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Real structure and magnetic properties of UN thin films

D. Rafaja[a,b], L. Havela[b,*], R. Kužel[b], F. Wastin[c], E. Colineau[c], T. Gouder[c]

[a] *Institute of Physical Metallurgy, Freiberg University of Mining and Technology, Gustav-Zeuner-Str. 5, D-09599 Freiberg, Germany*
[b] *Department of Electronic Structures, Charles University, Ke Karlovu 5, CZ-12116 Prague 2, Czech Republic*
[c] *European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany*

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Abstract

Uranium nitride thin films were prepared by reactive sputter deposition at temperatures between −200 and +400 °C. These conditions provided a large variety of microstructure. At low temperatures, nanocrystalline layers (mean crystallite size 17 nm) grew with a strong preferred orientation {1 1 1} perpendicular to the substrate, with a large compressive residual stress and with a high density of structure defects (i.e. with large microstrain). At elevated temperatures, the crystallites had only a moderate preferred orientation; the residual stress was partly relaxed and the density of structure defects lower. For the first time, for an actinide material, we have investigated how the microstructure influences the formation of magnetic moments and magnetic ordering. Bulk UN is an itinerant antiferromagnet. The increasing disorder suppresses the long-range antiferromagnetism and induces a ferromagnetic component in exchange interactions, leading to a cluster glass type of ordering at low temperatures. In highly disturbed thin films (low temperature deposition), UN exhibits a weak Pauli paramagnetism.

Keywords: Magnetic films and multilayers; Nanostructures; X-ray diffraction; Magnetic measurements

1. Introduction

Amorphous and nanocrystalline magnetism has been studied so far mainly in cases relevant for technical applications, i.e. in ferromagnets based on 3d or 4f elements. The 5f magnetism of light actinides, which can be characterized as narrow-band magnetism with large orbital moments, was not investigated systematically yet. As to fundamental interest, the insight in the 5f magnetism obtained by possibility of variable disorder is rather intriguing.

From scarce existing information on the influence on non-crystallinity on the 5f magnetism, a part was obtained when studying systems with potentially large magnetooptical rotations [1–4], including multilayers containing actinide components. These studies indicated that both critical temperatures and types of magnetic ordering can differ substantially in amorphous and crystalline phases. In particular, even compounds known as antiferromagnets (e.g. UAs) exhibit ferromagnetism in the amorphous phase. Critical temperatures are, as a rule, lower in the amorphous phase. This is also the conclusion of the study [5], deducing a considerable reduction of the Curie temperature T_C in the amorphous ferromagnet UGa_2.

Thin film deposition techniques enable samples to be prepared with very different amount of structure defects (grain boundaries, lattice strain, dislocations, etc.) depending on the deposition conditions. We have been using the reactive sputter deposition to produce thin actinide films, mainly for photoelectron spectroscopy studies [6,7]. Results obtained on the U–N system were presented in [8]. In the present work, we report on the relationship between the real structure of UN layers deposited at various conditions and their magnetic properties.

According to the U–N phase diagram [9], three uranium nitride phases are thermodynamically stable below 400 °C, namely UN, α-U_2N_{3+x} and UN_2. Two of them (UN and UN_2) are line compounds, i.e. phases with a very narrow homogeneity range. The intermediate phase α-U_2N_{3+x} exists actually in the range from $UN_{1.54}$ to $UN_{1.75}$. The stoichiometric UN crystallises within the cubic space group $Fm\bar{3}m$ [10] (lattice parameter $a = 4.8897$ Å [11]). The crystal structure of the next nitrogen-richer phase, α-U_2N_{3+x}, is also cubic, having the space group $Ia\bar{3}$ [10]. Its lattice parameter is ranging between 10.628 and 10.682 Å depend-

* Corresponding author. Tel.: +420-224261265; fax: +420-224261265.
E-mail address: havela@apollo.karlov.mff.cuni.cz (L. Havela).

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ing on the nitrogen content (higher nitrogen content leads to a smaller lattice parameter [10–12]). The nitrogen-richest phase UN_2 crystallises within the space group $Fm\bar{3}m$ [10] and with the lattice parameter $a = 5.301$ Å [11] (original work [10] gave $a = 5.31$ Å). In single-phase samples, the non-stoichiometric phase α-U_2N_{3+x} with ordered vacancies could be clearly distinguished from the stoichiometric phase UN_2 [13].

In the process of the reactive sputtering, the composition of the uranium nitride thin films (the UN/U_2N_3 ratio) can be adjusted via the N_2/Ar ratio in the working atmosphere [8].

UN is known to undergo antiferromagnetic ordering with the Néel temperature $T_N = 53$ K. A small ordered moment $(0.75 \pm 0.1)\mu_B$/U at $T = 12$ K [14] and a moderate γ-coefficient of the low temperature specific heat of 25 mJ/mol K^2 [15] point to an itinerant character of UN magnetism. The susceptibility behaviour in the paramagnetic range can be characterized by the Curie–Weiss (CW) law with the effective moment $\mu_{eff} = 2.66$–$2.76\,\mu_B$/f.u., while strong antiferromagnetic interactions are reflected by a large negative paramagnetic Curie temperature $\Theta_p = -247$ K [16].

2. Experimental

Thin films of uranium nitrides were deposited by a reactive DC sputtering at various substrate temperatures T_s ranging from −200 to 400 °C. Employing in-situ photoelectron spectroscopy, the parameters of the deposition process were tuned to obtain approximately stoichiometric UN. The photoelectron spectroscopy was also used to check the stoichiometry of the thin films after finishing the deposition process, whereas the phase composition of the films was concluded from X-ray diffraction (XRD). Typical deposition parameters are the target voltage −800 V and the ion current 2.5 mA. The plasma was maintained by injecting electrons with energy between −50 and −100 eV emitted from a heated thoriated tungsten filament. The deposition rates of the order of 0.1 nm/s led to about 1 mg of material deposited in 2–3 h. One additional deposition at $T_s = -200$ °C was undertaken with a higher ion current (7 mA) to see the influence of the ion current on the microstructure of the thin film.

As a substrate we used Spectrosil quartz glass, which exhibits diamagnetic susceptibility independent of temperature and magnetic field. Thus, its magnetization can be easily subtracted in the magnetization measurement. The mass of the substrate and that of the deposited material were determined, using an electronic microbalance with a resolution of 0.01 mg.

XRD experiments were performed at room temperature on an XRD-3003 diffractometer (Seifert) in the parallel beam geometry. Radiation of the Cu anode was made parallel by means of a parabolic Goebel mirror (graded multilayer). Radiation diffracted by the sample was detected by a scintillation detector; a good angular resolution was guaranteed by a Soller collimator with the acceptance angle of 0.4° and by a flat graphite monochromator inserted in the diffracted beam. Basic microstructure parameters (stress-free lattice parameter, residual stress, crystallite size and microstrain) were obtained from detector scans performed at a small angle of incidence of the primary beam with respect to the sample surface (3°). Small angle of incidence reduces substantially the penetration depth of the radiation into the bulk of the sample; this is a typical geometry used to increase the contribution of the thin surface layer to the total diffracted intensity. In selected samples, the detector scans were carried out for several angles of incidence (2°, 6° and 10°), which enables to check the depth homogeneity of the thin films [17].

Supplementary diffraction measurements were performed to investigate the preferred orientation of crystallites and the anisotropy of the lattice deformation. The preferred orientation was quantified by the width of the Ω-scans (sample scan at a constant detector position), because the texture was fibre-shaped as typical for thin films. Anisotropy of the lattice deformation was investigated, using the $\sin^2\psi$ method [18] applied to different diffraction lines.

3. Results

3.1. Microstructure of UN thin films

In all uranium nitride thin films under study, the cubic face-centred UN was the dominant phase. Since UN is a line compound, a coexistence with neighbouring phases is anticipated if the nitrogen content differs from 50 at.%. In all our samples, UN co-existed with a small amount of the nitrogen-richer phase α-U_2N_{3+x}. Its amount was ranging approximately between 5 and 20%, depending on the partial pressure of nitrogen in the working atmosphere. Analysis of the diffraction patterns taken at the constant angle of incidence yielded the stress-free lattice parameters, residual stress, microstrain and crystallite size in all phases. Measurements performed at different penetration depths (with different angles of incidence) did not reveal any gradient of the above microstructure parameters in the films. Thus, we concluded that the thin films grew homogeneously from the substrate to the top.

The stress-free lattice parameter and the residual stress were calculated from the dependence of individual lattice parameters on the function $\sin^2\psi$ [19], where ψ denotes the current inclination of diffracting planes from the sample surface. The individual lattice parameters were determined from positions of individual diffraction lines, which can be done for cubic structures. The isotropic Poisson ratio and Young modulus, $\nu = 1/3$ and $E = 220$ GPa, were taken from Ref. [20] The stress-free lattice parameter was higher than the “bulk” value (4.8897 Å [3]) in all our samples. A slight decrease, observed with increasing substrate temper-