Two-stage PVD method for protective coating formation

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Abstract. The CVD methods are typically used for the formation of aluminum oxide coatings since aluminum oxide is a dielectric. The adhesion between the protective coating and the substrate material is normally improved by growing thin intermediate layers based on titanium oxides and nitrides. These intermediate layers are mainly formed using the PVD methods. In this paper, we propose a two-stage PVD method for forming a layered structure on the titanium substrate. The formation of intermediate layers was carried out by the magnetron method (first stage), and the main protective layer was deposited at the second stage using a fore-vacuum electron source. The dense beam plasma generated during the electron beam transport in a fore-vacuum gas medium compensates for the negative electrical charge accumulating on the surface of the aluminum oxide target and facilitates its effective evaporation. The electrical properties of the intermediate layers and the resulting layered coatings have been investigated, including the tangent of dielectric loss angle, the real and imaginary parts of the conductivity and the dielectric constant dependencies on frequency.

1. Introduction

Aluminum oxide, being a simple chemical compound with high chemical inertness and temperature stability, is an ideal component to be used for protective coatings of various alloys against high temperature and chemical types of wear and tear [1, 2]. Since such coatings are dielectric, they are formed using the CVD methods [3]. The use of the PVD methods for this purpose is difficult because it requires taking special measures to prevent the change in the discharge parameters due to the electrode surface poisoning in the oxygen atmosphere [4]. For improved adhesion between the protective coating (Al₂O₃) and the main material of the substrate, thin intermediate titanium oxide and nitride layers (hundreds of nm) are introduced [5]. The intermediate layers are mostly formed using the PVD methods [6]. As a result, the deposition of protective coatings with adequate adhesion requires using several technological installations.

The use of an electron beam generated in the fore-vacuum range of pressure to form aluminum oxide ceramic layers by evaporation and depositing on the substrate allows one to keep the advantages of the PVD methods over the CVD techniques (an alleviated thermal load on the substrate), while carrying out the deposition in the atmosphere of either inert or reactive gases at a rate of tens of μm/min [7].

In this paper, we propose a two-stage PVD method of forming a layered structure on a titanium substrate. The intermediate layers were formed using the magnetron technique, while the main protective coating was created using a fore-vacuum electron source. We have studied the mass-to-charge composition of the magnetron and beam plasma ions during the formation of coatings, as well as the electrical properties of the intermediate layers and the created layered coatings, the tangent of
the dielectric loss angle, frequency dependencies of the real and imaginary parts of the conductivity and dielectric constant, and the hardness of coatings.

2. Experimental setup and methods

Figure 1 shows a schematic diagram of the two-layered coating deposition used in the experiment. The procedure consisted of two steps. At the first step, the films of titanium oxide and nitride were deposited on the substrate surface made of commercially pure titanium (VT1-0) by sputtering a magnetron discharge titanium cathode (50 mm in diameter) in a reactive gas atmosphere (oxygen, nitrogen).

![Schematic diagram of the experiment](image)

Figure 1. Schematic diagram of the experiment.

The 200 nm thick films were deposited at different gas consumption rates (table 1), with the chamber evacuated to a base pressure of 0.04 Pa using an nEXT300D turbomolecular pump at a rate of 300 l/s. The substrate was fixed to a grounded movable holder. The magnetron was also equipped with a positioning mechanism.

| Table 1. | The gases flow rate and hardness during the formation of the intermediate layer. |
|----------|--------------------------------------------------|
| Gas consumption (sccm) | Sample No | Sample No | Sample No | Sample No | Sample No | Sample No | Sample No |
| Ar       | #1     | #2     | #3     | #4     | #5     | #6     | #7     | #8     |
| 47.5     | 45     | 42.5   | 40     | 50     | 50     | 50     | 50     |
| O₂       | 12.5   | 15     | 17.5   | 20     | -      | -      | -      |
| N₂       | -      | -      | -      | 1      | 2      | 3      | 4      |
| Hardness (GPa) | 4 | 3 | 5 | 5 | 13 | 15 | 16 | 20 |

At the second stage, the substrate with the formed titanium oxide or nitride layer was transported to the region of electron beam interaction with the target made of alumina ceramics. The electron beam was generated by a fore-vacuum electron source, design and working principle of which is discussed in detail in [8]. Upon the electron beam reaching the power density sufficient for the onset of the alumina target evaporation, the target material vapor formed in the process of evaporation deposited on the substrate with the already formed layer of titanium oxide or nitride. The thickness of alumina
ceramic layers was about 1 µm for all samples. The ceramic target evaporation was carried out in the oxygen atmosphere at a pressure of 5 Pa. The two-layered coating was performed in a single vacuum cycle. During the second stage of the deposition, in order to maintain a high pressure in the chamber, the pump lock valve was partially closed.

The mass-to-charge plasma composition during the coating formation (titanium oxide and nitride) in the magnetron discharge plasma and the composition of coatings formed during the evaporation of alumina oxide ceramics were studied using a retrofitted quadrupole residual gas analyzer RGA-100 according to the technique described in [8, 9]. The hardness of the sample surface was determined using a Nanotest 600 hardness tester according to the Oliver-Pharr method using a Berkovich three-sided pyramid with an angle of 65.03° between the axis and the face.

The complex dielectric constant (DC) at frequencies up to the decimeter wavelength range was measured using the widely adopted capacitor method, which is based on placing a dielectric sample between the plates of a flat capacitor and measuring its parameters. The titanium substrate served as the capacitor lower plate. The upper plate was the copper layer deposited via the thermal evaporation in high vacuum onto the upper layer of the coating under study (titanium oxide or nitride, or alumina ceramic layer). The frequency dependence of the real and imaginary parts of the dielectric constant was used to calculate the corresponding parts of the specific electrical conductivity.

3. Results and discussion

Figure 2 illustrates typical spectra of the mass-to-charge composition of the magnetron discharge plasma operating in oxygen (figure 2a) and nitrogen (figure 2b). It has been found that during the formation of oxide and nitride coatings in the magnetron discharge plasma (at the indicated consumption rates of active gases), there are registered ions of the puffed gases (argon, oxygen, and nitrogen), ions of the magnetron target material (titanium), and ions of the residual atmosphere.

![Figure 2](image-url)  
**Figure 2.** Typical spectra of the mass-to-charge ratio of ions in the magnetron discharge plasma during the formation of (a) titanium oxide (sample #1) and (b) titanium nitride films (sample #8).

With increasing consumption of an active gas (within the range indicated in table 1), the portion of target material ions decreased and the portion of active gases increased, while the ratio of argon ions changed insignificantly.

The mass-to-charge spectrum of the beam plasma during evaporation of the alumina ceramic fragment is qualitatively similar to [8], namely, the spectrum contains traces of sodium, aluminum, nitrogen, and oxygen ions as well as ions of their compounds.

Figures 3 and 4 show respectively the dielectric properties of titanium oxide coatings and layered coatings of titanium oxide and alumina ceramic for different flows of oxygen.
Figure 3. Dielectric properties of TiO$_2$ films.

Figure 4. Dielectric properties of TiO$_2$+Al$_2$O$_3$ films.
Comparing the data in figures 3 and 4, one may arrive at the following conclusions. All coatings in question have dielectric properties. The increased values of the real and imaginary parts of the dielectric constant at low frequencies are due to the near-contact phenomena. It should be noted that \( \varepsilon' \) decreases with increasing portion of oxygen (figure 3a) in the total gas flow, which is related to additional oxidation of the deposited coating. However, despite the high values of the dielectric constant of the TiO\(_2\) coating (figure 3a), these coatings are characterized by large losses, which is reflective in the increased imaginary part of the dielectric constant and the tangent of the dielectric loss angle (figure 3c). Adding an additional layer (alumina ceramics) results in a noticeable improvement of dielectric properties: significantly lower values of \( \varepsilon'' \), \( \sigma'' \) and \( \tan \delta \) (figure 4c). The lower level of losses (i.e., lower values of \( \varepsilon'' \)) for TiO\(_2\)+Al\(_2\)O\(_3\) coatings results in lower values of the tangent of the dielectric loss angle as compared with the TiO\(_2\) coatings, despite the fact that the two-layered coatings have smaller values of the dielectric constant.

The hardness of titanium oxide coatings is practically independent on the oxygen consumption in the indicated range (table 1) and equals about 5 GPa, while that of the upper layer of alumina ceramics is 12 GPa for all samples.

All titanium nitride films are electrically conductive and their hardness directly depends on the nitrogen consumption (table 1). With an additional layer of alumina ceramics applied, the films acquire dielectric properties; however, their characteristics are inferior to those of the alumina ceramic films formed with a titanium oxide sublayer.

4. Conclusion
We have demonstrated a method of layer-wise deposition of TiO\(_2\)+Al\(_2\)O\(_3\) and TiN+Al\(_2\)O\(_3\) coatings that combines the magnetron sputtering of a titanium target in the active gas media and the electron beam evaporation of alumina oxide ceramics. It is found that increasing the oxygen flow results in an increased portion of oxygen ions, and decreased \( \varepsilon' \) does not affect the coating hardness. An increase in the nitrogen flow results in an increased portion of nitrogen ions in the magnetron discharge plasma and an increased hardness of nitride coatings. The formation of an additional alumina ceramic layer improves dielectric properties of coatings as a whole.

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