SURFACE EROSION OF MULTILAYER CrN/a-Si_3N_4 FILMS UNDER HE IONS IMPLANTATION

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The effect of He ions implantation on surface erosion in multilayer CrN/*a*-Si_3N_4 films was studied using scanning electron and atomic force microscopy. The CrN/*a*-Si_3N_4 multilayer films with deferent thickness of CrN and Si_3N_4 layers on a Si (100) substrate were grown via magnetron sputtering. These multilayer films were implanted with 40 keV He^{2+} ions with doses of (3-11)·10^{17} cm^{-2}. AFM studies of the surface of implanted films showed the formation of open blisters consisting of two levels. Low surface erosion in multilayer films with a thickness of the amorphous layer exceeding crystalline was found in comparison with mononitride CrN films. Studies have shown the promising use of crystalline/amorphous boundaries to increase the resistance of materials to radiation erosion.

Keywords: radiation tolerant materials; blistering; nanocrystalline CrN/amorphous Si_3N_4.

Introduction

Increasing the intrinsic security and the performance of next-generation nuclear plants is a key issue for the development and public acceptance of nuclear energy. One of the conditions to achieve this goal is the elaboration of advanced materials tolerant to a high irradiation dose and to gas accumulation (He and/or H transmutation products) at high temperature [1].

Much attention is being paid to the study of materials with multiple interfaces (grain and phase boundaries), which act as defect absorbers that reduce the effects of radiation damage, and as traps for implanted gases such as helium [2]. A large number of grain and phase boundaries can be achieved by the forming of nanostructured materials such as multilayers. Among them, Me (metallic) and MeN (metal nitride) multilayer systems with different interface structures (bcc/fcc, fcc/fcc and bcc/bcc) have attracted much attention over the past few years [3]. Thus, the increased radiation resistance of Cu/Nb, Cu/V, Cu/Cu–Zr, V/Ag, Ag/Ni metallic multilayer systems was shown in [4-8].

In addition to multilayer films having a crystalline/crystalline structure, multilayer films with a crystalline/amorphous structure are of great practical interest. Besides immiscibility between constitutive elements, a high strength of the multilayer structure is essential to prevent slip and swelling in a radiation environment [8]. Recent findings have unambiguously revealed that crystalline/amorphous nanostructured multilayers exhibit a high radiation tolerance, due to their unique properties of crystalline/amorphous interfaces and amorphous nanolayers associated with excellent defects absorption capability. A maximum radiation resistance of the films is typically obtained at layer thicknesses of 2-5 nm, i.e. at a high density of interphase boundaries [7-8].

The formation of blisters (defects on the surface of materials with bubble form) He ions irradiation is a process leading to the changes in the surface physicochemical properties and loss of the structural integrity of the material [9-10]. Blisters are formed due to the nucleation and growth of gas-vacancy clusters. The introduction of He into the film often leads to an increase in compressive stresses. The subsequent relaxation of stresses can lead to stratification (crack formation) in the film, which leads to the formation of a blister or exfoliation (exfoliation of the film material without visible deformation of the surface layer) of the film [11-12]. The presence of additional effluents in multilayer nanostructured films can significantly affect the nucleation and growth of gas-vacancy clusters, leading to the formation of blisters.

The aim of the work was to study the surface erosion of the multilayer CrN/Si_3N_4 films after irradiation by He^{2+} ions with energy of 30 keV and doses up to 1.1·10^{18} cm^{-2}.

Materials and methods

Multilayer CrN/Si_3N_4 films were grown by reactive magnetron sputtering in a high vacuum chamber (base pressure < 10^{-5} Pa) equipped with three confocal targets configuration and a cryogenic pump (max. 500 l/s). Films were deposited on Si substrates covered with 10 nm thick thermally grown SiO_2 layer. A constant bias voltage of -60 V was applied to the substrate during deposition.

Water-cooled, 7.62-cm-diameter Cr (99.95 % purity) and Si_3N_4 (99.99 % purity) targets, located at 18 cm from the substrate holder, were used under Ar+N_2 plasma discharges at constant power mode. The Cr target was operated in magnetically unbalanced configuration using a DC power supply, while a RF power supply was used for the Si_3N_4 target in balanced mode. The total working pressure was 0.21 Pa, as measured using a Baratron capacitance gauge.

Multilayer CrN/Si_3N_4 films with the thickness of CrN and Si_3N_4 elementary layers of 2 and 5 nm (the number of bilayers 43), 5 and 5 nm (the number of bilayers 30), 5 and 10 nm (the number of bilayers 20) were formed at 500°C.

Ion implantation of the multilayer and CrN films was carried out using 40 keV He^{2+} ions at the DC-60 heavy ion accelerator of the Astana branch of the Institute of Nuclear Physics at a fluence of 3×10^{17} cm^2 to 1.1×10^{18} cm^{-2}.

The morphology of the films surface was studied by the method of scanning electron microscopy (SEM) on plan-view specimens using a JEOL JSM-7500F Field

Emission Scanning Electron Microscope (SEM) and by the method of atomic-force microscopy (AFM) using scanning probe microscope Solver P47Pro.

All specimens were analyzed using a JEOL JEM 2100 LaB6 transmission electron microscope operating at 200 kV and equipped with an energy-dispersive X-ray spectrometer (EDS).

Results

XRD studies of the films showed that cubic CrN is formed with a preferential orientation (200). The position of the CrN (200) diffraction peak for multilayer films is shifted relative to the CrN mononitride peak towards smaller angles, which indicates an increased value of the CrN lattice parameter (increase in compressive stresses). It was found, that films with a small thickness of the CrN crystal layer (2 nm) have the highest lattice parameter (high compressive stresses).

The XRD spectra shows a significant broadening of the diffraction peak (200) in multilayer films. This is due to a decrease in the size of the ZrN crystal layer from 5 to 2 nm, which limits the growth of ZrN grains (Fig. 1). The diffraction peaks of Si_3N_4 were not observed in multilayer CrN/Si_3N_4 films, this shows that the Si_3N_4 phase is amorphous.

In order to estimate microstructural features of CrN/Si_3N_4 multilayer films a microscopic examination of its cross - sections were carried out. TEM investigations of the as-deposited multilayer CrN/Si_3N_4 (5 nm/5 nm) system have shown that the film consisting of the alternating layers of nanocrystalline CrN and amorphous Si_3N_4 is formed as shown in Figure 1.

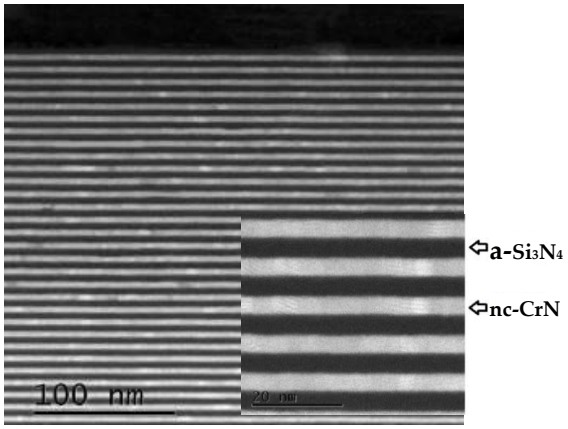


Fig. 1. TEM micrograph of multilayer CrN/a-Si3N4 (5 nm/5 nm) film. HRTEM micrograph of this film is shown in the insert

CrN layers have a polycrystalline microstructure, while Si_3N_4 layers showed no crystalline appearance. Columnar structure extends through the multilayers. The thickness of the layers, according to the TEM data, was 4.7 (CrN) and 4.8 nm (Si_3N_4). Thus, the as-deposited CrN/Si_3N_4 multilayer films are alternating layers of nanocrystalline CrN and amorphous Si_3N_4.

SEM data of the CrN mononitride films irradiated with 40 keV He^{2+} ions in the dose range from 3×10^{17} to 1.1×10^{18} cm^{-2} made it possible to experimentally estimate the critical dose of blister formation (i.e., the dose at which the radiation erosion of surface begins) of 6×10^{17} cm^{-2}. Opened blisters are on the surface of irradiated CrN, as well as a small number of closed ones. The diameter of the blisters varies in the range from 2 to 10 microns.

On the border of large blisters visible craters (opened blisters) of small diameter of about 1.2 microns. An increase in the radiation dose to 1.1×10^{18} cm^{-2} leads to an increase in the number of blisters per surface unit (Fig. 2). The large blisters have small opened blisters with a diameter of 1.2 μm on their border, as well as closer to the center (Fig. 2. Inset).

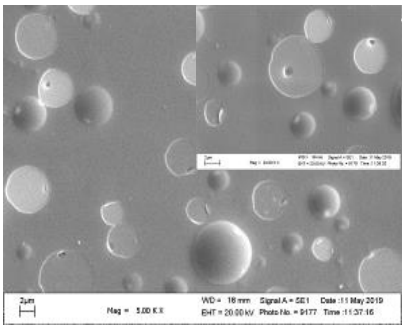


Fig. 2. SEM image of the surface of monolayer CrN films irradiated with He^{2+} ions (40 keV, dose - 1.1×10^{18} cm^{-2})

According to AFM data, two-layer blisters on the CrN surface after irradiation with 40 keV He^{2+} ions are formed. The depth of a large blister located near the surface is about 75 nm, and a small one is 120-150 nm. The diameter of the small blister is 1.2 microns. The total depth of blisters is 195-225 nm and is close to R_p (181 nm) calculated by SRIM program.

In order to evaluate the radiation resistance of the CrN films, the erosion of its surface (the ratio of the area occupied by blisters to the surface area of the film) was calculated (Fig. 3).

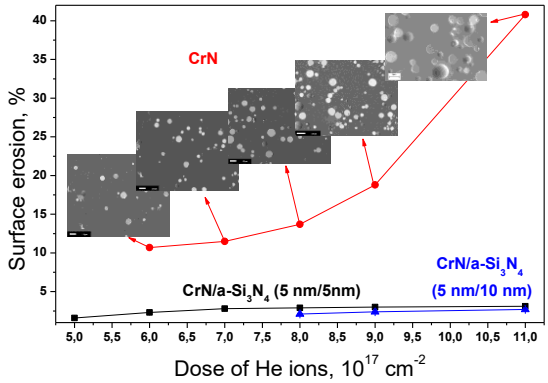
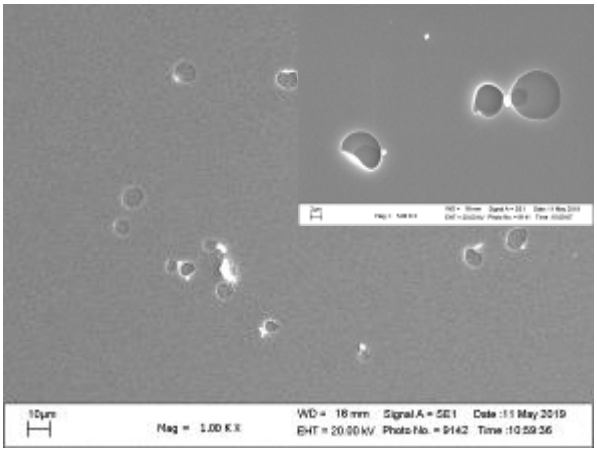


Fig. 3. The dependence of surface erosion on the dose of implantation with He ions (40 keV) of mononitride and multilayer films. Inset SEM micrographs of the surface of the CrN film implanted with He ions with different doses

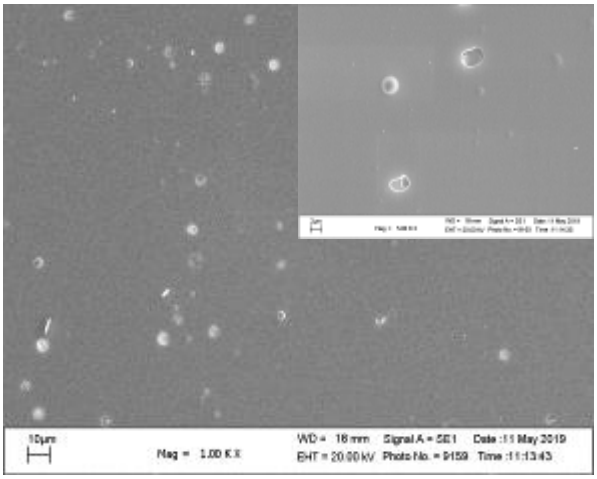
Figure 3 shows that increasing the dose of He implantation from 6×10^{17} to 1.1×10^{18} cm^{-2}, the surface erosion increases from 10.7 to 40.1%.

To study the effect of crystalline/amorphous boundaries on the blister formation, implantation of 40 keV He^{2+} ions into multilayer CrN/*a*-Si_3N_4 films was carried out. SEM studies of the films surface showed no blistering or exfoliation after implantation with He ions and dose less 5×10^{17} cm^{-2}. Blister formation was

found at the dose of 5×10^{17} cm^{-2} for a multilayer CrN/*a*-Si_3N_4 film (5 nm / 5 nm) (Figure 4 *a*). Only opened blisters with a diameter of 7-10 microns are visible on the surface (Figure 6 *a*. Insert). Blisters have an elongated, elliptical shape. Surface erosion is small compared to CrN mononitride and is equal to 1.6% (Fig. 3). An increase in the dose to 1.1×10^{18} cm^{-2} leads to an increase in surface erosion to 3.1%



a



b

Fig. 4. SEM image of: *a* - multilayer CrN/*a*-Si_3N_4 (5 nm/5 nm) *b* - multilayer CrN/*a*-Si_3N_4 (5 nm/10 nm) films after 40 keV He^{2+} implantation with doses of and 1.1×10^{18} cm^{-2}

As in the case of the CrN film in this multilayer CrN/*a*-Si_3N_4 (5 nm/5 nm) film, the blisters have a two-level structure (Figures 4 *a*). The size of the upper part of the blister is 14 μm (ellipsoid blister) and a depth is 260 nm and the bottom one with a diameter of 7.5 μm and a depth of 90 nm.

SEM studies of He^{2+} ions implanted with multilayer CrN/*a*-Si_3N_4 films (5 nm/10 nm) revealed an increased critical dose of blister formation up to 8×10^{17} cm^{-2} (Figure 4 *b*). The blister diameter is 4-7 μm and the surface erosion is 2.1% (Fig. 3). A small amount of closed blisters with a diameter of 1.5-1.7 microns is also present on the surface. The surface erosion slightly increases and reaches 2.7% with a dose of 1.1×10^{18} cm^{-2}. The blister structure is similar to the structure of multilayer CrN/Si_3N_4 film (5 nm / 5 nm): the upper part is 180 nm deep and 4 μm in diameter and the lower part is 95 nm deep and 3.2 μm in diameter.

SEM and AFM studies have shown that a critical dose of blister formation exceeds 1.1×10^{18} cm^{-2} for the multilayer CrN /*a*-Si_3N_4 system (2 nm / 5 nm).

Discussion

The features of blister formation in mononitride CrN and multilayer CrN/Si_3N_4 films implanted with He^{2+} ions (40 keV) at doses up to 1.1×10^{18} cm^{-2} were investigated. It was found, that multilayer films in which the thickness of the amorphous layer exceeds crystalline layer have a higher critical dose of blister formation than mononitride CrN. Surface radiation erosion of the multilayer films is significantly lower than mononitride CrN. The growth of surface erosion of monolayer CrN films was observed with increasing doses of implantation, while surface erosion slightly increased in multilayer films.

Blisters formation in mononitride films is described on the basis of the mechanism of inter-bubble fracture [13], which occurs due to the high overpressure in pores located at depths close to R_p. In accordance with this mechanism, helium-vacancy complexes are formed during He implantation, which are combined into bubbles. At some critical dose and at a depth close to R_p, the bubbles can have enough pressure to coalesce by breaking the film and creating an internal crack. The resulting tensile stress created in the crack region will be directed perpendicular to the crack plane, and, therefore, will tend to expand this plane. If the excess bubble pressures in the bubble layers adjacent to the crack falls well higher these pressures (in the crack), then it seems possible for the difference to be great enough for each individual bubble to break into the crack - in essence each bubble will act as a “microblister”. The overall result will be a wider crack. The process could repeat itself and involve several layers of bubbles. The process would stop when the pressure difference between the gas in the crack and the gas in the bubbles adjacent to the crack was insufficient to allow the microblisters to form. While this process of “unzipping” layers of bubbles is proceeding the pressure in the crack could be sufficient to start deforming the layer of material above the crack to give the final blister cross-section. High pressure in the blister leads to the destruction of blister cup and the formation of cracks in the cup (for plastic materials) or tearing off the cup (for fragile materials).

In our case, the density of blisters in CrN and multilayer films is small, this causes a high pressure in the blister, leading to the destruction of its cups. In mononitride films, an increase in the dose leads to the growth of helium bubbles number and an increase in the surface erosion of the film. The mechanism of blister formation of multilayer films is different due to the presence of amorphous layers. In this case, the formation of blisters occurs due to the fusion of gas bubbles in the amorphous layer. Since the amorphous layers are strong sinks of radiation defects, this does not lead to the formation of bubbles in the CrN crystal layer. Helium-vacancy complexes and their clusters diffuse into amorphous layers and dissolve into them to form gel bubbles. This leads to the swelling of the multilayer film without surface erosion. When the critical concentration of He in the amorphous layers is

reached, helium bubbles combine to form other bubbles with a pressure sufficient to deform the upper layer. The high radiation resistance of the multilayer CrN/a-Si_3N_4 film (2 nm/5 nm) is associated with a large number of amorphous layers separated by a thin crystalline layer that prevents diffusion of helium-vacancy complexes from neighboring amorphous layers.

Thus, multilayer films with a thickness of the amorphous layer exceeding the crystalline layer have an increased resistance to radiation erosion. SEM and AFM studies of mononitride CrN films revealed the formation of two-level blisters. The formation of the bottom blister corresponds to the theory of interbubble fracture. The blister crater depth is close to R_p. Apparently, blister growth process leads to a film rupture and the formation of a crack near the surface (depth - 75 nm) leading to exfoliation of the film (a significant increase in the area of the blister). This leads to the formation of a large blister. In multilayer films, blistering occurs through the exfoliation mechanism, since blister is formed in the amorphous layer. Therefore, blisters of large diameter (3-7 microns) are formed. The formation of the bottom blisters, apparently, is due to repeated exfoliation.

Conclusions

Multilayer CrN/*a*-Si_3N_4 films were formed by reactive magnetron sputtering. The films are alternating crystalline CrN and amorphous Si_3N_4 layers.

It was shown, that multilayer CrN/a-Si_3N_4 films are less sensitive to surface erosion compared to the CrN film.

Multilayer CrN/*a*-Si_3N_4 films (2 nm/5 nm) have a higher critical dose of blister formation (1.1×10^{18} cm^{-2}) compared to mononitride CrN (6×10^{17} cm^{-2}).

The specific features of blister formation in mononitride CrN and multilayer CrN/*a*-Si_3N_4 films implanted with He ions are revealed. They consist in the formation of blisters in mononitrides according to the interbubble fracture mechanism, and the exfoliation mechanism with bubble fusion in amorphous layers in multilayer films.

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