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Surface reactions and bulk diffusion of U overlayers on Pd

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Abstract

Thin layers of U on polycrystalline Pd and Pd(100) have been prepared by magnetron sputter deposition at room temperature. Mode of growth, annealing-induced surface rearrangement, bulk diffusion, reactivity towards CO and O_2, and surface electronic structure have been studied by Auger electron spectroscopy, X-ray photoelectron spectroscopy and UV photoelectron spectroscopy. At low coverages the U 5f electrons are localized and the reactivity is suppressed up to the point where CO dissociation becomes and activated process. The U stays on the top surface where it is atomically dispersed. At higher coverages U becomes reactive as shown by the spontaneous U–Pd interdiffusion and the dissociation of CO. O_2 always reacts with the surface oxidizing U to UO_2 and annealing always triggers diffusion of U into Pd. Two types of diffusion are observed: one at temperatures below 250 °C which results in U–Pd surface compound formation and one at temperatures above 300 °C, which is associated with bulk diffusion of U.

1. Introduction

Study of thin layers of uranium compounds is interesting from both a practical and a fundamental point of view. Thin layers can be used to model uranium–transition metal interfaces, and the study of the stability and corrosion resistance of such systems may contribute to the understanding of long-term storage behavior of nuclear waste [1]. Because of their particular electronic structure, *i.e.* almost localized 5f electrons which participate only weakly in bonding and highly reactive 6d7s electrons, U shares chemical properties with the late as well as the early transition metals; thus, actinides are well suited to explore the interplay of localized and delocalized electrons in a catalytic process [2]. Finally many of the interesting physical solid state properties of the early actinides, such as the formation of heavy fermions, are related to the high correlation of the 5f electrons, which may even be enhanced by decreasing the coordination of the actinide atoms, *i.e.* by depositing them on the surface of a low reactive substrate [3].

2. Experimental details

Thin layers of U have been prepared *in situ* by magnetron sputter deposition. This method was preferred to the conventional evaporation technique because of the difficulties associated with the latter: U has a low vapor pressure at the melting point and has a strong tendency to alloy with most filament or crucible materials. The experimental details are described elsewhere [3]. We used as substrates an ultrahigh purity, polycrystalline Pd foil and a Pd single crystal cut in the (100) direction. Spectral information were obtained using X-ray and UV photoelectron spectroscopies (XPS and UPS) and Auger electron spectroscopy (AES).

3. Results and discussion

At low dosages U was found to stay on the top surface, *i.e.* interdiffusion does not take place. All U atoms are in the same chemical environment, which points to the atomic dispersion of U on Pd and the absence of U clusters and islands. The high binding energy (BE) of the U 4f lines is typical for U in UPd_3 [4] and thus we conclude that U–P bonds govern the electronic structure of surface U (Fig. 1). At this stage the U 5f electrons are localized, which may be due partially to the decreased coordination at the surface, but also to the Pd substrate, which forms UPd_3 with U, where the U 5f electrons are also localized [3]. The electronic structure of the Pd is modified, too: U deposition results in the filling of the Pd 4d band. With increasing coverage the surface becomes heterogeneous as shown by the broadening of the XPS U 4f signal and its shift to low BE. Islands of U start growing on

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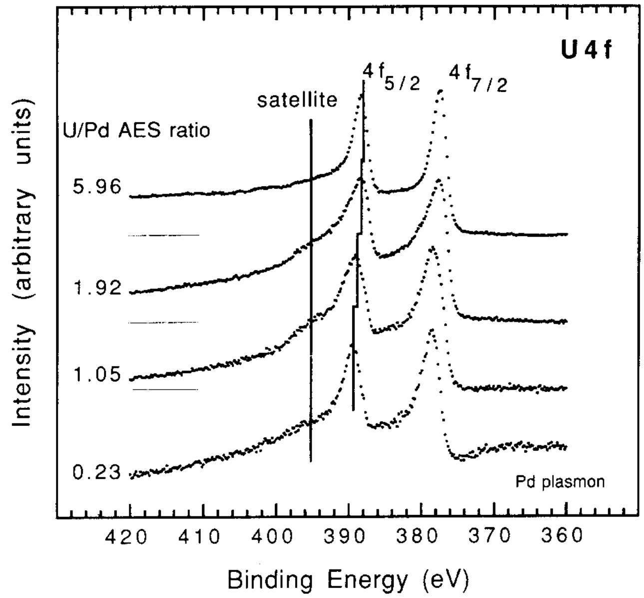

Fig. 1. U 4f spectra at increasing U dosage, expressed as average composition of the first three monolayers. The U:Pd = 0.25 curve corresponds to half a monolayer of U. With increasing U dosage the U 4f BE decreases and the peaks become more asymmetrical, *i.e.* they take shape and position of U metal. The broad shape in the interim region is due to a heterogeneous surface.

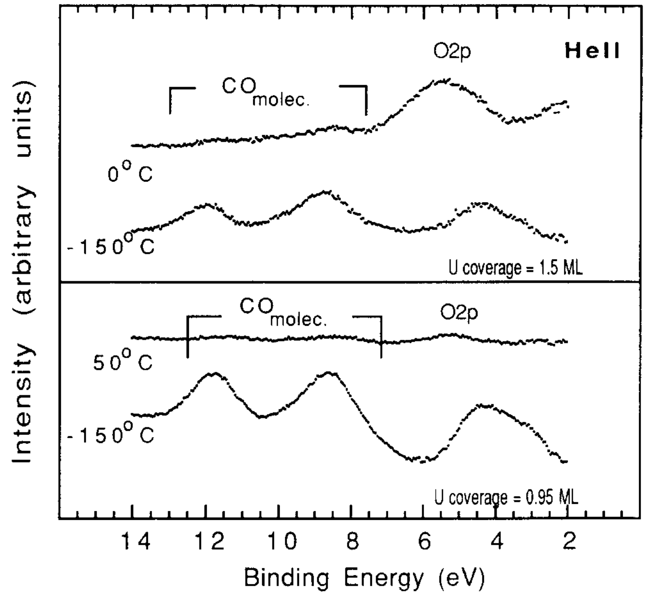

Fig. 2. UPS He II spectra for U–Pd surfaces after CO adsorption at low temperature and after heating. For low U coverage CO desorbs (top) while for high U coverage it partially dissociates (bottom), which is attributed to an increased reactivity of U.

the U overlayer and the surface becomes unstable as shown by the spontaneous U–Pd interdiffusion at room temperature, probably triggered by the high heat of formation of UPd_3 [3]. The 5f electrons become delocalized (asymmetrical U 4f emission) and the electronic structure of U becomes more similar to that of U metal, which results in a decreasing U 4f BE. The high affinity between U and Pd controls electronic structure and surface reactivity. This is also manifested during adsorption and annealing experiments.

We probed the reactivity of the surface by exposing it to low and high reactivity gases (CO and O_2 respectively). Below a critical surface concentration of U of less than one monolayer CO adsorbs exclusively molecularly at room temperature (Fig. 2). This shows that the U atoms, which sit on the top surface, lose their capacity to dissociate CO at room temperature. Loss of reactivity is also shown by annealing experiments where, below a coverage of about one monolayer U, heating results in the desorption of CO instead of its dissociation. This surface passivation is attributed to the interaction between Pd and U, which places the 6d7s electrons in stable solid state bonds making them less available for interaction with CO. The adsorption properties of the Pd surface atoms are modified, as well. Thermal desorption spectroscopy (TDS) spectra display a decreasing CO desorption temperature with increasing U concentration. The magnitude of the temperature drop (up to 180 °C) cannot be explained by a pure geometrical factor but points to an electronic effect [2]. We think it to be the filling of the Pd 4d band by U valence electrons. In spite of its passivation, the surface U still retains much of its reactivity as shown during the adsorption of more reactive O_2. Even at the lowest U coverage O_2 adsorption results in the oxidation of surface U to UO_2. In cases where we produced a near surface alloy by low temperature annealing (see below), this alloy decomposed and the U segregated back to the surface where it was oxidized to UO_2.

Thermal stability of U, UO_2 and U oxycarbide overlayers and the bulk diffusion of U have been investigated using a technique very similar to TDS. We recorded the evolution of the concentration of surface species (U, Pd and O) while heating the sample linearly to 900 °C. This type of real-time experiment is very useful in the study of the evolution of heterogeneous systems such as thin layers, which may go through a series of transitional near-surface alloys before U eventually dissolves in the bulk. By ramping the temperature we are certain to observe all diffusion phenomena within a short time frame, which is not the case for adiabatic annealing experiments. Annealing curves exhibit regions of a steep slope, which correspond to an ongoing diffusion process, and flat regions, where no change in surface composition is recorded. By differentiating the curves we produce diffusion peaks which have a similar meaning to the desorption peaks in TDS (Fig. 3). One has to be careful in interpreting the exact positions of the peaks, because they appear when the reaction front of a given diffusion process reaches the AES information region, which takes longer for thicker overlayers.

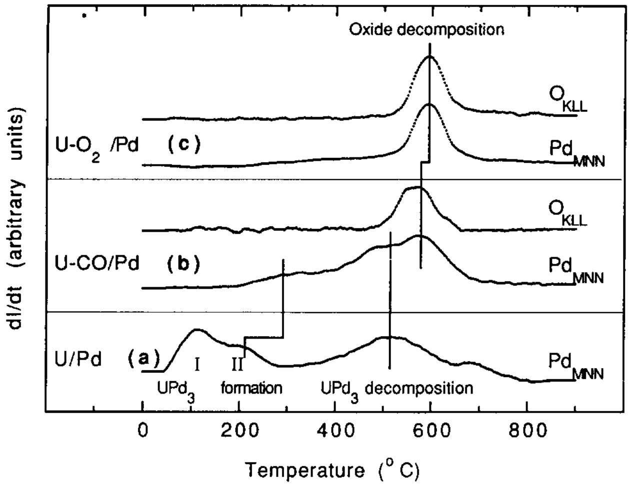

Fig. 3. Evolution of U, Pd and O AES signals when heating a Pd surface covered by (a) U metal, (b) U metal exposed to 20 L CO and (c) U exposed to 20 L O_2. The differentiated curves are shown.

The diffusion curves of U metal overlayers exhibit two diffusion peak systems (Fig. 3(a)). That at low temperature is due to the reactive interdiffusion of U and Pd that results in the formation of UPd_3, as proven by XPS and by quantitative AES. It has two components (I and II), one of which (I) is primarily seen at low coverage. We attribute it to the reaction of overlayer U with the Pd substrate: this peak is seen at coverages where island formation does not take place and can be suppressed by exposing the surface to CO (Fig. 3(b)), which reacts only with the top surface U (above the critical U concentration; see above). The second low peak component (II), which grows with increasing U dosage, is attributed the the reactions of island U with the Pd substrate. It is not suppressed by CO adsorption, because the U metal atoms in a thick island are protected by an inert U oxycarbide overlayer [2, 5]. The high temperature peak (above 300 °C) is attributed to the dissolution of UPd_3 and the bulk diffusion of U. It is observed even for very low coverages, where the low alloy formation peaks (I and II) are missing. This agrees well with our finding that at low coverage U is atomically dispersed and U–Pd bonds predominate: a submonolayer U film behaves like a single alloy layer. Grain boundary diffusion plays only a secondary role in the coverage range we investigated because a Pd(100) single crystal behaves almost identically to the polycrystalline Pd foil.

CO adsorption results in the suppression of the overlayer dissolution peak while the island dissolution peak stays (Fig. 3(b)). The high temperature alloy dissolution peak also stays, which confirms that some of the U diffuses into the surface immediately after deposition. There it forms a near surface alloy, which is not attacked by CO, because the latter reacts only with the top surface. A new high temperature peak appears and coincides with the oxygen dissolution peak (Fig. 3(b)): it is attributed to the decomposition of the U surface oxycarbide, formed by the reaction of CO with a thick U overlayer. This takes place far below the decomposition or evaporation temperatures of bulk U oxycarbide. It is triggered by the strong chemical affinity between U and Pd. O_2 adsorption results in the disappearance of all alloy formation and decomposition peaks (Fig. 3(c)). This confirms that the near-surface alloy is attacked by O_2 and decomposes into a UO_2 overlayer on the Pd substrate; therefore there is only one diffusion peak left which coincides with the disappearance of the oxygen signal, and which we assign to the decomposition of the UO_2 overlayer.

4. Summary and conclusions

Electronic structure and reactivity of thin U overlayers deviate considerable from those of bulk U. This is in part due to the low coordinated environment in thin layers, which trigger 5f localization, but also the U–Pd interactions which strongly passivate the surface. By varying the U dosage the reactivity may be modified within some range, down to a residual reactivity which becomes coverage independent and which was observed during O_2 exposures. Real-time study of the near-surface and bulk diffusion of U metal overlayers showed the process to proceed through the initial formation of a transition near-surface alloy (UPd_3). UO_2 and U oxycarbide also decompose and dissolve. The strong U–Pd affinity seems to be responsible for this low stability of the oxides.

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