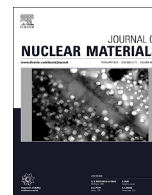
Journal of Nuclear Materials 509 (2018) 408–416

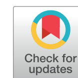
Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat



Thermal stability of uranium nitride and oxynitride films in an ultra-high vacuum environment



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ARTICLE INFO

Article history:
Received 23 November 2017
Received in revised form
14 June 2018
Accepted 14 July 2018

Keywords:
Uranium nitride
Uranium oxynitride
Heat treatment
Thermal stability

ABSTRACT

Uranium nitride ($UN_{1.66}$) and oxynitride ($UN_{1.42}O_{0.23}$) films have been prepared on the substrate of Si by radio frequency (RF) magnetron sputtering. The films have been studied by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Auger electron spectroscopy (AES). Then, vacuum heat treatment of uranium nitride and oxynitride films were in situ investigated in an ultra-high vacuum chamber of AES. The experimental results show that the $UN_{1.66}$ and $UN_{1.42}O_{0.23}$ films fabricated by radio frequency magnetron sputtering method are dense and uniform. The surface of the $UN_{1.66}$ films changes into UN_xO_y at the beginning of the heat treatment. Then the surface changes into UO_2 with the increasing temperature. When the temperature exceeds 573 K, UO_2 phase gradually changes back into UN_xO_y phase due to the out diffusion of decomposed N atom in $UN_{1.66}$ subsurface with increased N content of the surface. $UN_{1.42}O_{0.23}$ film exhibits good stability until 573 K. UN_xO_y and UO_2 mixed phases form on the surface of the $UN_{1.42}O_{0.23}$ after initial oxidation. Owing to the decomposed nitrogen from the $UN_{1.42}O_{0.23}$ subsurface, the UO_2 phase turns back into UN_xO_y again when the temperature exceeds 573 K.

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1. Introduction

Uranium is a chemically active metal, prone to oxidize in atmospheric environment. Uranium oxide film can form on the surface of uranium even under the condition of room temperature and vacuum. In order to improve the corrosion resistance of uranium, usually in the absence of change or reduce its performance, the dense protective film is deposited on the surface of the materials [1–3]. However, the interface between uranium materials and protection film will affect the stability of the structure and properties of uranium materials. On the other hand, surface modification is explored to improve the corrosion resistance of uramium metal. Uranium nitriding treatment can improve the corrosion resistance and the nitride layer can be a smooth transition to the uranium matrix. Raveh et al. [4,5] found that uranium nitride formed on the uranium surface by N_2^+ implantation has considerable protection against corrosion by H_2 and H_2O than that required for untreated uranium metal. Long et al. [6] implanted nitrogen ion into uranium surface forming uranium nitride with plasma immersion ion implantation method. They found that the sample surface had not changed during five months in atmosphere and the dot-corrosion appeared after two months in heat–humid environment. Furthermore, uranium nitride is considered as a potential nuclear fuel for the fast reactors in the generation IV nuclear reactor owing to the high thermal conductivity and high uramium density [7,8]. However, the properties of uranium nitride are much less studied than that of uranium oxide fuel.

In addition, the existence of uranium oxynitride in the process of oxidation is suspected because of the lack of the direct evidence [9–11]. There are few reports about the uranium oxynitride (UN_xO_y) system. Eckle et al. firstly fabricated thin films of UN_xO_y by reactive DC sputtering of metal uramium in an argon atmosphere containing N_2 and O_2 mixtures, and the itinerant 5f character of UN_xO_y was demonstrated [12] and the structure of UN_xO_y was considered to be a solid solution of Nacl-type UO and UN. Carley et al. prepared UN_xO_y from the interaction of NO and NO_2 with clean uranium surface [13]. The present work is motivated by the investigation of thermal stability of uranium nitrides. The

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https://doi.org/10.1016/j.jnucmat.2018.07.032
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theoretical investigation reveals that if the oxygen is introduced to the UN_x, i.e. the ternary UN_xO_y system, the oxidation performance can be improved [10], but further experimental evidence is needed. Also, whether the oxidation mechanism is based on the replacement of nitrogen atoms by oxygen atoms as well as the influence of temperature on the diffusion behavior of oxygen and nitrogen atoms is still need to be investigated.

The oxidation behaviors of uranium and uranium nitride have been extensively studied by X-ray photoelectron spectroscopy and thermogravimetry [14–17]. However, these methods are not suitable and sensitive enough for the detection of surface changes. Our interest is mainly related to the in situ detection and identification of the phase and composition changes during the thermal annealing using AES. The use of AES allows data to be collected more quickly because it has higher sensitivity to light elements, including nitrogen and oxygen. This advantage is of special significance for the study of initial surface oxidation and vacuum thermal annealing. Younes et al. [18] used AES to study the surface oxidation of uranium-niobium alloy in a UHV environment containing primarily H_2, H_2O and CO. Compared to XRD, AES have high depth and lateral resolution, giving access to the distribution and quantification of the uranium nitride films. Besides the elemental information, chemical state information is also very important. It is known that any change in the chemical environment of an atom can have an effect on its Auger peak, e.g. energy shift of the peak, change in the relative intensity of different peaks of the same element, and change in the shape of the peak. The last effect particularly concerns nitrides [19].

In the present study, we have investigated the thermal stability of uranium nitride and oxynitride while annealing at different temperatures by exposing these materials to oxidative residual gases in an ultra-high vacuum environment. The results will be benefit for further understanding of oxidation behavior and thermal stability of uranium nitride and oxynitride.

2. Experimental procedures

Uranium nitride films were prepared by RF magnetron sputtering by changing the partial pressure of Ar/N_2. The detail of RF magnetron sputtering deposition process of uranium nitride films was as follows. Low carbon depleted uranium was used as target with a diameter of 25.4 mm × 3 mm. Si substrates were ultrasonic cleaned with acetone and deionized water for 10 min, transferred into the magnetron sputtering deposition chamber (the base vacuum of 2.3×10^{-7} Pa) after drying. Under the condition of opening mechanical pump, Ar passed to the chamber to clean the pipes, repeating 3 times. Under the Ar partial pressure of 7 Pa, the uranium target was cleaned for 30 min, and the RF power was 100 W. During the process of uranium nitride film deposition, firstly the partial pressure of Ar was reduced to 4 Pa, and then a certain pressure of N_2 was passed through. Finally, the substrate baffle was opened and uranium nitride film was plated on the Si substrate for 1 h by magnetron sputtering. In the process of preparing uranium oxynitride films, a small amount of O_2 was needed at the same time, forming admixture of O_2 and N_2.

The surface morphology and structure of the uranium nitride films were characterized and analyzed by the Sirion 200 scanning electron microscopy (SEM), the Empyrean X-ray diffraction (XRD) and PHI-650 scanning Auger electron spectroscopy (AES). The XRD patterns, for the 2θ range between 25° and 60° with a step of 0.013°, were recorded for freshly prepared uranium nitride and oxynitride samples. Thin Al film was prepared on the $UN_{1.66}$ film against air corrosion before XRD analysis. Uranium nitride and oxynitride samples were detected in the AES analysis chamber to carry out the in situ vacuum heat treatment experiments. The deposited Al layer on the uranium nitride film was sputtered cleanly by Ar^+ with a 5 mm × 5 mm area before the sample was heated and analyzed by AES, while the uranium oxynitride film was not protected by the deposited Al layer. Under 6.5×10^{-7} Pa base vacuum, the annealing temperature of the samples was slowly increased to 773 K, and the atomic percentages of U, N and O elements on the surface of uranium nitride films were analyzed by AES. Finally, the composition and valence state changes of the surface layer during vacuum heat treatment were analyzed via AES in situ analysis.

In order to identify the residual gaseous species in the UHV chamber of AES, under the experimental background atmosphere applied, mass analyses were performed using a residual gas analyser (RGA). The results of these analyses, displayed in Fig. 1, revealed that the UHV atmosphere was mainly comprised of H_2, H_2O, CO/N_2, Ar and CO_2. It should be noted, however, that exposing the clean sample surfaces to this residual gas mixture could lead to some uncertainties in the description of the adsorption and the oxidation reaction processes involved. Residual oxygen come from H_2O/CO_2 and the samples will oxidize in the residual gas.

3. Results and discussion

3.1. Microstructure of uranium nitride films

Fig. 2 shows the SEM and AFM images of the surface of the deposited uranium nitride and oxynitride films deposited on the Si substrate by RF magnetron sputtering. It can be seen that both of the film surface is uniform and compact. The AFM image (scan area: 2 μm × 2 μm) of the uranium nitride film and uranium oxynitride film are presented in Fig. 2c and d, and the continuity of the films can also be observed. The bright and dark spots that present in SEM images is indicative of variation in Z of the different regions of the film.

AES have high surface sensitive (0.5–2 nm) and lateral resolution (less than 20 nm), giving access to the distribution and quantification of the uranium nitride film and uranium oxynitride film. So AES can easily detect the adsorption and the oxidation reaction processes involved with residual gas mixture on the uranium nitride film and uranium oxynitride film. However, the chemical homogeneity should also be proved by the AES analysis. Considering spatial chemical mapping will cost more time than line scanning and avoiding the influence of the adsorption and the oxidation with residual gas mixture. As seen from Fig. 3, AES line scans on the $UN_{1.66}$ film and the $UN_{1.42}O_{0.23}$ film were captured to substantiate the uniformity of the deposited films.

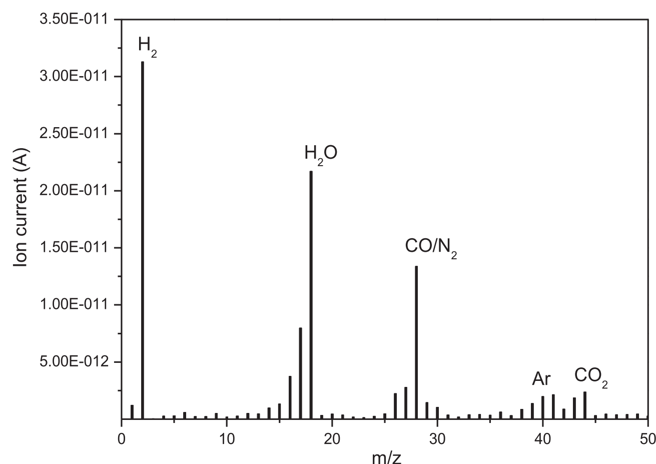

Fig. 1. Ion currents of the residual gases in the UHV chamber of AES.

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