FORMATION AND PROPERTIES OF ISLAND ALUMINUM-IRON ALLOY NANOMETER FILMS AT ION-ASSISTED DEPOSITION ON GLASS

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In this work the morphology, topography and wetting of nanometer films of lightly doped Al–1.5 at. % Fe alloy depending on the mode of deposition on glass substrates using a resonant ion source of vacuum electric arc plasma were studied. The coating deposition rate was 0.1-0.2 nm/min. Analysis of film growth and nanoscale irregularities on the surface of films were carried out using scanning probe microscopy. Using sessile drop method, the measurements of contact angles of the films were carried out. Quantitative relations correlating the surface microgeometry of Al-Fe alloy films to conditions of passive (U=0) and ion-assisted (U=3.0 kV) deposition modes have been established. The detected patterns of the evolution of submicron cone-like film morphology during ion-assisted deposition allowed us to determine that the wetting of films with distilled water has a heterogeneous character and is described by the Cassi-Baxter model.

Keywords: ion-assisted deposition; scanning probe microscopy; wettability; Al–Fe alloys.

Introduction

Practical and scientific attention to the synthesis of optical metal films on dielectric substrates using ion-beam coating deposition methods is caused by the prospects of their use in modern electronics and solar photovoltaic devices [1]. To modify the characteristics and control the properties of thin metallic coatings it is necessary to understand the impact of deposition conditions on the surface structure and properties of the coating/substrate system. Therefore, the purpose of this work is to perform profile and topographic analysis of island aluminum-iron alloy nanometer films on glass substrates prepared using a resonant ion source of vacuum electric arc plasma. In combination with scanning probe microscopy (SPM) data of the equilibrium contact angle (ECA) of the surface of the films with distilled water were used to estimate the surface conditions of the coating/substrate system.

Materials and research methods

The metallic coating (Al–1.5 at. % Fe alloy) was deposited on glass substrates using a vacuum resonant plasma-arc source (vacuum 10^{-2} Pa) [2] that simultaneously generated a neutral atom flow and an ion flow of the deposited alloy in two modes. In the

absence of accelerating potential (passive deposition mode) coating deposition time was 3 and 6 h, and with accelerating voltage U=3kV (ion-assisted deposition mode) - 6 and 10 h. The coating deposition rate was ~0.1-0.2 nm/min. In a number of papers, the mechanisms of defect formation during bombardment of solids by ions are discussed based on ideas about atomic collision cascades. The cascade development time is ~ $10^{-13} - 10^{-12}$ s. According to some evaluations [3] average kinetic energy of atoms in the cascade is equivalent to dynamic temperature $\sim 10^4$ K and taking into account cooling time (10⁻¹¹ s), the rate of "crystallization" (cooling of atomic collision cascades) was 10¹²-10¹³ K/s.

The morphology and topography, including roughness, of the surface of nanometer film nanostructures were studied by the SPM method on the NT-206 atomic force microscope with CSC-38 probes in contact mode in air. The roughness parameters of ISO standards together with dimensionless complexes (the ratio of step parameters of the profile $\psi = S/S_m$ and the research hybrid factor $k = R_{10z}/S$ [4]) were applied to describe the nanorelief of the films. The wettability of the surface of the Al-

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Fe/glass system was measured by the sessile drop method. The measurement error of ECA θ did not exceed 5%.

Results and their discussion

The SPM study of thin film nanostructures of Al-Fe/glass system showed the formation of submicron cone-like morphology. By changing the alloy application conditions (deposition time and mode), films of various thicknesses with different values of roughness and ECA were obtained. The results of analytical analysis of the data obtained by SPM are given in the Table 1. It was obtained that in the mode of passive deposition of a neutral flow of metal atoms generated by an ion source without turning on the accelerating voltage on the target holder, the arithmetic average rough-ness remains practically unchanged, being on average about 22 nm, which is 129 times higher than R_a of a glass substrate. Because of changing the deposition mode when metal alloy films are deposited on glass under an accelerating potential of 3.0 kV on the target, an increase in the R_a is observed, reaching 38.52 nm after 10 h of deposition under ion assisted conditions.

resulting distribution roughness The histograms of Al-Fe alloy films have a distinct maximum and are close to the Gaussian distribution. Analysis of histograms using asymmetry and peakedness parameters allows us to evaluate how accurately the experimental histograms of glass substrate and films are approximated by the probability density function f(z)of the normal distribution. An example of the smallest deviation of the height distribution of the sample surface topography from the normal one $(R_{sk} = 0, R_{ku} = 3)$ is glass, see Table 1. At the same time, asymmetry of film histograms is observed in the region of positive z values $(R_{sk} = 2.07 - 4.05)$, which indicates a greater number of local maximums relative to the midline of the surface profile as compared to the Gaussian distribution. It should also be noted that with increasing R_{sk} parameter R_{ku} grows. The nanometer film formed after passive deposition for 6 h is characterized by

Table 1. Parameters of morphology and roughness of glass substrate and films of Al-1.5 at.% Fe alloy deposited on glass

Parameter	Specimen					
s	Glas	Al–Fe				
	s	<u>U</u> =0		<i>U</i> =3.0 kV		
<i>t</i> , h	_	3.0	6.0	6.0	10.0	
R_a , nm	0.17	22.8	21.1	23.4	38.5	
		7	1	2	2	
R_q , nm	0.22	37.7	40.9	36.9	58.3	
		0	2	8	3	
R_q/R_a	1.29	1.65	1.94	1.58	1.51	
R_{sk}	-0.40	2.66	4.05	2.27	2.07	
R_{ku}	4.03	17.1	30.6	12.2	11.4	
		3	9	8	5	

the highest kurtosis (R_{ku} =30.69).

Values of the boundary contact angle of wetting with distilled water of the surface of films formed during ion-assisted deposition reach 80° and higher in contrast to films deposited at U=0, for which $\theta \approx 52^\circ$, see Table 2. In spite of the fact that deposition of Al-Fe alloy films regardless of the formation conditions reduces the degree of hydrophilicity of the glass substrate surface $(\theta = 22^{\circ})$, it was found that in case of U=3 kV with deposition time of 6 h the ECA value jumps by 52% to 78.2° compared to passive deposition without irradiation, although the film roughness increase is insignificant (11%).

Table 2. Morphological parametric complexes and wettability of glass substrate and films of Al-1.5 at.% Fe alloy deposited on glass

Specimen	t.h	<i>U</i> ,	ψ	<i>k</i> ,	θ, °
	- ,	kV		10-2	
Glass	_	-	1.23	0.04	22.0
Al–Fe	3.0	-	1.13	2.90	51.90
	6.0	_	1.26	6.10	51.60
	6.0	3.0	3.13	1.20	78.20
	10.0	3.0	1.33	3.20	81.90

Based on these results, it can be assumed that using only amplitude parameters is not sufficient to describe the aperiodicity of the nanostructure elements of the thin films. The correlation between R_a and R_q parameters is such that the coefficient of proportionality varies in the range of 1,7–1,9 times for films deposited under passive deposition conditions, decreasing to values of 1.5–1.6 times after ion-assisted deposition, see Table

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1. As a result, for this group of specimens for a selection of n=4 it was obtained that the selection regression coefficient is equal to 1.25, and the type of the selection linear regression equation $R_q = 1.25R_a + 10.27$ (Pearson's correlation coefficient r = 0.96) differs from the known equation for the Gaussian random surface by the presence of a free term. Comparison of the values of the parameter ψ for the surfaces deposited at U=0 and 3.0 kV shows that the values measured for the films match quite well, being in the range 1.26–1.33, and are close to the value ψ =1.23 of the glass substrate, except for the films deposited for 3 h (U=0) and 6 h (U=3.0 kV), see Table 2. The hybrid parameter k of films changes non-monotonically with the growth of their roughness. As the duration of the deposition process, and hence the film thickness, increases, the value of k increases. At the same time, the value of k decreases when an accelerating potential is applied. While the maximum value of $k=6.10 \cdot 10^{-2}$ corresponds to the case of film deposition for 6 h at U=0, in the mode of ion-assisted alloy deposition the obtained thin film coating is characterized by the minimum value of k=1.20 (t=6 h at U=3.0 kV). The increase in values of both parameters R_a and k for the film deposited for 10 h at U=3.0 kV, apparently, is connected with formation of microdrop fraction of the deposited alloy. It is known that the size of the drops and their concentration significantly affect the roughness of the coating.

The nature of the ECA dependence on R_a indicates a metastable heterogeneous mode of wetting of Al–Fe alloy films by water and is described by the Cassi–Baxter model [5]. Apparently, this explains the nonlinear relation between the amplitude of surface irregularities and the degree of its wettability, since water does not fill all the cavities of the nanorelief due to the presence of air in the recesses. At the same time, the regularities of changes in the topography of the coatings detected during passive deposition (see the change in the ψ and k parameters in the Table 2), indicate that the island films are at different growth stages depending on the time of deposition. The combination of island and layer-by-layer film growth mechanisms at t=6 h (U=0) results in a slower growth of islet height than the increase in longitudinal size.

Conclusion

Evolution of submicron cone-shaped morphology of island Al-Fe alloy nanometer films deposited on glass was studied by SPM and sessile drop method. The average roughness of Al-Fe alloy films varies in the range from 21 to 39 nm. In comparison with passive deposition without irradiation, the formation of films with a developed surface topography was found in all cases of ionassisted deposition. With increasing film thickness, the degree of relief heterogeneity decreases with a decrease in the proportion of abnormal protrusions on the surface. The growth of roughness leads to deterioration of film wettability, which is well described by the heterogeneous nature of film wettability by water. The regularities of structure formation of iron-doped aluminum films discovered in this work can be used to control the properties of nanometer metallic film structures, particularly to predict their wettability.

References

- 1. Mozetič M., Vesel A., Primc G., Bauer J., Eder A., Schmid G. et al. Recent developments in surface science and engineering, thin films, nanoscience, biomaterials, plasma science, and vacuum technology. *Thin Solid Films* 2018; 660: 120-160.
- 2. Tashlykov I.S., Belyj I.M. Coating methods: patent BY 2324; 1999; (1): 30. (in Russian).
- 3. Kinchin G.K., Piz R.S. Smeshhenie atomov v tverdykh telakh pod dejstviem izlucheniya. *Uspekhi fizicheskikh nauk* 1956; 60(4): 590-615. (in Russian).
- 4. Tashlykova-Bushkevich I.I., Stoliar I.A. Surface nanorelief of thin films of Al–Mn and Al–Ni alloys in the case of ion-assisted deposition on glass. Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques 2023; 17: 338–351.
- 5. Huang, F., Motealleh, B., Wang, D., Cornelius C.J. Tailoring intrinsic hydrophobicity and surface energy on rough surface via low-T Cassie–Wenzel wetting transition method. *AIChE Journal* 2023; 69: e17908.

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