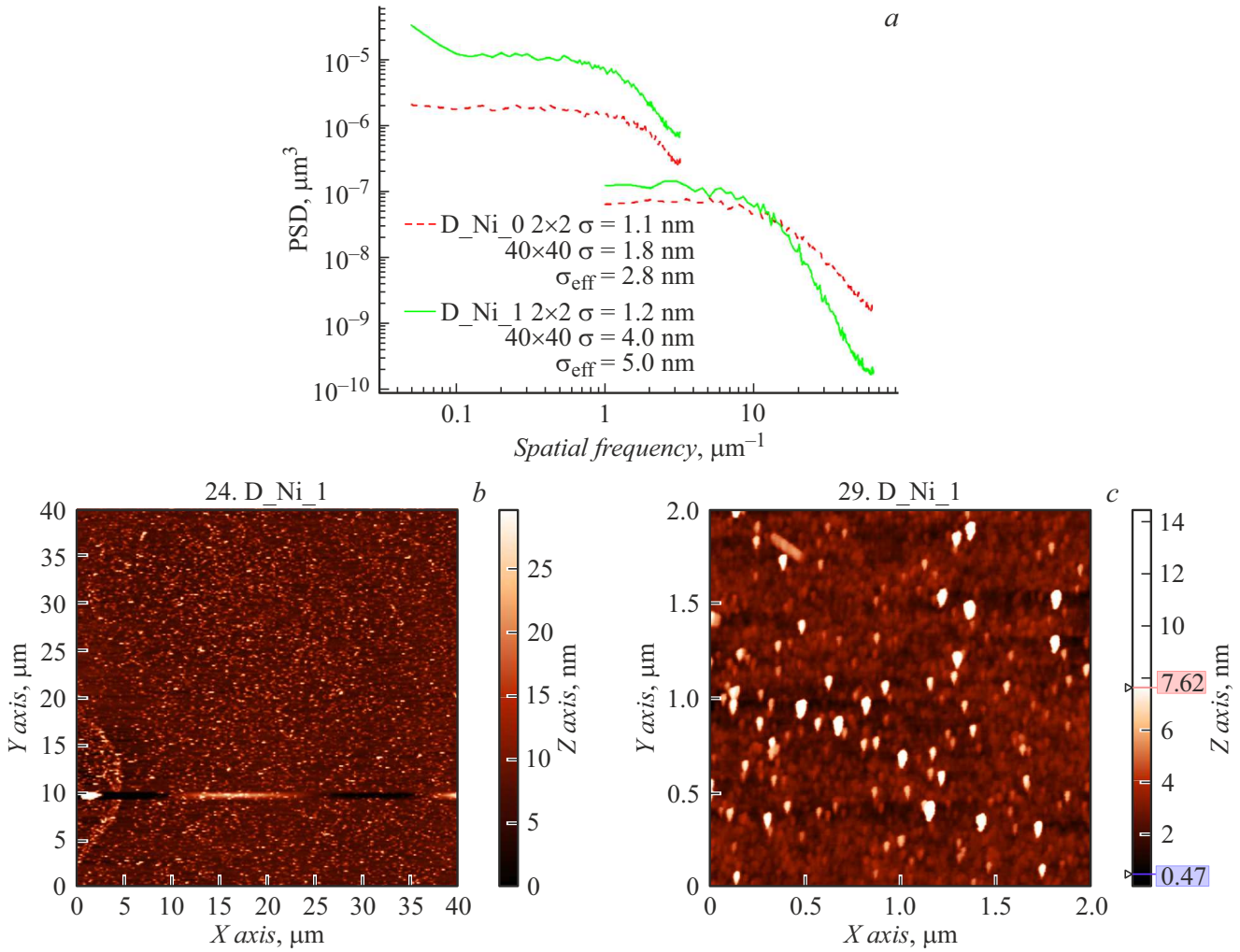


**Figure 6.** *a* — PSD-function of the Ni film surface (discontinuous line — initial roughness, solid — surface after applying liquid glass); *b, c* — AFM frames of the nickel surface after applying liquid glass 40×40 and 2×2 $\mu$m respectively.

during solidification is more of a polymer structure in which urea actively interacts with silicon oxides and silicic acid. In addition, the absence of products of interaction with chromium makes it possible to state that the liquid glass is inert to the coating to which it is applied.

## Conclusion

In the course of the work, it was discovered that the studied composition of liquid glass containing urea and showing a record smoothing of surface roughness on chromium films, unfortunately, is completely unsuitable for smoothing the surface of nickel and quartz films, which may indicate the need for an individual approach to smoothing each type of surface. We cannot explain the reasons for such a different result on different substrates at this stage of research. Thus, it is necessary to either look for a new technological coating, or replace amorphous nickel with chromium for space mirrors to solve the defined tasks.

Studies of the liquid glass film using SIMS helped to establish its approximate composition, as well as to prove the absence of chemical interaction with the surface on which it is applied.

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### Conflict of interest

The authors declare that they have no conflict of interest.

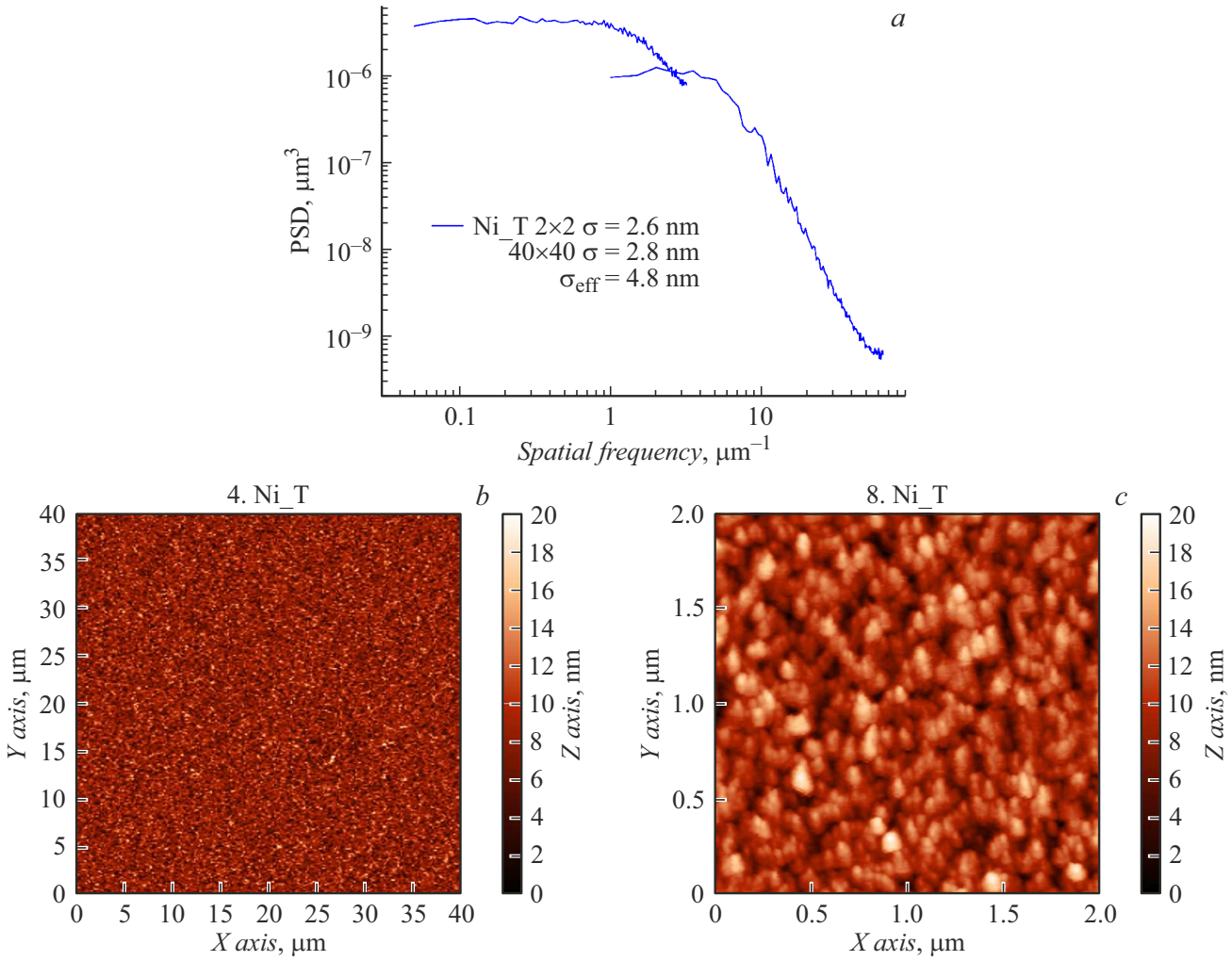


**Figure 7.** *a* — PSD-function of the Ni film surface after etching; *b, c* — AFM frames of the nickel surface after etching liquid glass 40×40 and 2×2 $\mu$m respectively.

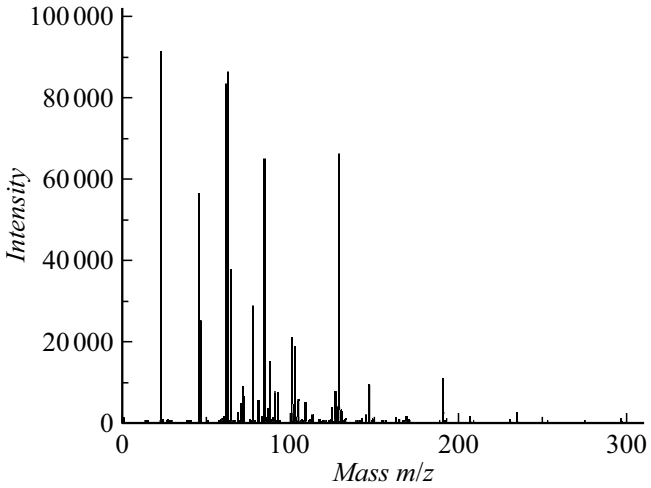


**Figure 8.** The spectrum of SIMS for a layer of liquid glass with urea deposited on the surface of a chromium film.

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