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# Structure and magnetism of thin UX layers

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**Abstract**

US layers (thickness 0.1–0.3 μm) were prepared by sputter deposition from US target in Ar atmosphere at temperatures 298–573 K. For US thin films, magnetism tends to be suppressed comparing to the bulk US, which is a band ferromagnet with $T_C = 177$ K. $T_C$ decreases down to 85–105 K for the layers deposited at room temperature (depending on the deposition parameters) and increases with the increase of the temperature of substrate. Spontaneous magnetization in the ordered state is suppressed considerably for the deposited layers: down to 0.1 $\mu_B$/f.u. or less for all samples studied (compare with 1.55 $\mu_B$/f.u. for bulk US). The changes in the magnetic properties are correlated with the microstructure of the films. Microstructure studies indicated that the US thin films contain a mixture of "nanocrystalline" and "amorphous" parts. The crystallite size in the nanocrystalline parts is approximately 100 Å. In all samples, a compressive residual stress was observed, which caused a strongly anisotropic lattice deformation with the easy deformation direction {1 1 1}. The compressive residual stress was below −3 GPa in most samples. Results are compared with UN layers synthesized by reactive sputtering.
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## 1. Introduction

Amorphous and nanocrystalline materials on the basis of 3d- and 4f-elements attract a considerable attention due to their application potential. The 5f-materials are so far mainly matter of a fundamental interest—studies of nanocrystalline materials bring information on the influence of atomic disorder and of microstructure details on magnetism of actinide compounds. Few studies undertaken so far reveal very dramatic effects. The magnetic properties of bulk and amorphous or nanocrystalline 5f materials differ substantially: in the few documented cases, the suppression of ordering temperatures, magnetic moments or even vanishing of magnetic ordering was observed [1]. In general, still very little information exists on 5f systems in conditions of nanocrystalline and amorphous structures. Because of the very specific character of magnetism in light-actinide intermetallics, we cannot take it as simply analogous to the d-magnetism, although it has essentially an itinerant character, and a systematics remains to be explored.

Two compounds with the NaCl-structure type, UN and US, have been chosen as objects for such studies. As reported previously [2], in the case of UN (the bulk form is antiferromagnetic, $T_N = 53$ K [3]), magnetic behaviour of the deposited layers shows a strong dependence on synthesis conditions, such as the temperature of substrate. For UN thin layers, no anomaly around 50 K is observed. If deposited at the temperature $T_d = 293$–573 K (the deposition temperature $T_d$ is the temperature of substrate), their suscetibility exhibits a small ferromagnetic component developing gradually below $T \approx 100$ K, which can be attributed to the not fully compensated antiferromagnetic moments at grain boundaries and/or at numerous structure defects. Decreasing $T_d$ leads to the suppression of the ferromagnetic component, which can be explained as due to the suppression of the local magnetic moments of uranium. For $T_d = 673$ K, an anomaly appears around $T = 50$ K, which can be associated with incipient bulk antiferromagnetism of UN.

Microstructure studies of such sputter-deposited (reactive sputtering) thin layers of UN revealed preferred

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orientation with the direction {1 1 1} perpendicular to the substrate, which gets more pronounced at lower deposition temperature $T_d$, a large compressible residual stress, and a high density of structure defects (i.e. large microstrain).

In the present work, we compare the results obtained on UN with those obtained on ferromagnetic US thin films, prepared by sputtering from a US target. US crystallizes with the space group $Fm\bar{3}m$ (lattice parameter $a = 5.484$ Å). The compound is characterized by a narrow homogeneity range (≈2 at.%) in the binary phase diagram U–S [4]. US is a band ferromagnet with $T_C = 177$ K and ordered magnetic moment of 1.55 $\mu_B$/U at. [5].

## 2. Experimental

The US thin films were prepared by dc sputtering from a US target in Ar atmosphere. The substrate temperature was varied in the range 298–573 K. The in situ photoelectron spectroscopy was used to check the stoichiometry of the thin films after the deposition process. A very weak oxygen contamination and the absence of other elements prove that we deal indeed with US, and the observed variations of physical properties have to be attributed to specific features of the structure. Typical deposition parameters are the target voltage 730–750 V and the ion current about 0.5 mA. The average thickness of the layers obtained under such conditions is 0.1–0.3 μm.

Similar to the UN films, Spectrosil quartz glass was used as a substrate. It exhibits diamagnetic susceptibility independent of temperature and magnetic field. And therefore, the values of magnetization could be easily corrected for the substrate magnetization. The mass of the substrate and of the deposited material was determined using an electronic microbalance with a resolution of 0.01 mg.

The microstructure study of the US thin films was done using the glancing angle X-ray diffraction (GAXRD) at the angle of incidence of the primary beam of 3° on XRD-3003 diffractometer (Seifert). The radiation of the copper anode ($\lambda = 1.5418$ Å) was used for the measurement. A divergent primary beam (the divergence was approximately 1°) was diffracted by the sample; the angular resolution of the detector was defined by a long Soller collimator with an acceptance angle of 0.4° and by a flat graphite monochromator. The small angle of incidence (3°) reduces substantially the penetration depth of the radiation into the bulk of the sample, what increases the contribution of the thin film to the total diffracted intensity.

Supplementary diffraction measurements were performed to investigate the preferred orientation of crystallites and the anisotropy of lattice deformation. The preferred orientation was quantified by the width of the Ω-scans (sample scan at a constant detector position), because we expected a fibre-shaped texture as found earlier for UN thin films [2]. Anisotropy of the lattice deformation was investigated using the modified $\sin^2\psi$ method [6] applied to different diffraction lines. It is based on the assumption that crystallites are deformed by the residual stress depending on their orientation with respect to the substrate. Stress-free lattice parameters can be determined for the direction, in which the compression along the substrate is just compensated by the expansion perpendicular to it. The mean crystallite size, $D$, and microstrain (fluctuations of the lattice parameters), $e$, were determined using the Willianson–Hall analysis of the integral line broadening, $\beta$:

$$\beta = \frac{1}{D} + 4e\frac{\sin\theta}{\lambda}$$

where $\theta$ is a diffraction angle and $\lambda$ is the wavelength of the radiation.

Magnetic susceptibility of US thin films was studied in various magnetic fields; the SQUID magnetometer (Quantum Design) was used for dc susceptibility measurements. The ac susceptibility (to determine $T_C$ in low magnetic fields) was measured using the PPMS system (Quantum Design).

## 3. Results

In all samples under study, the cubic phase of US was found. No other crystalline phase was observed, but the US thin films consist probably of a mixture of "nanocrystalline" and "amorphous" parts. The nanocrystalline regions contribute to the broad diffraction lines, the "amorphous" regions to the diffuse scattering (the latter absent for UN). The latter is obvious in the low-angle region of the XRD patterns (see Fig. 1). The crystallite size in the nanocrystalline parts is approximately 100 Å. In all samples, a large anisotropy of the lattice deformation was observed, similarly to that in UN [2]. The easy deformation direction was again {1 1 1} as typical for fcc systems—for details, see Ref. [7]. This anisotropy is extremely strong in the samples deposited at room temperature at lower deposition rates and at $T_d = 200$ °C.

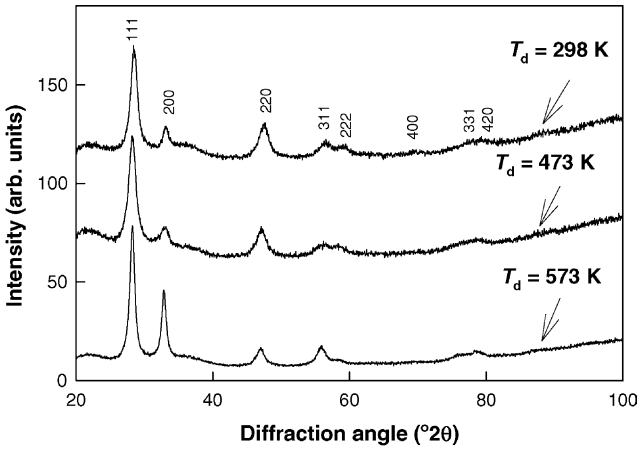


Fig. 1. X-ray diffraction patterns of US thin films deposited at various temperatures. Diffraction lines are labelled by diffraction indices.

Table 1
Microstructure parameters and Curie temperatures of the US thin films deposited at different substrate temperatures ($T_d$) and ion currents ($I$)

| $T_d$ (K) | Deposition current (mA) | Stress-free lattice parameter (Å) | Residual stress (GPa) | Crystallite size (Å) | Microstrain ($10^{-3}$) | $T_C$ (K) |
|---|---|---|---|---|---|---|
| 298 | 1.10 | $5.389 \pm 0.006$ | $-2.3 \pm 1.0$ | 90 | 7.6 | 105 |
| 298 | 0.50 | $5.469 \pm 0.035$ | $-3$ (?) | 80 | 6.2 | 94 |
| 298 | 1.35 | $5.447 \pm 0.048$ | $-1$ (?) | 180 | 16.5 (?) | 85 |
| 473 | 0.45 | $5.430 \pm 0.018$ | $-2.8 \pm 2.0$ (?) | 95 | 9.1 | 113 |
| 573 | 0.50 | $5.439 \pm 0.006$ | $-2.2 \pm 1.0$ | 100 | 8.5 | 117 |
| Bulk | – | 5.484 | – | – | – | 177 |

The results marked with question marks should be taken as semi-quantitative.

The anisotropy of the lattice deformation is usually enhanced by a large compressive residual stress and by a strong preferred orientation of crystallites [7]. The compressive residual stress was found in all samples, but the values were rather low, below $-3$ GPa, in most cases (see Table 1). The samples are almost texture-free (or have a very weak preferred orientation of crystallites) with the exception of the sample deposited at the room temperature at the lowest deposition rate, which shows the $\{1\,0\,0\}$ texture. The stress-free lattice parameters are smaller than the intrinsic lattice parameter of the uranium sulfide ($a = 5.484$ Å). A possible reason could be a slight departure from the expected stoichiometry of the samples.

Magnetization measurements indicated that the magnetism in the US films tends to be suppressed with respect to the bulk compound. No anomaly was observed at 177 K (bulk $T_C$). Instead we found ferromagnetism at lower temperatures, depending on $T_d$. $T_C$ decreased down to 85–105 K for the layers deposited at room temperature (depending on the rate of deposition) and grew with the increase of $T_d$ (see Table 1). The observed temperature dependence of the magnetic susceptibility is characteristic for a two-phase system, in which one phase is a temperature-independent paramagnet (tentatively associated with the amorphous phase), while the other one is ferromagnetic with a lower ordering temperature than in the bulk samples (Fig. 2).

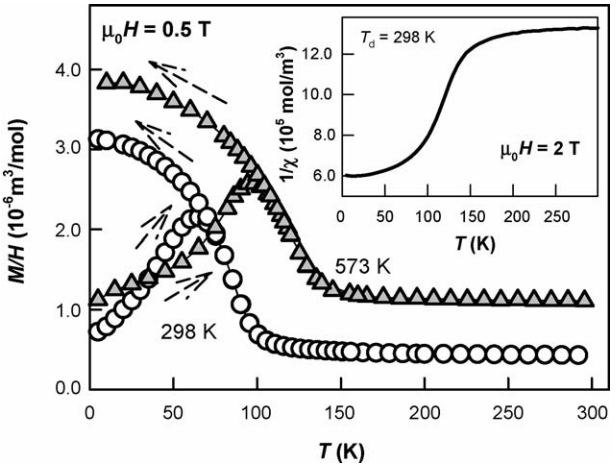


Fig. 2. Temperature dependence of magnetic susceptibility of US layers synthesized at $T_d = 573$ K (full triangles) and at 298 K (empty circles) in 0.5 T. Arrows indicate the regime of the measurement (field cooled or zero-field cooled). The inset shows the temperature dependence of inverse magnetic susceptibility of the US thin film ($T_d = 298$ K) measured in 2 T.

Also the spontaneous magnetization is considerably suppressed in the deposited thin films: its value is below 0.1 $\mu_B$/f.u. for all samples under study (compare with 1.55 $\mu_B$/f.u. for bulk US [5]), but there is relatively large high-field susceptibility. We may assume that only a part of the suppression is due to the presence of amorphous non-magnetic phase.

## 4. Discussion and conclusions

In contrast to the UN thin films, no straightforward relationships between the synthesis conditions, microstructure details and magnetism have been found for US layers, although the magnetic properties depend on the temperature of deposition also in this case. The amount, size, shape and distribution of the "amorphous" domains as very important microstructure parameters could not be investigated by XRD. The lowest Curie temperature is for the samples prepared at room temperature and gradually increases with increasing deposition temperature. The value of magnetic susceptibility in the paramagnetic region also increases with increasing $T_d$. Assuming that the amorphous phase is a temperature independent paramagnet, we may speculate that the fraction of the amorphous phase increases for the higher $T_d$.

Another possible reason for the magnetism weakening may be the small observed reduction of the stress-free lattice parameters. However, the comparison of the results with the high-pressure studies of US [8,9] shows that such a volume change corresponds to a decrease of the Curie temperature of 2 K only. Although the effect of compressive residual stress is different from that of hydrostatic pressure, we deduce that it cannot be reason for the dramatic suppression of $T_C$, observed in US layers.

We can summarize that unlike for UN films, we did not observe any dramatic difference between the microstructure parameters for the samples synthesized at different

conditions: the grain size is approximately 100 Å, the residual stress is less than −3 GPa (much lower than for the UN) and there is typically no preferred orientation of the crystallites. The strong anisotropy of the lattice deformation was found in all samples with the easy deformation direction {1 1 1}, which is also typical for other nitrides crystallizing with the NaCl structure, e.g. TiN or UN [2,9].

The behaviour of US thin layers partly follows the behaviour of UN thin layers (weakening of magnetism, easy deformation direction {1 1 1}), but other microstructure parameters (residual stress, microstrain, grain size) have different tendencies. The possible reason can be found in different mechanism of deposition.

Based on the results obtained we can conclude:

- US thin layers consist of two phases—nanocrystalline, which is ferromagnetic and amorphous, which is presumably nonmagnetic.
- Largely reduced magnetization at low temperatures points to a reduction of the uranium moments even in the nanocrystalline phase (influence of the disturbed crystallite boundaries) and to a glassy character of the magnetism (frustration due to large microstrain).
- Unlike for UN, in which the evolution of the 5f magnetism is related to the real structure (i.e., the deviation from the ideal crystallinity), the direct dependence of the Curie temperature on the microstructure parameters has not been established yet in US.

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