Investigation of Ta-Si-N coatings obtained by pulsed magnetron sputtering of multicomponent Ta5Si3-TaN-Si3N4 SHS target

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Abstract. The coatings were obtained by pulsed magnetron sputtering of Ta5Si3-TaN-Si3N4 target. Reverse pulse duration was varied during deposition. The structure, composition, mechanical characteristics and oxidation resistance have been investigated. It was found that an increase in the pulse duration does not significantly affect the structure and hardness of the coatings but control the growth rate and nitrogen content in the coatings. Ta-Si-N coatings showed high hardness in range of 20-22 GPa and good oxidation resistance up to 800 °C.

1. Introduction
Tantalum silicide TaSi2 is a promising candidate as a material for multifunctional protective coatings, since it has a high melting point of 2200 °C and a good hardness of 15.6 GPa in comparison with titanium silicide (1500 °C, 8.6 GPa) and tungsten silicide (2160 °C, 13.1 GPa) [1]. It is known that TaSi2 coatings show good oxidation resistance [2, 3]. The technological properties of TaSi2 coatings can be improved by alloying with various elements. The included of nitrogen atoms into the composition of coatings based on TaSi2 is promising [4-6]. Nitrogen-containing coatings are characterized by a hardness of ~ 25 GPa, a low friction coefficient of 0.23 at high temperatures due to the formation of TaSiOx fibers, good wear resistance and thermal stability up to 800 °C [6]. Ta-Si-N coatings with a high silicon content are resistant to high-temperature oxidation up to 1300 °C, which is achieved due to the formation of a barrier oxide layer based on Ta2O5 [7].

The most common method for producing Ta-Si-N coatings is magnetron sputtering [2-6]. The introduction of nitrogen into the composition of coatings during magnetron sputtering is usually carried out by injecting a reaction gas of N2 into a vacuum chamber [5–7]. Chemical interaction of tantalum and silicon atoms with nitrogen atoms occurs. The second method of introducing gaseous elements into the composition of coatings is the use for sputtering of multiphase targets obtained by the method of self-propagating high-temperature synthesis (SHS) and containing the corresponding ceramic phases. Previously, this approach was used for deposition of Ti–Si–N, Ti–B–N, Ti–Al–Si–B–N, and Ti–Si–Ca–C–O–N coatings by sputtering of multicomponent Ti3Si1+TiN, TiB2+TiN, TiB2+Ti5Si3+TiAl+Ti2AlN and TiC0.5+CaO+Si3N4 targets, respectively [8-10]. This route can be applied for manufacturing of coatings in the Ta-Si-N system. It is important to note that there are no data on non-reactive deposition of coatings in the Ta-Si-N system in the literature.
The aim of present study is deposition of Ta-Si-N coatings by pulsed magnetron sputtering of a Ta$_5$Si$_3$-TaN-Si$_3$N$_4$ target with variation of pulse duration, investigation of composition, structure, mechanical characteristics, and oxidation resistance of coatings.

2. Experimental Part

The Ta-Si-N coatings were deposited by pulsed magnetron sputtering of a Ta$_5$Si$_3$-TaN-Si$_3$N$_4$ target. The powders for the manufacture of the target were obtained by the SHS method by the interaction of the initial powders of tantalum and silicon in a nitrogen atmosphere at a pressure of 200 atm. After that, the products of the SHS reaction were milled and subjected to hot pressing. Deposition was carried out in Ar (99.9995%) medium with the following parameters: current of 2 A, power of 1 kW, deposition time was in range of 15-40 minutes. Pinnacle Plus power supply (Advanced Energy, USA) maintained the magnetron power at the frequency of 50 kHz and pulse durations of 0, 0.5, and 5 μs. Single-crystal (100) silicon wafers were used as substrates. The substrates were preliminarily cleaned in isopropyl alcohol using ultrasonic UZDN-2T setup and directly in a vacuum chamber using etching by Ar$^+$ ions with an energy of 2 keV for 2-20 minutes. The structure and elemental composition of the coatings were studied by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) on a Hitachi S-3400N microscope equipped with a NORAN 7 Thermo device. The phase composition was studied by X-ray diffraction (XRD) on a Phaser D2 Bruker diffractometer using CuKα radiation. To determine the mechanical properties of the coatings, a nanoindentation at load of 4 mN on Nano-Hardness Tester (CSM Instruments) was used. The oxidation resistance of the coatings was evaluated by air annealing in a SNOL 3.3.2 / 1200 muffle furnace at temperatures of 700-1000 ° C for 60 min.

3. Results and Discussion

Sample numbers, pulse duration values, and compositions of Ta-Si-N coatings are shown in Table 1.

Table 1. Elemental composition and growth rate of Ta-Si-N coatings.

| №   | Pulse duration, μs | Elemental composition, at.% | Growth rate, μm/min |
|-----|------------------|-----------------------------|---------------------|
|     |                  | Ta  | Si  | N   |                        |
| 1   | 0.0              | 55.1| 16.9| 28.0| 0.155                  |
| 2   | 0.5              | 55.6| 20.5| 23.9| 0.160                  |
| 3   | 5.0              | 57.2| 31.7| 11.1| 0.127                  |

Coating 1 had the following composition: 55.1 at.% Ta, 16.9 at.% Si and 28.0 at.% N. When passing from 0 to 0.5 μs (sample 2), a slight change in the concentration of Ta was observed as well as an increase in the concentration Si by 20%, and a decrease in the N content by 15%. An increase in the pulse duration from 0.5 to 5 μs led to an increase in the concentration of metallic elements Ta and Si by 3 and 55%, respectively, and a decrease in N by 54%.

Thus, the coating deposited with a pulse duration of 0 μs showed the minimum concentration of metallic elements and the maximum nitrogen content. An increase in the pulse duration led to a growth in the concentration of tantalum and silicon and a decrease in the concentration of nitrogen. During the deposition process, the target surface is additionally nitrided, as a result of which a modified layer is formed on its surface [11]. With a raise of reverse pulse duration, the time of electron bombardment of target increases, and the amount of nitrogen in the modified layer decreases because of its etching as a lighter element [12, 13].

According to SEM images, all coatings showed a dense homogeneous structure (Fig. 1).
The growth rates calculated by measuring the coating thickness from SEM data are summarized in Table 1. Samples 1 and 2 showed similar growth rates of 0.155 and 0.160 μm/min. An increase in the pulse duration to 5 μs led to a decrease in the growth rate by ~20%. This effect can be associated with a decrease in the duration of the direct pulse, under the action of which the coating is deposited [14].

Fig. 2 shows the sections of the diffraction patterns of the Ta-Si-N coatings in the range of 2Θ =20-50°.

According to XRD, coatings 1–3 are X-ray amorphous. The diffraction patterns of the coatings revealed a strongly broadened peak in the range 2Θ = 30-45°. It is close to the reflection from the hexagonal phases of h-TaSi₂ (JCPDS 89-2941), h-Si₃N₄ (JCPDS 83-0700), and cubic c-TaN (JCPDS 32-1283). Thus, the coatings contain Ta-Si, Si-N, Ta-N bonds with equal probability. Note that changing the pulse duration did not affect significantly the phase composition and structure of the coatings. The mechanical characteristics of the coatings are shown in Table 2.

Table 2. Nanoindentation data for Ta-Si-N coatings.

| №  | H, GPa | E, GPa | W, % | H/E     | H/E², GPa |
|----|--------|--------|------|---------|-----------|
| 1  | 22     | 250    | 65   | 0.088   | 0.170     |
| 2  | 21     | 224    | 65   | 0.094   | 0.184     |
| 3  | 20     | 215    | 65   | 0.093   | 0.173     |

Coatings 1-3 showed similar values of hardness (H) in the range of 20-22 GPa and the identical elastic recovery W = 65%. Elastic modulus (E) decreased with increasing pulse duration and amounted...
to 250, 224, and 215 GPa for coatings 1, 2, and 3, respectively. According to the literature data, the Ta-Si-N coatings obtained by magnetron sputtering in an N$_2$/Ar mixture had hardness in the range of 14–18 GPa [15, 16], which is ~20–50% lower than the values for samples 1–3.

Since the pulse duration does not seriously affect the structure and properties of the coatings, the oxidation resistance was determined for sample 2 deposited with an average pulse duration of 0.5 μs. The kinetic curve of the oxidation of coating 2 annealed at temperatures of 700–1000 °C is shown in Fig. 3.

![Figure 3. The kinetic curve of the oxidation of coating Ta-Si-N.](image)

At temperatures of 700 and 800 °C, an increase in the sample mass change (Δm/s) by 0.05 and 0.29 mg/cm$^2$ was observed, associated with the formation of an oxide layer based on Ta$_2$O$_5$ and SiO$_2$. The difference in the color of samples at these temperatures is due to the different thicknesses of the oxide layer. With an increase in temperature to 900 and 1000 °C, the mass of the sample sharply decreased because of complete oxidation and delamination of the coating. Also, the decrease in weight can be associated with the evaporation of nitrogen [17]. Thus, the maximum operating temperature of the coatings was 800 °C.

4. Conclusion
Ta-Si-N coatings were obtained by magnetron sputtering in pulsed current mode using a multicomponent nitrogen-containing Ta$_5$Si$_3$-Ta$_2$N-Si$_3$N$_4$ target. All coatings had a dense, homogeneous structure. According to XRD data, the Ta-Si-N coatings are X-ray amorphous. All samples were characterized by hardness of 20–22 GPa and the same elastic recovery of 65%. Annealing of the Ta-Si-N coatings showed that the maximum temperature at which the coatings retain their protective properties is $T = 800$ °C.

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