Thin Solid Films 636 (2017) 658–663

Contents lists available at ScienceDirect

Thin Solid Films

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

Structural and compositional characterization of single crystal uranium dioxide thin films deposited on different substrates

Mohamed S. Elbakhshwan *, Brent J. Heuser

Department of Nuclear, Plasma, and Radiological Engineering, University of Illinois Urbana Champaign, USA

ARTICLE INFO

Article history:
Received 18 October 2016
Received in revised form 7 July 2017
Accepted 8 July 2017
Available online 10 July 2017

Keywords:
Uranium dioxide
Magnetron sputtering
Thin film
Single crystal
X-ray diffraction
Different substrates
Peak splitting

ABSTRACT

Uranium dioxide thin films were deposited on single crystal TiO_2, Al_2O_3, YSZ, ZnO and $NdGaO_3$ substrates to optimize conditions for the growth of high quality single crystal films. X-ray diffraction results show that all the films have one growth direction and well defined peaks in the specular scans with the expected symmetry for each growth orientation. The UO_2/Al_2O_3, TiO_2, and ZnO films have high concentration of misfit dislocations that increase with the lattice mismatch. The UO_2 film on YSZ is found to be in registry with the substrate. The film has narrow mosaic component that is imposed upon a broader component arises from the diffuse scattering due to defects in the film. Meanwhile, $UO_2/NdGaO_3$ film shows a splitting of the X-ray diffraction peaks which is attributed to the in-plane asymmetry of the orthorhombic substrate.

1. Introduction

Uranium dioxide properties have been intensely studied over decades because it the main fuel in nuclear power plants. Most of the studies were performed on bulk and powder samples however there were few attempts to study UO_2 properties in the thin film geometry deposited by various growth methods.

The first known trial to grow thin film of UO_2 was done by Bierlein et al. using vacuum evaporation [1]. They deposited the films on carbon substrate to study radiation damage in nuclear fuel. The evaporation technique was also used in several other studies and for various applications [2–6]; Birjega et al. evaporated polycrystalline UO_2 thin film on three types of NaCl substrates; pure, and doped with Pb or Ag to study the effect of adding impurities to the substrate on the film structure [7]. Shoichi et al. prepared polycrystalline UO_2 thin films on NaCl substrate to study the He ions energy loss in UO_2 [8].

Chemical vapor deposition was used by Shiokawa et al. to grow UO_2 thin films on quartz substrates [9]. They deposited polycrystalline α-U_3O_8, UO_{2+x} ($x > 0.25$), and U_4O_9 at different growth conditions. Amorphous UO_2 was grown from solution on Fe foil by Qiu et al. but several U_4O_9 peaks appeared after annealing [10]. Sol-gel technique was used to deposit films on sapphire and MgO substrates by Meek et al. to study the optical properties of intrinsic and doped UO_2 [11]. Polycrystalline UO_2 thin films were grown at room temperature on Ni substrates using electrodeposition by Adamska et al. [12].

The growth of single crystal UO_2 thin films on a substrate was reported for the first time by Burrell et al. [13] using polymer-assisted chemical solution deposition to grow single crystal UO_2 thin film on $LaAlO_3$ substrate [13,14]. The XRD spectra showed that the film had a strong (100) peak and small (111) peak with intensity <2% relative to the (100) peak.

Sputtering techniques were employed in several studies to grow the thin films. Navinsek used cathode sputtering to grow fine grained polycrystalline and nearly perfect single crystal UO_2 thin films on sodium chloride crystals [15]. Low crystalline UO_2 thin films were deposited on quartz substrate by Miyake et al. [16]. Miserque et al. deposited films on polycrystalline gold disc, single crystal Si, and amorphous glass substrates [17]. Chen et al. succeeded to grow preferentially oriented UO_2 thin films with (111) planes on Si (111) substrate, and also noticed that the crystallinity of the film increased with the thickness [18].

In 2012, we successfully deposited single crystal UO_2 thin films on YSZ and sapphire substrates using reactive gas magnetron sputtering [19]. Our study showed that the change in the oxygen partial pressure can lead to the formation of single crystal UO_2, U_4O_9 and U_3O_8. Following that, we studied the change in the mechanical properties of the thin films under heavy ion irradiation and high temperature and results were similar and relevant to data collected using bulk nuclear fuel samples [20]. This work will open the doors for further research on the usage of thin films as a surrogate for nuclear materials.

* Corresponding author.
E-mail address: elbakhs1@illinois.edu (M.S. Elbakhshwan).

http://dx.doi.org/10.1016/j.tsf.2017.07.020
0040-6090/

The reactive gas magnetron sputtering technique was later adapted in several studies; Bao et al. deposited single crystal UO_2 films on $LaAlO_3$ and CaF_2 substrates to study the magnetic properties [21]. Teterin et al. deposited single crystal and preferentially oriented UO_2 thin films on YSZ and LSAT substrates with different crystallographic orientations [22]. Springell et al. deposited (001), (110) and (111) single crystals UO_2 to study the interfacial interactions between water and spent nuclear fuel [23]. Popel et al. used it to study radiation damage in nuclear fuel [24–27], and finally Cakir et al. used it to study the thorium effect on the oxidation states of UO_2 thin films [28].

The current study shows the ability to grow single crystal UO_2 thin films in various crystallographic orientations by depositing the UO_2 on TiO_2, Al_2O_3, YSZ, ZnO, and $NdGaO_3$ single crystal substrates using the magnetron sputtering technique.

2. Experimental procedure

We deposited Uranium dioxide thin films on different substrates using reactive gas magnetron sputtering [29]. Argon ions were used as a sputtering gas at partial pressure of 8.3×10^{-2} Pa. The sputtering process performed at the current controlling mode, the ion current was fixed during the whole process at 0.056 mA while the power and voltage were around 20 W and 352 V respectively. Before the deposition, the substrates were annealed at 400 °C for two hours followed by another two hours annealing at 750 °C, while the temperature was kept at 700 °C and oxygen partial pressure of 1.3×10^{-5} Pa during the deposition. The substrates were kept rotating at 60 RPM to insure uniform heat distribution and the growth rate was around 6.2 Å/s.

Thin films were deposited simultaneously on five different single crystal substrates which were all oxides to avoid anion diffusion through the film-substrate interface; TiO_2, r-plane Al_2O_3, YSZ (8%moleY_2O_3), ZnO (C-plate), and $NdGaO_3$. All substrates were supplied by MTI Corporation, USA, except Al_2O_3 substrate was supplied by Crystal Gmbh, Germany. Substrates were selected to have different crystal structures and a broad range of lattice parameters as summarized in Table 1.

The film structure and thickness were investigated by X-ray diffraction (XRD) and X-ray reflectivity (XRR) using Philips X'pert machine of Cu K_α radiation of wavelength 1.54056 Å. Fitting of the XRR measurements was performed using the REFLFIT software package from the National Institute of Standards and Technology. Furthermore, Rutherford backscattering (RBS) was done using High Voltage Engineering Van de Graaff accelerator with 2 MeV He^+ ions and the spectrum was fitted using SIMNRA software package [30].

3. Results

The UO_2 thin films were deposited on substrates that have different crystal structure and a broad range of lattice parameters. They have smaller and larger than the lattice parameter of UO_2 (5.47 Å) which has a fluorite crystal structure and space group of Fm3m [31]. The structural and compositional properties of the thin films deposited on each substrate are summarized as follow:

Table 1
Substrate structure and properties.

Substrate	Crystal structure	Orientation
TiO_2 (Rutile)	Tetragonal $a = 4.59$ Å, $c = 2.95$ Å	(100)
Al_2O_3 (*r*-plane)	Hexagonal $a = 4.77$ Å, $c = 13.04$ Å	$(1\bar{1}02)$
YSZ (8% mole Y_2O_3)	Cubic $a = 5.125$ Å	(100)
ZnO (*c*-plate)	Hexagonal $a = 3.25$ Å, $c = 5.31$ Å	(0001) O-face polished
$NdGaO_3$	Orthorhombic $a = 5.43$ Å, $b = 5.50$ Å, $c = 7.7$ Å	(100)

3.1. TiO_2 substrate

The TiO_2 (Rutile) substrate is a single crystal with (100) orientation. It has a tetragonal crystal structure and a space group of p42mnm with lattice parameters of $a = 4.59$ Å and $c = 2.95$ Å [32], as summarized in Table 1. The epitaxial relation between the substrate and the deposited film indicates that the UO_2 lattice is rotated by 26.6° degrees with respect to the surface normal, with d spacing of $(a^2 + c^2)^{1/2} = 5.45$ Å, which fits the UO_2 (100) plane with $a = 5.47$ Å. Therefore, the UO_2 lattice is found to be under compression of −0.3% with respect to the substrate.

XRD shows that the UO_2 thin film deposited on TiO_2 substrate has single (220) growth orientation as shown in Fig. 1. The in-plane ϕ scan shows a broad but well defined peaks with two-fold symmetry for the (110) reflections of the fluorite UO_2 as shown in Fig. 2. The mosaic of the UO_2 film is investigated using the rocking curve scan. The film has a broad mosaic width with FWHM of 5.09, as shown in Fig. 3, indicating that the UO_2 film is not in register with the TiO_2 substrate due to the large difference in the lattice parameters. However the XRD (out-of-plane) and in-plane ϕ scans show that the film is a single crystal. This is an indication that the film has a lot of low-angle tilt boundaries due to the high dislocation density [19].

XRR shows that the film is smooth and uniform with a thickness of 370 Å as shown in Fig. 4. Furthermore, RBS measurement shows that the film-substrate consists of three layers; an oxygen rich layer on the film surface due to air exposure, a stoichiometric UO_2 layer, and finally the substrate. No interdiffusion was observed through the film-substrate interface.

3.2. Al_2O_3 substrate

A single crystal *r*-plane sapphire substrate with $(1\bar{1}02)$ orientation was used for the deposition of UO_2 films. It has a hexagonal crystal structure with a space group of R3c and lattice parameters of $a = 4.77$ Å and $c = 13.04$ Å, as summarized in Table 1.

The deposited film is found to have a single growth orientation of (200) as shown in Fig. 1, with four-fold symmetry in the in-plane ϕ

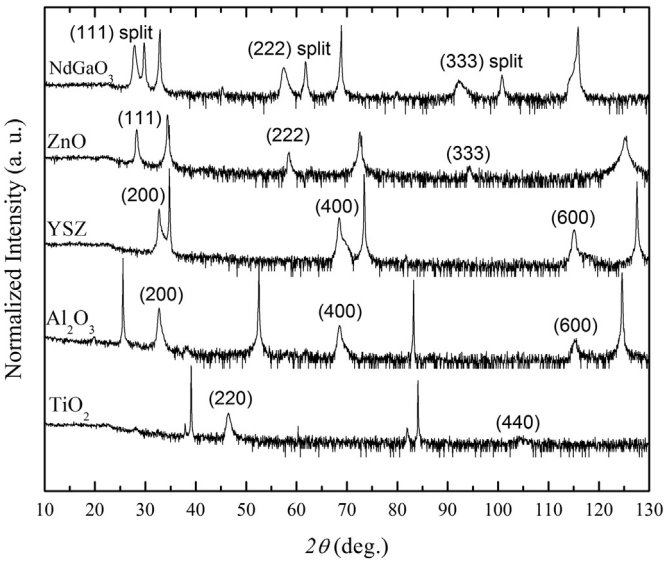

Fig. 1. X-ray diffraction patterns for UO_2 thin films on TiO_2, Al_2O_3, YSZ, ZnO, and $NdGaO_3$ single crystal substrates. The unmarked peaks are for the substrates.