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Thin layers in actinide research

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Abstract

Surface science research at the ITU is focused on the synthesis and surface spectroscopy studies of thin films of actinides and actinide compounds. The surface spectroscopies used are X-ray and ultra violet photoelectron spectroscopy (XPS and UPS, respectively), and Auger electron spectroscopy (AES). Thin films of actinide elements and compounds are prepared by sputter deposition from elemental targets. Alloy films are deposited from corresponding alloy targets and could be used, in principle, as replicates of these targets. However, there are deviations between alloy film and target composition, which depend on the deposition conditions, such as pressure and target voltage. Mastering of these effects may allow us to study stoichiometric film replicates instead of thick bulk compounds. As an example, we discuss the composition of U–Ni films prepared from a UNi_5 target. © 1998 Elsevier Science S.A.

Keywords: Photoemission spectroscopy; Electronic structure; Thin films; Sputter deposition

1. Introduction

Surface science studies of actinides and actinide compounds are motivated both by fundamental and applied aspects. On the one hand, the specific bonding situation at the surface, in particular the decreased coordination, results in systems of a highly interesting electronic structure. On the other hand, the surface constitutes the contact part between the solid and the environment. Thus, material exchange, corrosion and dissolution reactions, interdiffusion, etc., which all influence the handling and disposal of nuclear systems, take place at the surface and depend on its properties. Thin films are particularly well suited to do research in these two areas. They allow to prepare overlayers of known thickness and texture, and thus give a good control of atom coordination and electronic structure. They allow preparation of off-stoichiometric compounds, impurity doping and variation of defect concentrations, which are used in the study of nuclear waste behavior. They give access not only to the solid–gas interface, but also to the overlayer–bulk interface, which may be studied by surface spectroscopies because it is covered only by little material. Chemical interdiffusion and the stability of actinide-containment material systems may thus be investigated as a function of temperature and corroding conditions.

In this paper we report first on the preparation of thin films and, in this part, concentrate on UNi_5 alloy films. In the second part we discuss the role of thin films in the study of the electronic structure of actinides. As an example, we present a study of U films on Mg and Al, and Pu films on Al.

2. Synthesis of actinide thin films and study of their composition

Thin films are prepared by the sputter deposition technique, which is preferred to evaporation because of the high chemical reactivity and low vapor pressures of the actinide metals. Working with actinides requires use of small target samples, and excluded common commercial magnetron sputter deposition devices. We developed, instead, a triode source, where the argon plasma is produced and maintained by energetic electrons (50–200 eV) emitted from a ring electrode close to the target. The target itself does not play an active role in maintaining the plasma, which gives us freedom in choosing its size, shape and position. Target discs of 4 mm diameter and 0.5 mm thickness were used at pressures of 5×10^{-3} T argon, which makes the device entirely UHV compatible. Films of a fraction of a monolayer up to several microns in thickness were produced, with a high purity. We barely observed some Ar incorporation during the sputter process. Oxides, nitrides, etc., are produced by adding a reactive gas to the plasma. To a certain extent the composition of such compounds may be controlled by the partial pressure

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of the reactive gas. Recently we investigated the ability of sputter deposition to prepare thin film replicates of multicomponent targets. This appears to be a particularly important aspect. If sputter deposition produces stoichiometric replicates of complex materials, surface science investigations could be performed without cleaving or scraping the bulk materials, which allow only a very limited number of measurements to be performed on one sample. We did initial experiments using UNi_5 targets, which had been studied earlier as bulk compounds [1]. We investigated the film composition as a function of Ar pressure, which seems to be the decisive factor.

Fig. 1 shows the evolution of the film surface composition with pressure, monitored by comparison of the Ni_{LMM} (60 eV)/U_{OVV} (75 eV) Auger, and the Ni2p/U4f XPS intensity ratios. The two studies differ by their information depth. The Auger measurements are very surface sensitive with an information depth of 1.2 monolayers, in contrast to the XPS lines with an information depth of about 6 monolayers. All values in Fig. 1 have been normalized using the corresponding values of scraped samples. Both spectroscopies show films to be strongly enriched in Ni at low pressures, while at highest pressures they are enriched in U. But the variation of the Ni surface concentration is more pronounced for the more surface-sensitive AES. This indicates that the films are not homogeneous, but the variation of composition is strongest at the top surface. There are two possible explanations for this: either there is only a top surface enrichment in Ni, with the film itself being stoichiometric, and the less surface-sensitive XPS shows a composition closer to stoichiometry. Or, in addition to some surface enrichment, there is a also variation of the film composition. To solve this we did a depth profiling experiment on the UNi_5 films to see whether removal of the top layers made the films more stoichiometric. This was actually the case, and shows that surface reorganization under the influence of the plasma is responsible for an enrichment in Ni.

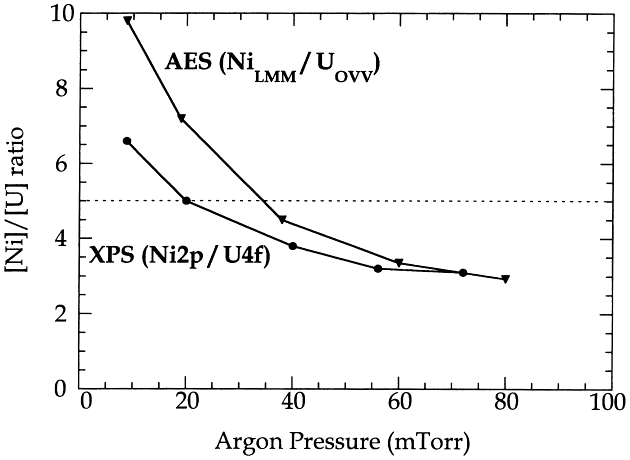

Fig. 1. U–Ni film composition as function of Ar pressure, as measured by AES (Ni_{LMM}/U_{OVV} intensity ratio) and XPS (Ni2p/U4f intensity ratio). All values have been normalized on those measured in scraped UNi_5 bulk compounds.

3. Electronic structure of thin films of actinides

Thin films are particularly interesting for the study of the electronic structure of actinides. Due to the lower coordination of actinides atoms inside the film, the 5f bandwidth is further decreased. This may even go to a point where the 5f electrons become localized, i.e. they no longer participate in the chemical bonding. Thin layers, or eventually clusters, show matter in the transition from solid state bonding to isolated atomic like behavior, and this transition can be expected to occur earlier for the more atomic-like, i.e. spatially restrained, 5f levels. Correlation effects can thus be expected to be emphasized, and it is interesting to follow the evolution of photoemission signals during that process. The electronic structure of thin films is also influenced by the chemical interaction between the overlayer and the underlying substrate. In a first approximation, we expected strong overlayer–substrate interactions to favor 5f delocalization, because it may compensate for the reduced U–U intralayer bonding in the overlayer. If the interaction is too weak, however, U surface atoms will agglomerate to form big clusters, which may acquire bulk-like properties and thus again favor 5f delocalization.

3.1. U on Mg and Al

To further investigate the influence of the substrate we prepared thin films of U on Mg and Al. These main group elements have weak UPS-VB signals of their own, and thus spectra of the U overlayers may be taken without strong background signals. Mg and Al exhibit very different bonding behaviors towards U. Al strongly interacts with U, forming the UAl_2 intermetallic compounds, while Mg does not interact with U at all. Mg and U are immiscible.

Fig. 2 shows U4f spectra of U overlayers on Mg, deposited at room temperature. In all cases the $U4f_{5/2}$ peak lies at 388.4 eV binding energy, which is typical for U metal. For thick overlayers the 4f peak is sharp and asymmetrical. It shows the usual step-like inelastic background (BG) at higher BE, produced by photoelectrons originating from deeper inside the bulk. The asymmetry comes from e–h pair excitation of conduction electrons at the Fermi level, and its extent depends directly on the density of state at the Fermi level [2]. For the light actinides, the DOS at E_F is dominated by 5f states, and a high asymmetry of core levels thus shows a high 5f DOS at E_F and points to a small width of the 5f band. U films in Mg are missing the correlation satellite, which is generally observed in highly correlated U systems, at about 6 eV higher BE than the main line. This satellite is found in heavy fermion materials [3], but also in UPd_3 [4], and thin films of U on Pd [5] and Pt [6]. The U films on Mg behave

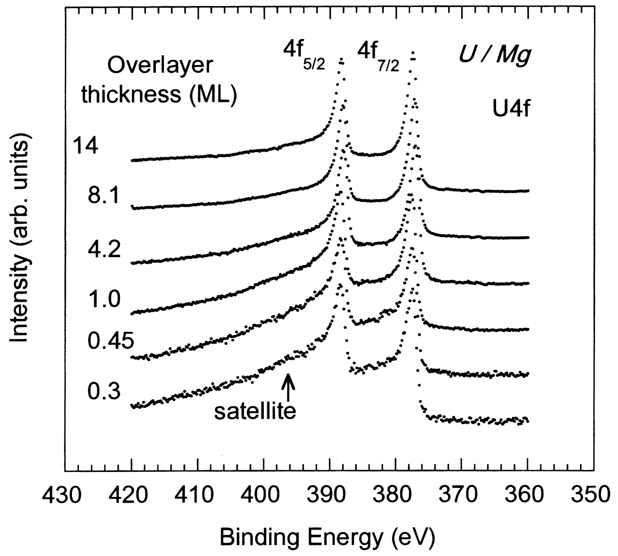

Fig. 2. U4f spectra of thin films of U on Mg.

very much like U metal, where the satellite is missing, too. As the overlayer thickness decreases, the inelastic background also decreases. At low coverage there are no U4f photoelectrons from deeper inside the bulk, which are mainly responsible for the inelastic background. This shows that all U atoms stay at the surface, and thus U–Mg interdiffusion does not take place.

Fig. 3 shows U4f spectra of thin U films an Al. For thick overlayers, the U4f spectra are similar to that of U bulk metal, with the sharp asymmetrical U4f line, the step-like background and the absence of correlation satellites. As the overlayer thickness decreases, the U4f peak moves to higher BE. Since this shift was not observed for U/Mg is has to be attributed to U–Al bonding. Even at low coverage, there is an inelastic background pointing to U–Al interdiffusion. The additional peaks at 405 and 395 eV binding energy, which increase at low coverage, are partially explained by bulk and surface plasmon losses of the U4$f_{7/2}$ peak, by comparison with electron energy loss spectra (EELS) taken on the same materials. However, part of the 395 eV is attributed to the 6 eV correlation satellite of the U4$f_{5/2}$ peak, because the corresponding 6 eV satellite of the U4$f_{7/2}$ peak is observed weakly at 384 eV BE.

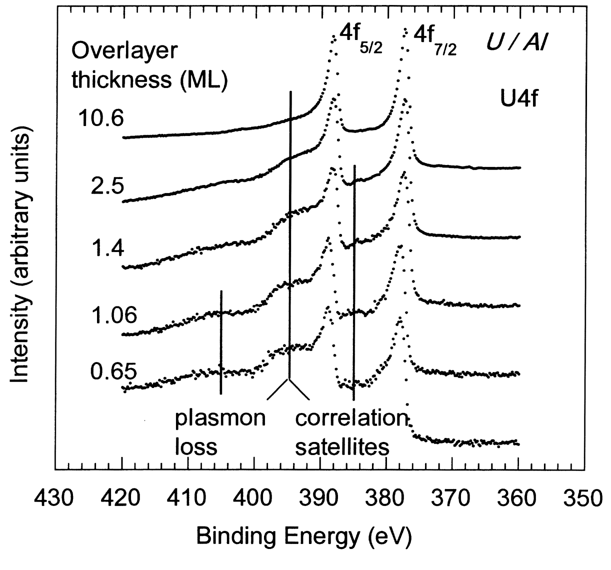

Fig. 3. U4f spectra of thin films of U on Al.

The correlation satellite shows band narrowing to take place for U–Al, while it is virtually missing for U–Mg, and this is explained as follows. U5f delocalization is favored both by direct U5f–U5f interactions and by U5f hybridization with the valence orbitals of the substrate. In alloys, direct U5f–U5f interactions are suppressed with increasing dilution of the actinide, and the bonding to the other elements may only weakly involve the 5f levels. This dilution effect is responsible for the small 5f band width in heavy fermion systems. On the surface, dilution translates as even dispersion of actinide atoms with decreased actinide–actinide bonding. When choosing a weakly interacting system one sacrifices this dilution/dispersion effect. If the interaction is too weak a stable bulk phase may not be formed and U–substrate intermixing does not occur, and on the surface cluster agglomeration takes place. Above a critical size these clusters will manifest bulk-like properties and direct f–f overlap, which would explain the absence of correlation effects in U4f levels of U/Mg. Dispersion/dilution seems to be more efficient in enabling localization than restricted bonding at the surface, which the system counteracts by favoring U agglomeration, thus minimizing the free energy at the surface. The correlation satellite thus may originate from surface U or from U atoms diluted in the near surface region.

Fig. 4 compares UPS-VB spectra of U metal, and thin U films on Mg, Al and graphite [7]. In all cases the spectra display a maximum emission at the Fermi level (E_F), attributed to the U5f peak. Its position at the Fermi level shows the U5f electrons to be delocalized. For U metal the peak at the Fermi level is fairly broad, while for the thin films on Mg and Al it is sharper. Sharpening seems to reflect the 5f band narrowing, and would be an initial state effect. There are no (final state) correlation satellites or supplementary structures between 0.5 and 2 eV BE, which are often observed for the U narrow band system [8]. In addition, the spectra of U/Al and U/Mg look virtually identical for similar coverages. The situation is very different for U on graphite. Here, an additional peak appears at 0.6 eV BE. It is most probably due to a correlation satellite, and shows that in this case 5f band narrowing is more pronounced than in U/Mg and U/Al. Graphite has been shown to have an affinity which lies between Mg and Al. While it is rather inert, modification of its electronic structure takes place at the graphite–U interface, as shown by C1s core level spectra [7]. This points to a weak bonding interaction, which would favor dispersion of U atoms on the graphite surface. Cluster

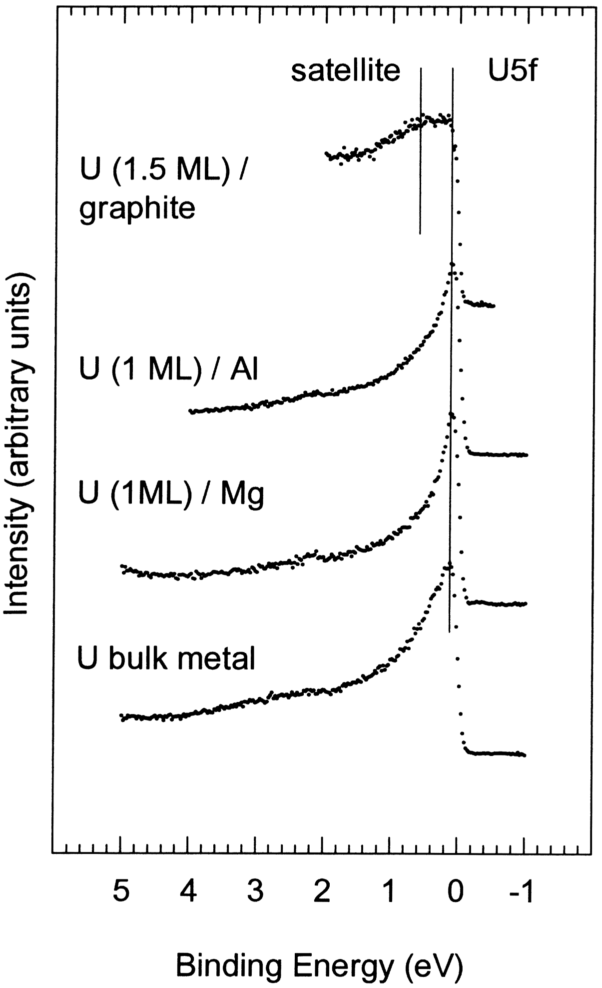

Fig. 4. UPS-HeII spectra of thin films of U on Mg, Al and graphite, and a UPS-HeII spectrum of a U bulk sample.

formation, which favors 5f delocalization, would thus be suppressed. Correlation satellites are also observed for the U4f core level data of U/graphite. To summarize the UPS data, we think that Al has a too strong binding interaction with U, thus favoring 5f delocalization in spite of U dispersion. Mg has a too weak interaction, and thus cluster formation takes place. Graphite seems to have the right affinity, favoring U dispersion but not involving the U5f electrons in bonding.

3.2. Pu on Al

Thin films of Pu have been deposited on Al. The films were of high purity, as checked by XPS and UPS. The signal of oxygen, the major contaminant on metallic actinide surfaces, is almost below detection limits. Pu is the actinide element, where localization effects should be observed most easily. It is right at the localization threshold, and the next higher actinide element, Am, has localized f electrons. Pu itself is present in different crystallographic phases, which differ in the degree of f delocalization, as shown, e.g. by measurements of the electronic specific heat. In particular the δ-phase shows an increased degree of localization, which was also seen in the XPS 4f core level spectra [9] and UPS 5f valence band spectra [10]. If localization effects can be produced in thin films, Pu should thus be the best element to observe them. Fig. 5 shows 4f spectra of Pu thin films on Al. Both the $4f_{5/2}$ and $4f_{7/2}$ lines present two peaks. The one at low BE (Fig. 5b) is attributed to the well screened or f-screened peak, while the high BE energy line (Fig. 5a) is attributed to the poorly screened (or ds-screened) peak [9]. If f electrons are well delocalized, they efficiently screen the photohole, and the intensity of the f-screened peak will be elevated. If, however, the f electrons become more localized, d-screening becomes more important and the high BE peak increases in intensity. Simple comparison of the two peaks thus gives a first hint to the degree of f delocalization. Fig. 5 shows that at low overlayer thickness the intensity of the well-screened peak decreases, which thus indicates that the f electrons become more localized. It should be noticed, however, that even for thick films the intensity of the well-screened peak does not reach that of α-Pu metal but stays smaller, at the level also observed in δ-Pu metal [9]. This would indicate that the structure of the films formed by sputter deposition is similar to δ-phase. At this stage we found indications that the exact height of the f-screened peak depends on conditions of sputter deposition (Ar pressure, target voltage, electron energy), which can be easily understood because surface reorganization may take place under the action of the plasma and depends on the properties of the plasma. Fig. 6 shows the corresponding UPS valence band spectra. Spectra do not resemble α-Pu, which has a maximum emission at the Fermi level. They can be understood when comparing the following systems with increasing degree of 5f localization: U [11], α-Pu [12], δ-Pu [10], Am [13]. Valence band spectra of U show a maximum emission, just at the Fermi

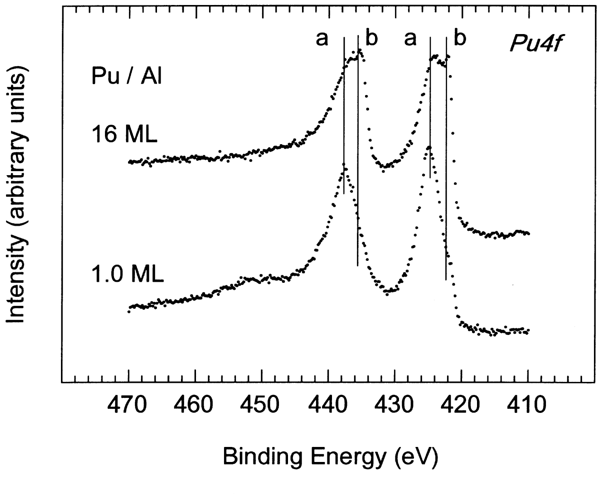

Fig. 5. Pu4f spectra of thin films of Pu and Al; (a) d-screened peak, (b) f-screened peak.

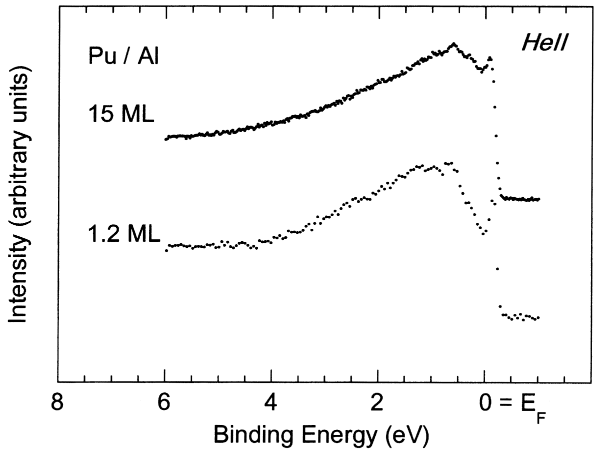

Fig. 6. UPS-HeII spectra of thin films of Pu on Al.

level, followed by an almost structureless decreasing tail at high BE. Spectra are understood in terms of a 5f emission at the Fermi level, and the absence of any final-state satellite at higher BE. In α-Pu, there is still a maximum at the Fermi level, but structures appear on the high BE tail, and may be attributed to final-state satellites. In δ-Pu, the emission at the Fermi level narrows, becoming a sharp pin, and the final-state satellites further increase in intensity. In Am, the emission at the Fermi level is suppressed, being neither a maximum nor a pin, and the entire f emission is shifted to higher BE and has a multiplet structure of a localized 5f photohole, thus showing the 5f electrons to be localized. Pu thin films seem to fall between δ-Pu and Am. There is still a sharp pin at the Fermi level, which is attributed to 5f emission. But the global intensity at the Fermi level is suppressed, with the spectral weight being shifted to higher BE, almost like in Am. This indicates a more pronounced f localization, and is in agreement with Pu4f core-level study. Let us also emphasize that the 5f emission looks similar to that of Pu_2O_3, except for the complete absence of the intense O2p peak. In Pu_2O_3, partial oxidation of the Pu results in collapse of the 5f orbitals and localization. For thin films, similar localization effects seem to be produced by the decreased coordination at the surface. These are preliminary results, and the exact influence of the surface phase and cluster formation remains to be studied in more detail.

Comparing the results from the U and Pu thin films, we conclude that localization effects are strong in Pu films, whereas in U films only weak effects have been observed. There is a clear influence of the substrate, as seen for the U films. Future work will concentrate on Pu films. In particular, we will investigate temperature-induced reorganizations of the films and overlayer–substrate interactions. Ultimately ordered films of Pu metal on single crystalline substrates will be investigated.

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