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Epitaxial UN and α-U_2N_3 thin films

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ABSTRACT

Single crystal epitaxial thin films of UN and α-U_2N_3 have been grown for the first time by reactive DC magnetron sputtering. These films provide ideal samples for fundamental research into the potential accident tolerant fuel, UN, and U_2N_3, its intermediate oxidation product. Films were characterised using x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS), with XRD analysis showing both thin films to be [001] oriented and composed of a single domain. The specular lattice parameters of the UN and U_2N_3 films were found to be 4.895 Å and 10.72 Å, respectively, with the UN film having a miscut of 2.6°. XPS showed significant differences in the N-1 s peak between the two films, with area analysis showing both films to be stoichiometric.

1. Introduction

Uranium mononitride, UN, is of significant interest to the nuclear industry due to its high melting point, high uranium density, and improved thermal conductivity in comparison to uranium dioxide, UO_2 [1]. In addition to the enhanced thermal conductivity, providing an improved accident response, the 40% higher uranium density of UN allows for lower enrichment or higher fuel burn-up [2]. Despite these known advantages, there are still many material properties of UN yet to be fully investigated, in particular, there are concerns over the rapid oxidation of UN in water [3, 4, 5]. This oxidation reaction has been shown to progress with the formation of a U_2N_3 interlayer between UN and UO_2, making it also of interest [6, 7]. A better understanding of this oxidation process, as well as fundamental fuel properties, such as thermal conductivity and irradiation performance, is required for UN to be considered as a viable accident tolerant fuel (ATF). Consequently, this area of research has had a renewal of interest, with several recent experiments utilising thin film samples [8, 9, 10].

Thin films provide an ideal way to research these properties, with their enhanced surface sensitivity being optimal for investigating surface reactions such as oxidation and hydrolysis, and ability to produce highly controlled samples, allowing for single variable investigations. These experiments improve fundamental understanding of materials and provide experimental data comparable to theoretical calculations which are of particular importance in an area of research that is restricted as a result of radioactivity. In addition, thin films contain such little radioactive material that they do not require dedicated facilities and are more likely to be classed as exempt from radioactive material transport regulations.

Polycrystalline UN and U_2N_3 films have previously been grown by reactive DC magnetron sputtering and epitaxial thin films of UN_2 have been grown by polymer assisted deposition [11, 8, 12]. However, prior to this study there have been no reports on the successful deposition of epitaxial UN and U_2N_3 films. It is noted that while the fabrication of bulk single crystal UN is documented, there have been no prior reports of single crystal U_2N_3 [13]. The ability to grow epitaxial UN and U_2N_3 thin films will therefore contribute to the advancement of ATF research, providing idealised samples on which to conduct fundamental material behaviour studies.

2. Experimental details

The films were grown in a DC magnetron sputtering system at the University of Bristol with 10^{-8} mbar base pressure, in-situ reflection high-energy electron-diffraction (RHEED), and substrate heating to 1200 °C, with the temperature at the substrate position calibrated using a pyrometer. The system uses 5.5 N argon at 0.7 Pa as the main sputtering gas, and houses a target of depleted uranium, producing deposition rates in the range of 0.5–1.5 Å/s, with a power density of 2.5 W/cm^2, at a distance of 200 mm from the substrate.

A partial pressure of 5.5 N N_2 is used to reactively deposit nitride films, with the pressure determining the phase deposited, as shown by Black et al. [11]. Polycrystalline samples were grown at room temperature to optimise the N_2 partial pressure required to deposit single

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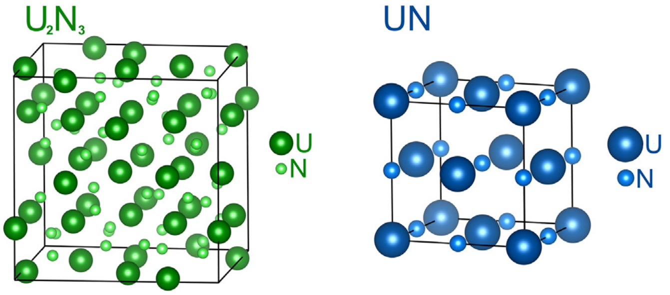

Fig. 1. Model of U_2N_3 an UN unit cells.

phase films of UN and U_2N_3, 2 mPa and 90 mPa, respectively, similar to that of Black et al.

In order to grow single crystal films, compatible substrates with epitaxial matches were chosen and heated during deposition. Substrates that did not contain oxygen were sought to prevent oxidation of the deposited nitride. The substrates used were 10 mm × 10 mm, supplied by MTI corporation, single sided polished to 1–3 Å root mean square (RMS) roughness and mechanically mounted onto sample holders.

Cubic [001] CaF_2 was used as the substrate to epitaxially deposit U_2N_3 in the [0 0 1] direction at 700 °C. It was selected as its bulk lattice parameter of 5.463 Å has only a 2.3% mismatch with that of α-U_2N_3 with a 1:2 relation [14]. Bulk α-U_2N_3 has a cubic bixbyite structure, with bulk lattice parameter of 10.678 Å, as shown in Fig. 1 [15].

Bulk UN is face-centred cubic with a lattice parameter of 4.890 Å, as shown in Fig. 1. It was matched to Nb in the (001) plane with a $1:\sqrt{2}$ relation and 45° rotation, Nb also being cubic with a lattice parameter of 3.300 Å [16, 17]. UN [0 0 1] was grown on a Nb [0 0 1] buffer layer on a Al_2O_3 [1 $\bar{1}$ 0 2] substrate, with the Nb layer acting as both a chemical buffer, protecting the UN layer from oxidation, and physical buffer, improving the epitaxial match. The Nb buffer and UN film were deposited at 800 °C and 500 °C, respectively.

All samples were deposited for 600 s and capped with a 50 Å layer of polycrystalline Nb or Au, deposited at room temperature, to prevent oxidation of the uranium nitride layers.

X-ray diffraction (XRD) and x-ray reflectivity (XRR) measurements were performed using a Philips X'Pert diffractometer with a Cu-Kα source. Specular and off-specular 2θ-ω, ω (rocking curves), and ϕ (azimuthal rotation) XRD scans were performed to investigate the crystallinity and epitaxy of the deposited films. XRR was used to measure the thickness and roughness of film layers and determine deposition rates.

XRD scans were fitted analytically using GenX software, which uses a differential evolution algorithm to optimise the fit [18]. The GenX reflectivity package, which models scattering length density as a function of depth, was used to fit XRR measurements and obtain layer thickness and roughness values.

X-ray photoelectron spectroscopy (XPS) measurements were performed at the Bristol NanoESCA facility, which employs a monochromatic Al x-ray source (1486.7 eV) and a ScientaOmicron XPS Argus analyser, and has an overall energy resolution of < 300 meV using a pass energy (PE) of 6 eV. The instrument houses a 0.5–1 keV Ar sputter gun, which was used to remove the capping layer on samples before taking measurements. Survey scans were taken with a PE of 50 eV, before scans of the N-1 s and U-4f states were taken with a PE of 6 eV. Peaks were calibrated using the Fermi edge and further analysed using the CasaXPS software [19].

3. Results

3.1. Structural characterisation

The XRR measurements and fits of the [0 0 1] U_2N_3 and UN samples are shown in Fig. 2. XRR data was fitted by modeling electron density as a function of depth though the sample, as shown in the inset in Fig. 2. From the fits, it was found that the [0 0 1] U_2N_3 sample comprised of a 310 Å U_2N_3 layer and 50 Å Au cap, whereas the [0 0 1] UN sample was found to have a 600 Å UN layer, and 120 Å and 40 Å Nb buffer and cap respectively. These values and the RMS roughness of each layer can be found in Table 1.

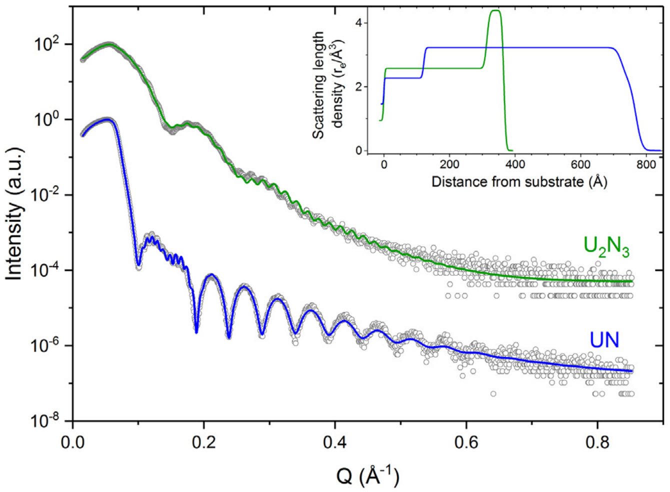

Fig. 2. XRR scans and fits, as a function of Q, the momentum transfer wavevector, of the U_2N_3 and UN samples, shown in green and blue, respectively, with the scattering length density plot obtained from the fit inset. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

RMS roughness of the CaF_2 and Al_2O_3 substrates obtained from XRR fitting are 1.6 Å and 2.7 Å, respectively. Though XRR is only sensitive to electron density in the specular direction, not structural or diffusive boundaries, these low roughness values show that any interaction region that is present must be small.

Fig. 3 shows the specular 2θ-ω XRD scans of the [0 0 1] U_2N_3 and UN samples, aligned to the specular film peaks. It can be seen that in U_2N_3 film, grown on CaF_2, only the (0 0 4) and (0 0 8) reflections of U_2N_3 and (0 0 4) reflection of CaF_2 are visible, showing the film is highly oriented in this direction. The same is true of the UN film grown on a Nb buffer on Al_2O_3, with only the (002) and (0 0 4) reflections of UN and (0 0 2) reflection of Nb visible. From these reflections, it was calculated that the U_2N_3.

c lattice parameter (in the specular direction) is 10.72 ± 0.01 Å and the UN c lattice parameter is 4.895 ± 0.001 Å.

The rocking curves or ω scans of specular reflections in both the U_2N_3 and UN samples are shown in Fig. 4, and the FWHM ($\Delta\omega$) of the fits shown in Table 1. The rocking curve of the (0 0 4) U_2N_3 reflection is very sharp, with a FWHM of only 0.03°, even narrower than the FWHM of the CaF_2 (0 0 4) substrate curve of 0.12°. A low intensity, broad component is also present in this curve, but not seen in that of the CaF_2 substrate, showing that there are areas of the U_2N_3 layer not completely commensurate with the substrate.

In the UN sample, both the Nb buffer and UN layer have broad rocking curves of 1.22° and 1.73° respectively, while the substrate curve is much narrower. These large values show that the film layers are not in complete registry with the layer below.

While the specular XRD scans shows only the orientation of this film perpendicular to the surface plane, the in-plane orientation of the [0 0 1] U_2N_3 and [0 0 1] UN samples can be seen in the ϕ scans shown in Figs. 5 and 7 respectively.

The clear ϕ dependence of the off-specular U_2N_3 (2 2 6) reflection shown in Fig. 5 indicates that there is a single domain present in the film. Though not displayed, the off-specular CaF_2 reflections showed that the U_2N_3 film is oriented in the same direction as the substrate. This is depicted in the model of the (0 0 1) planes of each of these in