Study of luminescent properties of Al-Si-N films

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Abstract. In this study, we analyzed the optical properties of Al-Si-N coatings applied on silica glass. Under the effect of optical radiation and electron beam, intense luminescence of Al-Si-N films with complex emission spectra is observed. Photoluminescence excited by the radiation with energy of 4.47 eV, which falls within the opaque range of the films, is likely connected with surface luminescence centers. The film luminescence demonstrates that luminescence spectra excited in different ways do not coincide. This indicates that there are different luminescence centers in Al-Si-N films. These centers are excited with different efficiency at different types of excitation.

1. Introduction

Al-Si-N films have many useful, from the viewpoint of their application, properties. These films are characterized by high microhardness up to 35 GPa [1] and temperature resistance to oxidation up to 1500°C [2]. Owing to these properties, Al-Si-N films can be used to increase the resistance of cutting tools for super finishing treatment of tough alloys [3].

Al-Si-N films are transparent in the visible spectrum of electromagnetic radiation [4]. The last property allows these films to be used in optical elements. In addition, diagnostics and examination of the films can be carried out by optical methods, such as absorption and luminescent spectrometry.

In the recent years, the protection of spacecraft illuminators against space debris has become a challenge. Illuminators are subject to continuous bombardment by a huge number of particles with size from 10 to 100 micrometers and speed up to 16 km/s. As a result, craters are formed, which decrease significantly the illuminator transparence. If illuminator glass is coated by Al-Si-N films, the number of craters decreases fourfold [1, 3]. To be noted is the high level of radiation in cosmic space. Therefore, it is necessary to know optical and luminescent properties of the considered films in radiation environment.

In this study, we analyzed physical-mechanical and luminescent properties of Al-Si-N coatings applied on silica glass and aluminum substrates. The coatings were deposited at the UVN-05MDKVANT vacuum setup in the argon-nitrogen gas mixture. The total pressure was 0.3 Pa, and the partial pressure ratio was Ar:N=3:1. The method of bipolar pulsed magnetron sputtering of a mosaic target based on aluminum with silica inserts was used. The magnetron discharge power was 1.2 kW, and the current pulse frequency was 50 kHz. The substrates were heated, and then their temperature was maintained constant in the process of coating application with a 10-kW resistive...
molybdenum heater. The coatings were applied onto silica glass for measurement of adhesion and microhardness and aluminum substrates for measurement of luminescence.

Adhesion was measured by a Revetest scratch tester (RST), while microhardness was measured by an AFFRI microhardness tester.

Cathodoluminescence was studied at excitation by an electron beam \( E_{av} = 250 \text{ keV}, \text{ duration } \tau = 12 \text{ ns} \) \[5\]. Aluminum substrates are used, because the electrons of e-beam with the mean energy of 250 keV pass through the film (10-20 µm) and excite luminescence of silica glass. This makes difficult measurement of coating luminescence. The mean free path of electrons in silica glass is about 250 µm. The measurements were carried out by two methods. The first method involved the use of a photomultiplier tube with separation of the measured wavelength by a monochromator and recording of the luminescence relaxation kinetics at an oscilloscope. The time resolution was 10 ns. The spectrum was constructed from oscillograms. In the second case, an AvaSpec-2048 high-sensitivity fiber optic spectrophotometer was used. It operates in the spectral range of 200-1100 nm with an optical resolution from 0.04 nm. The device records the integral luminescence from one electron pulse for the time of 200 µs.

The film thickness was determined by the weight method. The composition of coatings was measured with a LEO EVO50 raster electron microscope (CarlZeiss, Germany). An Oxford Instruments INCA X-act detector was used. The results of the analysis are given in table 1.

### Table 1. Elemental composition of Al-Si-N film specimens in atomic %.

| Elements, % | Specimens | 1   | 2   | 3   |
|------------|-----------|-----|-----|-----|
| N          | 51.31     | 51.80| 49.41|
| O          | 6.39      | 1.76 | 7.59 |
| Al         | 29.27     | 32.95| 30.36|
| Si         | 12.01     | 12.30| 11.41|
| Coating thickness, µm | 12.76 | 14.42| 9.72 |

2. Results and discussion
The measurements of adhesion of Al-Si-N films at KV specimens are presented in table 2.

### Table 2. Adhesion of Al-Si-N films on KV glass.

| Specimen # | Mean value of N |
|------------|-----------------|
| 1          | 16.6±0.8        |
| 2          | 14.5±1.8        |
| 3          | 17.7±0.4        |

The values of microhardness of Al-Si-N films applied on KV glass are given in table 3.

### Table 3. Microhardness of Al-Si-N films applied on KV glass.

| Specimen # | Mean values of microhardness at load of 9.8×10⁻² N, (GPa) |
|------------|----------------------------------------------------------|
| 1          | 34.1±1.7                                                 |
| 2          | 21.0±0.6                                                 |
| 3          | 29.9±1.7                                                 |

Cathodoluminescence (figure 1) of the films at the excitation by a nanosecond e-beam was recorded 10 ns after the pulse start. It has a rather complex structure. The depicted curves are smoothed. Luminescence peaks can be seen in the following ranges: 2.2 eV, 2.4 eV, 2.7 eV, 3.1 eV,
and 3.3 eV. The main part of the luminescence intensity decreases with a time constant smaller than 10 ns. In the recorded luminescence spectra, we can see the influence of the oxygen concentration (table 1) on the peaks nearby 2.2 eV, 2.4 eV, 2.7 eV, and 3.3 eV. This luminescence can be caused by the AlN phase [6].

![Figure 1. Cathodoluminescence spectrum of the Al-Si-N film excited by e-beam. Digits near the plots are the numbers of the specimens having different composition.](image1)

In [6], it was noted that this phase has luminescence bands nearby 2.1 eV, 2.7 eV and 3.2 eV, which coincide with the results obtained by us. The dependence of the luminescence intensity on the oxygen concentration additionally confirms the formation of this phase. As the concentration of O increases, the intensity at the high-energy front increases, while the intensity at the low-energy front decreases.

![Figure 2. Integral spectra of cathodoluminescence of the Al-Si-N film excited by e-beam. The spectra were recorded for 200 µs.](image2)
According to the literature data, the luminescence nearby 3.1 eV can be associated with O\textsuperscript{2−}V\textsubscript{a} oxygen centers [7]. At foreign excitation of this defect, the luminescence nearby 2.4 eV is observed. In our case at the pulsed recording of cathodoluminescence in all specimens, 3.1 eV and 2.4 eV bands are observed.

Figure 2 shows the integral spectra of cathodoluminescence recorded for 200 µs after the electron pulse. The presented curves are smoothed. Digits in the plots are the numbers of the specimens with different composition. Luminescence of the integral spectra differs significantly from that recorded 10 ns after the electron pulse. Peaks are observed in the following ranges: 1.6, 1.7, 1.9, 2.3, 2.5, 2.65, 2.85, 3.0 and 3.28 eV. The spectra are complex. As in the previous cases, their character is likely caused by the rich defect structure of the coatings and by the overlapping with interference. The recorded cathodoluminescence spectrum of the AlN film has demonstrated the luminescence bands nearby 2.6 and 2.9 eV and the absence of the band nearby 1.9 eV. Thus, the luminescence band nearby 1.9 eV can be assigned to the Si\textsubscript{3}N\textsubscript{4} phase [8].

3. Conclusion

Thus, under the exposure to optical radiation and electron beam, the intense luminescence of Al-Si-N films with complex spectra is observed. The recorded spectra of film luminescence excited at different times do not coincide. This fact indicates that Al-Si-N films contain a set of luminescence centers, which have different optical and time properties.

The results of analysis of cathodoluminescence spectra in different time intervals suggest the presence of two phases, namely, AlN and Si\textsubscript{3}N\textsubscript{4}, which form the total luminescence. The dependence of luminescence intensity on the oxygen concentration in the nanosecond time interval and on the silicon concentration in the microsecond interval serves an additional argument for formation of two phases. An excess of anions has a positive effect on the increase in microhardness and adhesion (see tables 1 and 2).

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