THE ROLE OF MONOLAYERS THICKNESSES RATIO FOR OXIDATION RESISTANCE OF AlN/SiN_X MAGNETRON SPUTTERED COATINGS

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Introduction

Physically-vapor deposited transition metal nitride coatings based on MeN mononitrides of transition metal (Me=Ti, Zr, Cr, Al and others) are widely used in the industry as solid protective coatings. However, mononitride films often lose their protective role under harsh external conditions like friction, high temperatures, influence of corrosive media or irradiation. At the present, the multilayer film structures show considerable promise for improvement of the coatings operating abilities. In particular, multilayer coatings, where the layers of transition-metal nitrides alternate with layers of SiN_x, are characterized by the mutual insolubility of these two phases and display good thermal and oxidation stability and properties [1–3]. The presence of a large number of interfaces between layers and fine-grained structure are the reasons of it.

As it was shown in our previous studies, the resistance to high temperature oxidation of ZrN/SiN_x and CrN/SiN_x coatings depends on the thicknesses ratio of elementary layers [4]. In this work, the stability of AlN/SiN_x coatings with different ratio of monolayers thicknesses upon annealing in air is investigated.

Experimental details

AlN/SiN_x multilayer coatings as well as reference AlN and SiN_x monolithic reference films were deposited by reactive magnetron sputtering method in a high vacuum chamber (base pressure < 10^{-5} Pa) equipped with three confocal targets configuration and a cryogenic pump. Coatings were deposited on Si substrates at 300 °C. A constant bias voltage of −60 V was applied to the substrate during deposition. Al (99.9995% purity) and Si_3N_4 (99.99% purity) targets were used under $Ar+N_2$ plasma discharges at constant power mode. The Al target was operated in magnetically unbalanced configuration using a DC power supply, while a RF power supply was employed for the Si_3N_4 target in balanced mode. The Ar/N_2 flow ratio was optimized to obtain stoichiometric nitrogen content in the coatings based on earlier results. AlN/SiN_x multilayers with AlN and SiN_x layer thickness varying from 2 to 10 nm were synthesized. The total film thickness was ~300 nm. Isothermal air annealing was performed at different sequential temperatures from 400 to 950 °C. The total duration of annealing procedure was 8-9 hours. The elemental composition of the coatings in their as-deposited and air-annealed states was determined using elemental probe microanalysis method by wavelength dispersive spectrometer attached to a JEOL 7001 TTLS scanning electron microscope. X-ray Diffraction (XRD) analysis for identification of phase composition and structure state of the coatings was performed using a Bruker D8 AXS X-ray diffractometer.

Results and discussion

As described in the previous section, the AlN/SiN_x coatings were formed with different AlN to SiN_x layer thickness ratios, namely, 5 nm/2 nm, 10 nm/5 nm, 5 nm/5 nm, 10 nm/10 nm, 5 nm/10 nm, 2 nm/5 nm. The elemental composition of the elementary layers in multilayer systems corresponds to the composition of AlN and SiN_x monolithic reference films: 43.6 at.% Al and 56.4 at.% N for AlN film, 43.3 at.% Si and 56.7 at.% N for SiN_x film.

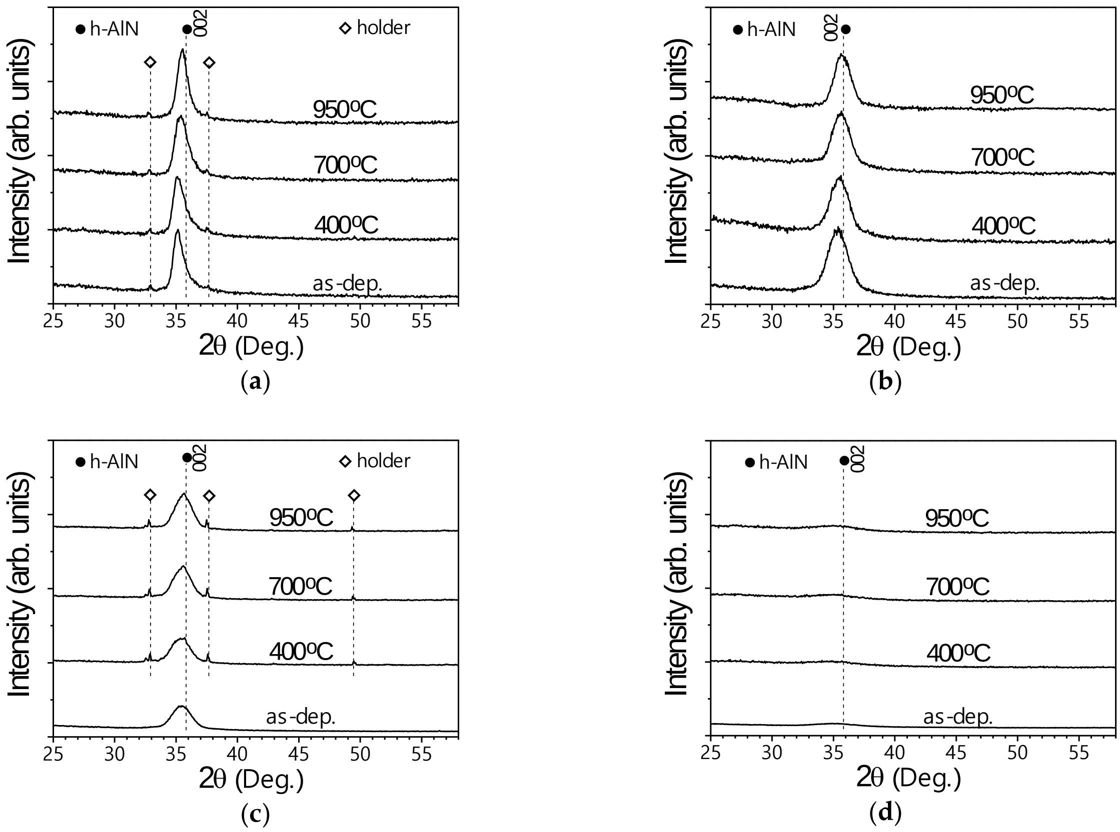

Fig. 1. Evolution of XRD patterns under air annealing for AlN reference coating (a); and AlN/SiN_x multilayer coatings with different thicknesses ratio of AlN and SiN_x elementary layers: (b) 5 nm/2 nm; (c) 5 nm/5 nm; and (d) 2 nm/5 nm.

The results of XRD analysis of AlN monolithic reference film in comparison with AlN/SiN_x multilayer coatings during annealing in air in the temperature range of 400–950°C are given in Fig. 1. It is known that SiN_x films are X-ray amorphous. That is why, in our case, the preferred orientation along the [002] direction for h-AlN layers is only observed. Broadening of AlN peak with decreasing AlN thickness takes place that can be connected with the decrease in grain size of AlN phase, and the coating appears to be nearly X-ray amorphous when the thickness of AlN layer is equal to 2 nm (Fig. 1d).

The main result consists in that no any change of phase composition for all synthesized coatings during annealing in air is detected by XRD method. The peak of the AlN phase retains its intensity up to a temperature of 950°C and oxide phases are not registered for AlN monolithic reference film as well as for AlN/SiN_x multilayers. There is a decrease in lattice parameter with an increase of annealing temperature that can be caused by a relaxation of the compressive stresses. The structure of the AlN/SiN_x multilayer coating with an elementary layer thickness ratio of 2 nm/5 nm remains X-ray amorphous at all temperatures of annealing (Fig. 1d).

The data of elemental analysis of the AlN, Si_3N_4 monolithic reference films and AlN/SiN_x multilayer coatings after annealing in air are given in Table 1.

Table. 1. Results of the oxygen content analysis for AlN, Si_3N_4 monolithic reference films as well as for CrN/SiN_x multilayer coatings after air annealing in the temperature range of 400–950 °C.

Type of coating	Oxygen content, at. %
AlN	33.9
Si_3N_4	28.0
AlN/SiN_x (5 nm/2 nm)	18.2
AlN/SiN_x (10 nm/5 nm)	6.8
AlN/SiN_x (5 nm/5 nm)	13.4
AlN/SiN_x (10 nm/10 nm)	6.0
AlN/SiN_x (5 nm/10 nm)	8.0
AlN/SiN_x (2 nm/5 nm)	15.6

Quite lower oxygen content in the AlN/SiN_x multilayer coatings exposed to annealing in air should be noted (Table 1). The minimal oxygen content in the AlN/SiN_x multilayer coatings after annealing is 6-8 at % in the case of elementary layer thickness ratios of 10 nm/5 nm, 10 nm/10 nm and 5 nm/10 nm, it means, in the case of bilayer period of 15 nm or higher. Such a result differs from earlier obtained results for the ZrN/SiN_x system where highest oxidation stability was observed for the case of ZrN to SiN_x thicknesses ratio of 2 nm/5 nm [4]. The oxidation rate of AlN/SiN_x multilayer coatings does not change significantly upon varying the MeN elementary layer thickness to that of SiN_x

that similar to the case of CrN/SiN_x coatings [4]. However, the main result consists in that the AlN/SiN_x multilayers are more resistant to high-temperature oxidation for all used MeN to SiN_x thickness-ratio values as compared with CrN/SiN_x and, especially, with ZrN/SiN_x multilayers.

Figure 2 shows the surface topography of the AlN/SiN_x (10 nm/10 nm) multilayer coating which is characterized by the best oxidation resistance. There are no any delamination of the coating and no presence of clearly defined surface centers of high-temperature corrosion.

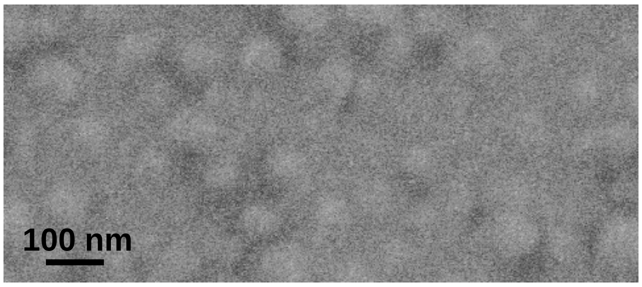

Fig. 2. Top-view SEM micrograph of AlN/SiN_x multilayer coating with the ratio of thicknesses of AlN and SiN_x elementary layers equal to 10 nm/10 nm after air annealing at 950 °C.

Conclusions

AlN/SiN_x multilayer coatings demonstrate higher resistance to high-temperature oxidation as compared to the AlN, Si_3N_4 monolithic reference films as well as ZrN/SiN_x and CrN/SiN_x multilayer coatings studied earlier. Observed relaxation of the compressive stresses during annealing can be one of the reasons of this fact. AlN/SiN_x multilayers with the elementary layer thickness ratio of 10 nm/5 nm, 10 nm/10 nm and 5 nm/10 nm are the most stable to oxidation at the high temperatures (only 6-8 at.% of oxygen in their composition after air annealing procedure). Further decrease in thickness of any elementary layer down to 5 or 2 nm leads to deterioration of their oxidation resistance.

References

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