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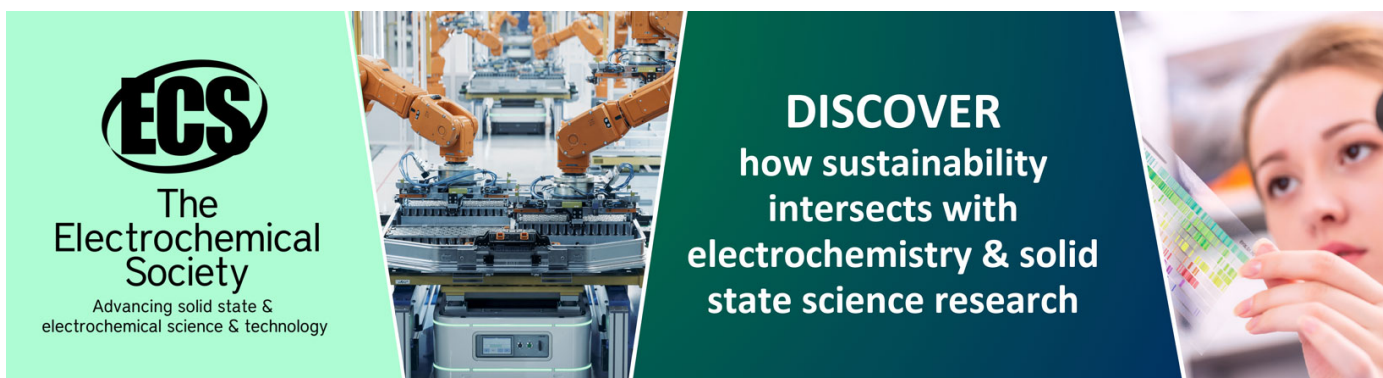
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Morphology of multilayer AlN/SiN coatings with layers of different thickness

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Abstract. Monolayer AlN coating and multilayer AlN/SiN coatings with single layer thickness of 10 nm and 5 nm were formed using reactive magnetron sputtering. The surface microstructure of these coatings was investigated using atomic force microscopy. Roughness, adhesion forces, and friction coefficient for different layers of coatings were determined.

1. Introduction

Materials multifunctionality is one of the actual trends of modern technology. Coatings based on aluminium nitrides are optimal for operation in the conditions of high temperature and mechanical stresses. Al-Si-N coatings are remarkable by a wide variety of properties, including optical, mechanical, heat-resistant, and tribotechnical ones [1-4]. The combination of different characteristics in one material is possible due to its controlled nanostructuring. On the one hand, the nanostructured state of the films, leads to a significant improvement of their mechanical and functional properties. On the other hand, excess surface energy at the interphase boundaries leads the nanostructure to a nonequilibrium state, which, in its turn, can lead to mechanical degradation of the films, especially at elevated temperatures under open air atmosphere conditions.

For Al-Si-N coatings, nanostructure can be created in two directions: with a uniform distribution of AlN nanocrystals in the amorphous matrix of Si₃N₄ or with alternation of nanosized AlN and SiN_x layers in a multilayer coating. In order to improve the mechanical properties and slow the cracks propagation, the coatings are formed as multilayer structures with a period of layers from several to a dozen nanometers. Such a composition can be a sequence of AlN/SiN layers.

In many applications, the surface is the working element of coatings. The destruction processes due to mechanical or thermal loading also begin on the surface. The adhesive forces and the specific surface energy of sublayers are essential in the process of products manufacturing, as well as in the preparation of surfaces for further tribological and heat resistant applications of coatings. To evaluate the morphology, tribological and adhesion properties, and the individual phases properties on the surface of coating with the 300 nm thickness and single layers of 5 and 10 nm, it is necessary to use a multifunctional atomic force microscopy (AFM) method with a high resolution both for topography and for force loading [5-8]. The forces interaction between the AFM probe and the coating surface in the mode of measuring the adhesion forces makes it possible to estimate the surface energy of the layers. AFM allows modifying the surface and carrying out tests for wear and friction [9-11]. The probe twist due to the contact with the surface can also be used to compare the properties of thin-coating surfaces [12-15]. The properties of Al-Si-N coatings in the form of nanocrystallites distributed



in the amorphous matrix are considered in Refs. [1-4]. The aim of this work was to study the surface of AlN/SiN coatings using the AFM method, to determine the morphology of their surfaces and to compare the friction coefficients, adhesion forces on the surface of AlN film, and AlN/SiN multilayer coatings with the thicknesses of individual layers of 10 and 5 nm.

2. Experimental details

AlN and AlN/SiN coatings were formed on silicon single crystal substrates with the (100) preferred crystallographic orientation by reactive magnetron sputtering with consecutive use of aluminum and silicon targets in Ar + N₂ plasma. The coatings thickness was about 300 nm. Multilayer coatings AlN/SiN were obtained with two thicknesses of single layer: 5 and 10 nm. The upper layer in the multilayer coatings was SiN.

Phase composition of the coatings was investigated using X-ray diffractometer RIGAKU Ultima IV with a Cu-K α source. Hardness and elastic modulus were determined using nanoindenter Hysitron Ti 750 Ubi (USA) equipped with the Bercovich diamond indenter with tip radius of 150 nm. The standard fused quartz sample was applied to control the calibration correctness of the device. The measurements were performed at loads 2-10 mN.

Cross-sectional TEM specimens have been prepared using FEI Helios Nanolab 650 FIB. The specimens were analyzed using JEOL JEM 2100 LaB6 transmission electron microscope operating at 200 kV.

The morphology investigations of the AlN coatings surface and multilayer AlN/SiN coatings surface were performed using Dimension FastScan AFM (Bruker, USA) in the PeakForce Tapping Quantitative Nanoscale Mechanical Mapping (QNM) mode with the standard silicon probe type NSC-11 (MicroMash, Estonia) with the curvature radius according to the passport less than 10 nm and the stiffness of the cantilever of 3 N/m.

After the probe evaluating according to the data processing program "NanoScope Analysis" using the "Tip Qualification" option, the tip radius was determined as 30 nm. The standard titanium sample RS-12M was used to calibrate the probe tip. For these hard coatings, the QNM mode using a silicon probe allowed estimating the distribution of adhesion forces over the surface, constructing an adhesion map, thus better revealing the different phases and boundaries of cluster formations. The adhesion forces were determined from the minimum of the probe detachment curves. The friction coefficient C_{fr} was determined by a two-pass technique of lateral forces microscopy (LFM) in the contact mode. The studies were carried out in air at 25°C and 40% relative humidity.

3. Results and discussion

The TEM image shows the right rows of atoms in the AlN crystal lattice (Fig. 1). The change in the orientation angle of atomic rows (crystalline planes) occurs every 1-10 nm. So the size of single crystallites in AlN layers of 5 nm thickness is 1-2 nm inside the coating. The atoms of the amorphous SiN layers are aligned in chains, most often curved and twisted, with ring formations (Fig. 1). The rare locations of regular crystalline organization include from 6 to 8 atoms.

The elastic modulus E of AlN coating was 189 GPa, in the case of multilayer coatings it was practically equal to 180-182 GPa. The microhardness H of AlN coating was 25 GPa, and that of multilayered coatings was 21-22 GPa (Table 1). The somewhat lower values of the elastic modulus for AlN coatings can be explained by their columnar structure, and for multilayer films – by the amorphous structure of SiN layers.

Typical images of the surfaces in the Al-Si-N coatings are presented in Figures 2 and 3. The monolayer AlN coating is crystalline according to the XRD and TEM results. The surface of AlN coating consists of rounded clusters (grains) with diameter 40 nm (Fig. 1a,b). The term «cluster» is used here as a larger structural formation, consisting of individual crystallites determined by TEM. In the case of using the term “grain” for these surface formation with uniquely defined boundaries, the term “subgrains” should be used for single nanocrystallites. Perhaps, in reality these clusters are somewhat smaller, since the probe radius can overestimate the size of the formations.

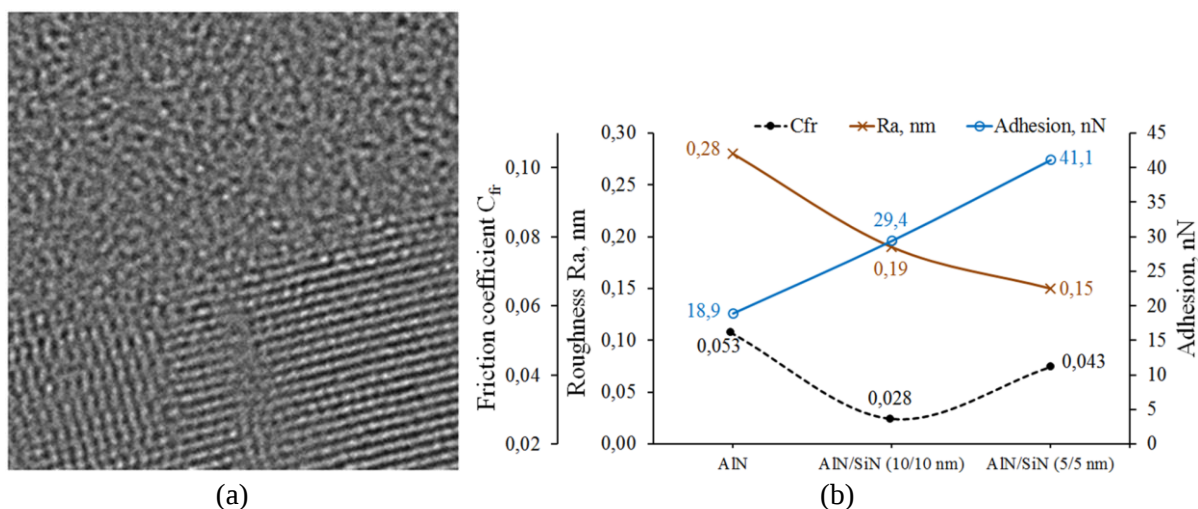


Figure 1. (a) TEM image of SiN (up) and AlN (down) layers with size of area $10 \times 10 \text{ nm}^2$. (b) Dependences of roughness, adhesion, and friction coefficient from coatings construction.

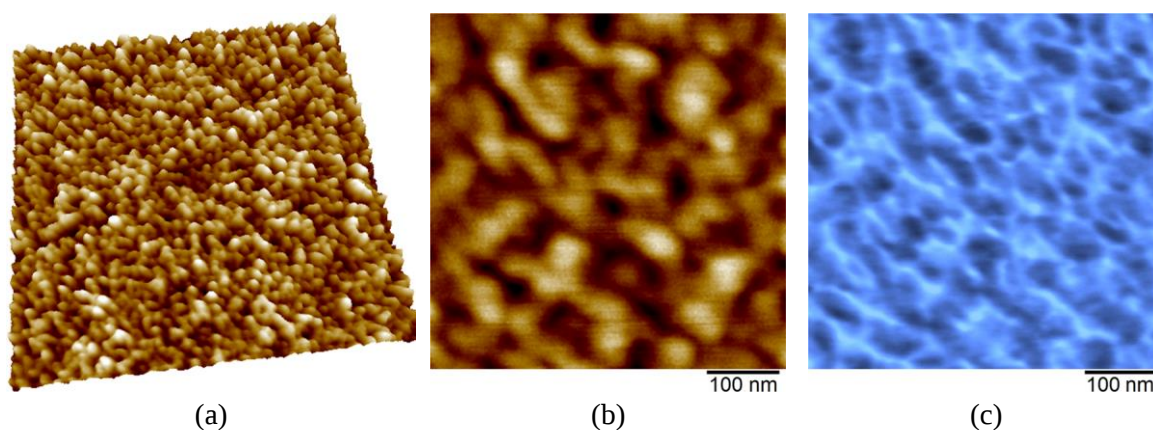


Figure 2. (a) Three-dimensional image of AlN coating on area $2 \times 2 \text{ }\mu\text{m}^2$. (b) Topography with Z range 1555 pm and (c) adhesion map with Z range 0.213 μN on area $500 \times 500 \text{ nm}^2$.

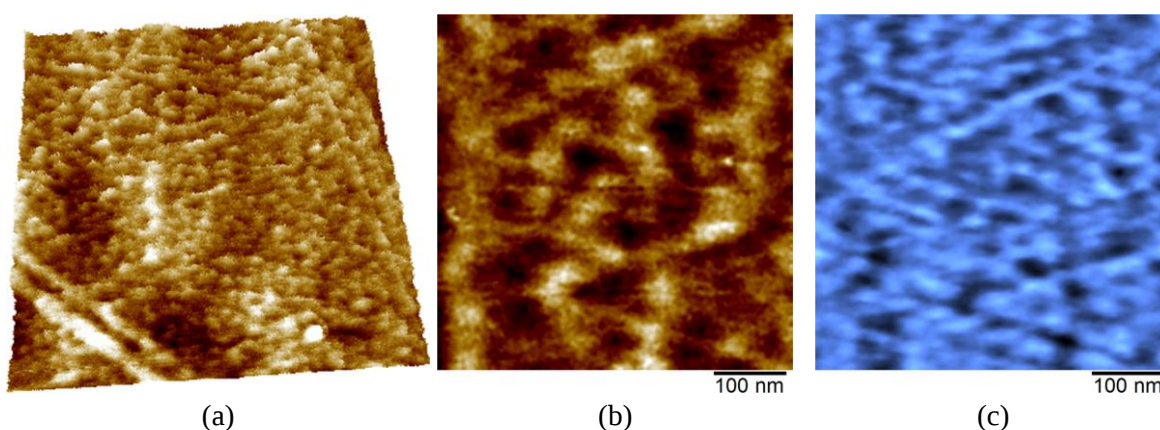


Figure 3. (a) Three-dimensional image AlN/SiN (5 nm) coating on area $2 \times 2 \text{ }\mu\text{m}^2$. (b) Topography with Z range 561 pm and (c) adhesion map with Z range 0.694 μN on area $500 \times 500 \text{ nm}^2$.

Table 1. The properties of AlN and AlN/SiN coatings investigated in this work: R_a , F_{ad} , C_{fr} , E, H, and the smallest diameter of structural formations D.

Number of samples	Content of samples	R_a , nm	C_{fr} by LFM	Adhesion forces S_a for F_{ad} , nN	The smallest diameter of structural formations D, nm	E, GPa	H, GPa
1	AlN	0.28	0.053	18.9	40	189 $\pm$ 3	25 $\pm$ 1
4	AlN/SiN 10/10 nm	0.19	0.028	29.4	50	183 $\pm$ 3	22,0 $\pm$ 0,7
8	AlN/SiN 5/5 nm	0.15	0.043	41.1	20	180 $\pm$ 3	21,3 $\pm$ 0,4

During the coatings deposition and AFM investigation, all silicon substrates of the [100] orientations were unrolled in the same way. So, the linear orientation of the cluster chains for all coatings was traced approximately at 45° to the X axis. This direction is typical for the exit of the (100) and (010) planes on the silicon plate surface with orientation [100]. In the crystalline AlN coating, these chains are the shortest, most often composed from two or three clusters, sometimes up to 10 clusters and chains lengths is about 150-300 nm (Fig. 2a,b). The roughness R_a of the AlN surface of 5x5 μm^2 area is 0.28 nm. The map of adhesion forces distribution over the surface shows that the dimensions of the structural formations are much smaller than that revealed on the topography (Fig. 2c). Adhesion forces F_{ad} in this study conditions can be associated with the capillary forces due to the nanometer layer of water between the probe and the coating surface. However, even in this case, the adhesion forces map expands the information about the surface microstructure, since different phases are covered with water atoms in different ways and, as a rule, the water can accumulate at the boundaries. The block structure with the average cluster size of 40 nm is more clearly revealed for AlN coating from the adhesion forces map (Fig. 2c). Z range of adhesion forces is 0.213 μN , and the arithmetic mean F_{ad} over the surface of 2x2 μm^2 was 18.9 nN.

Typical images of the amorphous SiN layers in Al-Si-N coatings are presented in Figure 3. The surface of SiN amorphous layers in AlN/SiN multilayer coatings is susceptible to texturing according to directions (100) and (010) of the silicon substrate in the highest degree. According to the topography image, the surface consists of asperities with fuzzy boundaries. The separate asperities with a diameter of about 100 nm for AlN/SiN (10 nm/10 nm) and about 50 nm for AlN/SiN (5 nm/5 nm) exist on the surface together with extended linear formations from 100 nm to 10 μm and more (Fig. 2). R_a of the surface is 0.19 nm for AlN/SiN (10 nm /10 nm) and R_a = 0.15 nm for AlN/SiN (5 nm/5 nm). The adhesion forces maps make it possible to reveal structural formations on the amorphous films surface and to determine their size more exactly. On the surface of amorphous SiN films, the adhesion forces and, consequently, the specific surface energy are significantly higher than those of crystalline AlN. The Z range of adhesion forces is 0.337 μN for AlN/SiN (10 nm/10 nm) and 0.694 μN for AlN/SiN (5 nm/5 nm), the arithmetic mean values of F_{ad} over the surface of 2x2 μm^2 area are 29.4 and 41.1 nN for these coatings, respectively. The size of the clusters is about 100 nm in length and 40 nm in width in the SiN layer in AlN/SiN (10 nm/10 nm) coating, and it is about 50 nm in length and 20 nm in width in AlN/SiN (5 nm/5 nm) coating.

The values of C_{fr} , determined by LFM for AlN and SiN surfaces differ almost twice being 0.028 and 0.053, respectively. The dependence of C_{fr} on the coating construction is presented in Figure 1b. Often, C_{fr} is bound either to the surface roughness or to the adhesive forces. The results obtained in this work show that none of these characteristics for Al-Si-N coatings have a single-valued relationship. The value of AlN C_{fr} is more likely to be affected by roughness, and the value of SiN C_{fr} in AlN/SiN 5/5 nm coating is more likely to be affected by adhesion forces.

The obtained surface morphology makes it possible to explain the good thermal stability of the studied coatings. The upper layer from amorphous SiN covers the surface of AlN layer with the columnar structure. Adsorption of water and gases in AlN layer occurs along the developed clusters (grain) boundaries, creating conditions for the oxidation reaction propagation into the coating. A layer from amorphous SiN closes the boundaries of AlN. In SiN layer, adsorption goes on the whole surface evenly, without creating nucleus of deepening. The increased thermal stability of multilayer structures is due to the presence of amorphous layers of the SiN_x phase, which are a barrier for the diffusion penetration of oxygen into the coating.

4. Conclusions

The surface microstructure of monolayer AlN coating and multilayer AlN/SiN coatings with thicknesses of separate layers of 10 nm and 5 nm was determined using AFM. The adhesion forces maps obtained in QNM mode allowed us to refine the size of structural formations on the surface of both the crystalline AlN film and amorphous SiN films. The dimensions of the cluster formations on the surface were 40 nm for AlN, 50 nm for AlN/SiN (10 nm/10 nm), and 20 nm for AlN/SiN (5 nm/5 nm). The values of the adhesion forces, friction coefficient and surface roughness of the coatings were determined. The increased surface energy for amorphous SiN layers in comparison with crystalline AlN was determined and the uniform distribution of adhesion forces over the surface was shown. The revealed microstructure explains the good thermal stability of multilayer AlN/SiN coatings.

Acknowledgments

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