Hf dissolution and surface alloy formation in Hf/W(011) adsorption system

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Abstract. The system Hf/W(011) was investigated using the STM, LEED, AES and CPD techniques. For low coverages (about 1 ML), dissolution of Hf in W and alloying on the W(011) surface was observed. For temperatures above 1200 K, mixing of the adsorbate and substrate atoms was observed. This process occurred at the edges of atomic steps. A surface alloy appeared at a temperature in excess of 1500 K. The alloy was being formed as large islands occupying one terrace each, and separated by atomic step bunchings of the substrate. At 1850 K the surface alloy decayed. The decay was followed by solution of the Hf in the subsurface layer of substrate.

1. Introduction

Surface alloys have attracted much attention recently, and studies on them is a growing research field [1, 2]. The Hf–W system is known to form a Laves intermetallic phase with the regular structure C15 [3]. Space filling in Laves phases is higher than that in the close packed structures of fcc and hcp metals, and obviously higher than in bcc W. The aim of this study was to investigate the intermixing processes for the Hf/W(011) adsorption system, which would lead to Hf dissolution in W and possibly to formation of a surface alloy. Since the majority of clean metal surfaces consist of steps that are one monolayer high, a special attention was paid to the role the steps played in the first stages of Hf adlayer formation, intermixing processes and finally a surface alloy’s formation.

Our previous LEED, AES and CPD study [4] of the Hf/W(011) adsorption system showed no evidence for Hf dissolution in the substrate in the temperature range 300–1500 K, though some evidence was found of Hf dissolution in the range 1500–1700 K and a possible surface alloy formation. In the present work, Hf layers of the thickness of a fraction of monolayer, deposited on W(011) at room temperature under ultrahigh vacuum (UHV) conditions, were annealed in the range 700–2300 K. Topographical and structural changes caused by annealing have been studied employing scanning tunneling microscopy (STM) beside the techniques of low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and contact potential difference (CPD) by the diode method.

2. Experimental

Two separate UHV systems were used, with the base pressure below $1 \times 10^{-10}$ torr in each. One of the systems was equipped with the four-grid reverse LEED optics, and electromagnetically focused electron gun for the diode method of work function (WF) measurement [5] by the electron beam technique. The
other system (commercial) was equipped with a variable temperature set of VT STM 100 RH/DH and a SpectaLEED optics (all from Omicron).

The sample under investigation was a single crystal of W(011)-oriented, cut and polished within 0.15° accuracy. The samples were cleaned by the routine procedure [6]. After cleaning no contaminants were detected by AES (using the LEED system in the retarding-field, the Auger mode) and good quality LEED patterns of clean W(011) were obtained. Sample temperature was measured by means of a thermocouple of W-Re 5% /W-Re 25% or by using an optical pyrometer of MINOLTA/LAND CYCLOPS 153A.

Hafnium was evaporated from resistively heated 0.25 mm diameter Hf wire of purity 99.97% (Alfa Johnson Matthey Company). The Hf source was outgassed prior to depositing a clean Hf film. Pressure during deposition of Hf was not higher than 1×10⁻⁹ Tr. The Hf-source efficiency, in this case, was estimated as 8.3×10¹³ atoms/cm² min. This value was obtained based on measurement of the time needed for deposition of the first atomic layer of Hf onto the W(011) at 600 K, when Hf dissolves weakly if at all. In the case of STM observations, no direct estimation was made for the source efficiency, and the amount of the material deposited was assumed to be about 1.0 ML. The Hf deposit was spread over the surface at a given temperature for 2 min in each step.

The STM measurements were carried out at room temperature in the constant-current mode, using probe tips from KOH-etched tungsten. All temperature treatments were performed on a separate heating stage in situ, by electron bombardment (for more detail see Ref. [7]). Image processing and height profile analysis was performed with the WSxM software from Nanotec [8].

![Figure 1. Work function changes: (a) measured during deposition of an Hf adlayer with coverage increasing to 6.3 ML (curve 2). The ranges of the appearance of respective LEED detected structures are indicated below, see text for denotation of A and B structures. Dashed line (curve 1) shows original WF changes for deposition of 3 ML Hf onto a new sample to begin with the experiment. The apparent WF difference of 0.2 eV between the curves is due to dissolution of a small amount of Hf in the substrate (b) measured during thermally spreading a predeposited Hf adlayer starting from a coverage of 6.8 ML. See text for denotation of C structure.](image-url)
3. Results
Hf atoms, after evaporation onto the W(011) substrate at 600 K, caused a monotonic lowering of the WF which, at saturation, reached a value lower by 1.1 eV than that of the clean substrate surface (fig. 1a). This was accompanied by a 1 eV shift in the Auger peak 38 eV towards the higher values of energy (fig. 2). The Hf adatoms at first filled the substrate lattice containing defects and improved its regularity, which was observed on diffraction patterns. At coverage $\theta = 1$ ML the first atomic layer of Hf revealed a structure of a deformed hexagonal lattice (denoted by letter A in fig. 1). Owing to this deformation the adlayer became isomorphic with the substrate. In Wood’s classification [9] such structure can be denoted as W(011) $\left( \frac{4}{9} \times \frac{10}{9} \right)$–o, which means that every 9 substrate lattice parameters and every 8 adsorbate lattice parameters the adsorbate and substrate atoms meet in the position coincidence along the W$<001>$ direction, and every 10 substrate lattice parameters and every 9 adsorbate lattice parameters another position coincidence occurs along the W$<011>$. The reticular density of the layer was the same as that of the perfect (0001) plane of bulk Hf, i.e. $1.14 \times 10^{15}$ atoms/cm$^2$. The second layer of Hf (denoted by letter B in fig. 1) revealed a lesser deformation with a structure of W(011) $\left( \frac{4}{9} \times \frac{10}{9} \right)$–o. Its reticular density was $1.25 \times 10^{15}$ atoms/cm$^2$, or exceeded by 10.6 % the density of reference. This condition was reached as a result of a closer Hf packing in the W$<001>$ direction. The third Hf layer, with a reticular density of $1.13 \times 10^{15}$ atoms/cm$^2$, showed a structure close to that of the Hf(0001). It was oriented with respect to the substrate with the directions such that Hf$<1\overline{1}2\overline{0}> \parallel W<001>$. No further changes in adlayer structure were found with increasing amount of deposition as monitored by LEED patterns. In the course of heating the Hf adlayer, an extra structure of W(011) $\left( \frac{4}{9} \times \frac{1}{9} \right)$–o appeared between the structures A and B, which is denoted by C in the figure. This superstructure was a result of loosing the packing of atoms in the W$<001>$ direction within the structure denoted by B. The changes of WF with increasing amount of Hf deposition at 600 K up to a 6.3 ML coverage as well as those with gradually increasing the heating of the adlayer are shown in figs. 1a and b.

Figure 2. (a) The result of extraction of 38 eV Auger peak of W from the background of secondary electrons. Area below each curve is a measure of the Auger current. The apparent shift of the peak by 1 eV toward high energy gives a measure of interaction between adatoms and the substrate (b) Auger current related to the 38 eV peak from substrate vs. amount of Hf deposition at 600 K. The straight line segments correspond to respective layers of Hf deposition.
The behavior of the Hf layer of 1 ML thickness in the course of heating was different. Diffraction
patterns indicated no changes in structure at this coverage and the observation was pursued by STM.
The clean W(011) surface exposed atomic steps of the mean width in excess of 100 Å and mean height
2.25 Å (fig. 3a). Room temperature deposition of Hf onto this surface led to a disordered adlayer.
Raising the temperature to 1000 K brought about accumulation of partial Hf into three-dim islands
which grew in size with increasing temperature and became irregular in shape. The rest of Hf adatoms
accumulated at terrace edges, which led to their irregular expansion (fig. 3b). At 1200 K a wiggling
border line emerged from the terrace edges with their height less by 0.5–0.6 Å relative to the original
height of the atomic step (fig. 3c). This process included more and more area of the atomic steps with
increasing temperature. At 1500 K, extensive terraces, separated by atomic step bunchings, were
observed instead of those islands of Hf atoms. The terraces clearly grew in size, up to 80 nm, with
increasing temperature whereas their formation of step bunching gradually expanded, too. At
a temperature of 1600 K a surface structure or surface alloy appeared, and the bunching formation
consisted of 6 atomic steps while at 1750 K there were as much as 12 or 14 (fig. 4). A detailed
structure of an extensive terrace could not, however, be imaged because of limited resolution, and the
STM image of the uniform surface is shown in fig. 3d. The insert image in the figure can illustrate the
possible occurrence of a surface alloy of Hf/W. To identify the surface alloy stoichiometry needs,
however, further investigation. After heating at 1850 K, the terrace image decayed and the topography
under investigation recovered its original form. The depicted cycle of Hf deposition followed by its
thermal desorption, when repeated many times, led to a WF change of 0.2 eV (fig. 1a).

Figure 3. STM images of
(a) The substrate surface
prior to Hf deposition.
White line indicates the
section across the atomic
steps shown below
(b) Hf adlayer of 1.0 ML
evaporated at room
temperature and spread at
1200 K
(c) Enlargement of the
white square marked
region of (b); the section
across the atomic steps is
shown below. Relaxation
induced contrast just at
the terrace edge is related
to the drop of the step
height by 0.5–0.6 Å
(d) The surface after
adsorbate spreading at
1600 K. Terraces with the
formation of surface alloy
are separated by a layer of
six atomic steps. Inset in
the lower-right corner shows
an enlarged image of the
terrace portion with
the surface alloy.
4. Summary
Room temperature deposition of Hf atoms onto the W(011) surface leads to an irregular distribution of adatoms on the surface. Structural changes in the adlayer appear after heating the adsorption system at 600 K. Hf deposition made at 600 K results in the intermediate growth of the Stranski–Krastanov type with a characteristic change in the Auger peak 38 eV. The peak shifts toward high energy by 1 eV, which is due to the interaction adatoms/substrate.

Upon 1000 K heating the Hf adlayer of the thickness slightly above 1 ML, the thermally activated surface diffusion process is observed. As a result, part of adatoms accumulate to form three-dim islands while the other concentrate at edges of the atomic steps. At 1200 K adatoms dissolve in substrate atoms at the edges, which is followed by relaxation of the surface with the step height shortened by 0.5–0.6 Å. This process spreads over all the atomic steps. The mixing of the surface atoms involves also the Hf islands and makes them decay. Nonuniform concentration of Hf adatoms on the respective steps leads to the formation of a surface alloy at the temperature raised above 1500 K. The alloying appears on terraces which are separated by step bunchings. The alloy structure remains unknown because of limited resolution. Size of the terraces increases with increasing temperature and also the amount of step bunching increases. The surface alloy decays at 1850 K. The observed step bunching and mixing results in closing the Hf atoms in the bulk substrate material. In consequence, the substrate stoichiometry is changed by the presence of excess hafnium. Repeated deposition and thermal desorption of Hf results in dissolution of Hf atoms in the bulk material. This is accompanied by a work function change of 0.2 eV.

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