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The effects of deuteration on the nanostructured zirconium films deposited by pulsed laser deposition for nuclear fusion applications

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HIGHLIGHTS

- Zirconium films deposited on Al_2O_3 (0001) substrate by PLD are obtained.
- The effects of deuterium on the resistivity and specular reflectivity of Zr films are investigated.
- The results will be useful to optimize the synthesis conditions for the First Mirror application in fusion devices.

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ABSTRACT

In this paper, zirconium films have been deposited on Al_2O_3 (0001) substrates by pulsed laser deposition (PLD) and then transferred to deuterium atmospheres. We find that the formation of $Zr_{0.38}D_{0.62}$ is under the deuterated temperatures of 923 K. The surface morphologies, electrical features and optical properties of as-grown zirconium films and zirconium deuteride films are systematically investigated as a function of three pulse repetition rates. It is found that the zirconium films show very smooth surfaces and high specular reflectivity. Moreover, exposure of the as-deposited zirconium films to deuterium atmospheres revealed that some pits formed on the surface of films. These defects induced by deuterium make the specular reflectivity and resistance of films change. The results of our investigation will be useful to optimize the environmental conditions for the First Mirror application in fusion devices.

1. Introduction

The optical diagnostics play a crucial role in controlling the nuclear fusion process. These devices (First Mirrors) must be exposed to the harsh environment, such as the high temperature, neutron flux, redeposition and sputtering. For the last few decades, it has been a great challenge to produce metallic films with high specular reflectivity and low sputtering yield. Furthermore, those films with good mechanical and resistance proprieties have drawn great attentions for the fabrication of First Mirrors working in nuclear fusion reactors [1,2]. For First Mirrors fabrications, the control of films structures and proprieties is one of the key issues.

Due to its special structures and proprieties, nanostructured metal films fabricated by PLD have mainly found applications on electrical sensors [3] and optical elements [4,5]. By controlling the laser parameters and experimental conditions, it is easy to obtain suitable crystalline structure and film surface [4,6–7]. Recently, Rhodium films [8,9] and molybdenum thin films [2,10] deposited by PLD have been investigated for the application of First Mirror.

Thanks to its properties such as low thermal neutron cross-section and exceptional corrosion resistance under high thermal load, zirconium is one of the ideal candidates for the exploration of First Mirror in fusion devices application [11,12]. Zirconium thin films have been produced by PLD for the exploration of deposition process [13], formation of zirconium silicide [14], and the First Mirror application in fusion devices [15]. Moreover, deuterium exposure is currently foreseen as one possible cleaning technique to remove the layers caused by the redeposition from the First Mirror, which will cause erosion of the mirror surface [16]. The understanding of the influence of deuterium on the electrical and optical properties is very significant to the applications of fusion devices. To the best of our knowledge, the zirconium films obtained by PLD have only been sparsely reported. Furthermore, the electrical and optical properties of zirconium films and zirconium deuteride films fabricated by PLD are also not clear.

In this paper, the effects of pulse repetition rates on the surface morphologies, specular reflectivity and resistivity properties of zirconium films and zirconium deuteride films are explored. This study is aim to find appropriate process parameters of PLD and

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obtain suitable films with good properties for the nuclear fusion applications.

2. Materials and methods

In our experiments, the nanosecond laser pulse (KrF excimer laser: wavelength 248 nm, pulse duration 25 ns, laser fluence 6.0 J/cm^2) was focused on the zirconium target (purity 99.9%) at an incident angle of 45°. zirconium films approximately of 70–100 nm were produced by PLD on the rolled sapphire substrates (Al_2O_3 (0001)). The deposition process was carried out under the substrate temperature of 473 K and at the base pressure of about 1×10^{-5} Pa. The pulse repetition rate (2, 5, 8 Hz) was varied to investigate the surface morphology, reflectivity and resistivity of zirconium films and zirconium deuteride films. To reduce the drilling of target, the zirconium target was also rotated continuously at a constant rate of 12 rpm. Before every experiment, the zirconium target was cleaned by 5000 laser shots to remove the surface contaminations. After every deposition process, the zirconium films were then degassed and loaded in deuterium atmospheres, respectively. Exposures on zirconium films were carried out for time periods of 4 h under the temperature of 923 K.

The microstructures of the zirconium films were identified by grazing-incidence X-ray diffraction (GIXRD). The morphologies were characterized by scanning electron microscope (SEM). Secondary ion mass spectroscopy (SIMS) was introduced to learn about the existence of deuterium element. A UV–vis–NIR PerkinElmer Lambda 1050 spectrophotometer was used to obtain the specular reflectivity of films. The four-point probe method was introduced to test the resistance variation of films during the process of deuteration.

3. Results and discussions

Fig. 1(a) displays the XRD patterns of the films unloading and loading deuterium. The zirconium film deposited at 5 Hz (films deposited at other pulse repetition rate are not showed in the patterns) is crystalline and all diffraction peaks are present. Compared with a standard bulk zirconium PDF card (JCPDS pattern #05-0665), the diffraction peaks of zirconium film are consistent with α zirconium phase. In Fig. 1(a), an apparent preferential orientation in the (110) direction is observed for the zirconium film. The X-ray diffraction study of the films loading deuterium has confirmed the existence of $Zr_{0.38}D_{0.62}$. Through the standard JCPDS cards and literatures [17,18], we confirm that the phase of $Zr_{0.38}D_{0.62}$ is face-centered-tetragonal structure. To get the information about the existence of deuterium, the SIMS experiments had been done for the sample unloading and loading deuterium. As showed in Fig. 1(b), the results are obtained by sputtering under the flux of oxygen. Fig. 1(b) indicates that the existence of deuterium is undoubtedly. The results obtained in Fig. 1 make the discussions processed in the next section significant.

In Fig. 2(a–f), the surface morphologies of as-deposited films are showed. Through the direct view, the films with very compact and smooth surface are depicted in Fig. 2(a–c). It is well known that the droplets formed on the surface of films during the deposition process cannot be avoided. In Fig. 2, some droplets are visible on the surface of as-deposited films. Due to its complex physical process during the target ablation and plasma plume expansion, the mechanism of the formation of droplets is still not clear.

By controlling the laser parameters, such as pulse repetition rate and laser fluence, the films with fewer and smaller dimensions of droplets on the surface can be obtained. In Fig. 2(a–c), we find that the films reveal a smooth surface with fewer liquid droplets compared with the molybdenum films [10] and Rhodium films [8] deposited by PLD.

In order to further study the effect of deuteration on the surface morphology of zirconium films, three samples are exposed to the deuterium atmosphere of 3000 Pa. The images of zirconium deuteride films are shown in Fig. 2(d–f). After the process of deuteration, some wrinkles and pits are formed on the surface of films and the surfaces become coarser. With increasing pulse repetition rate, the average diameter of theses pits increases obviously. During the process of deposition in the PLD, the droplets can be ejected from the target and mixed with the plasma plume [19].

In previous work, we found the dimension and density of the droplets increase with an increasing pulse repetition rate [13]. We suppose that the zirconium thin films are formed layer by layer through the mixture of plasma plume and droplets. The surfaces of the films are sparsely covered by droplets, and most of the droplets on the zirconium films vary in size from 10 nm to 300 nm. Because of their similar structure to bulk martial, these droplets (high purity zirconium) can react preferentially with deuterium during the process of deuteration. The volumes of zirconium deuteride droplets expand compared to zirconium droplets and the internal stress between the droplets and films become more intense. Because of above reasons, those droplets are easily striped off the surface of films, left wrinkles and pits (Fig. 3). In Fig. 3(a), it is observed that the maximum diameter of the pits is about 300 nm. It is well known that the hydrogen atoms can diffuse into the films and occupy the interstitial space, defects and crystal

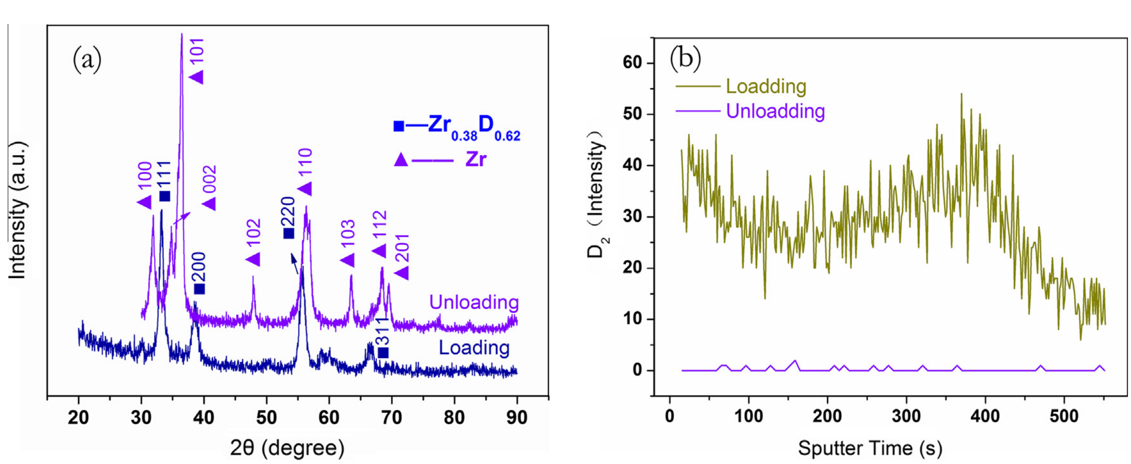

Fig. 1. XRD patterns of the films unloading and loading deuterium (a) and the SIMS results of Zr and deuteration elements by using the flux of oxygen (b).