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Reaction of hydrogen with uranium catalyzed by platinum clusters

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Abstract

The surface-reaction of hydrogen with uranium in the presence of Pt clusters was studied using scanning tunnelling microscopy (STM). Uranium was deposited on highly oriented pyrolytic graphite (HOPG) and annealed at temperatures up to 1200°C to obtain atomically flat surfaces. Platinum clusters were then formed using evaporation from a Pt source onto the surface and were subsequently annealed. As a result, hydrogen primarily attacked U in the vicinity of Pt clusters and formed hydride, which expanded non-linearly over time. A simple model to explain this expansion behavior is proposed. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

In previous studies, the interactions of hydrogen and water with pure and slightly oxidized U have been reported. The sticking probability and binding energies were deduced from temperature programmed desorption (TPD), and the hydride formation and recombination probabilities were determined by modulated molecular beam techniques [1]. In addition, using atomic force microscopy, it was shown that exposure of a slightly oxidized surface of U to di-hydrogen (H_2) leads to raised features mainly along the grain boundaries. The features were postulated to be regions where hydriding had been initiated, since the U to U hydride transformation involves a volume increase by a factor of 1.8. These features continued to grow in size with exposure while the density of features did not change noticeably. By assuming that the hydride at particular sites grows isotropically (forms a half sphere cavity into the U surface that is filled with hydride) and that the density of these sites does not change, the total number of U metal atoms that react to form hydride during a particular exposure was calculated. The hydride formation probability was defined as the ratio of the number of the UH_3 molecules formed to the number of di-hydrogen striking a unit area times 1.5. It was shown that the probability of hydriding increased by three orders of magnitude in 20 min with H exposure at 6.7 Pa but levelled off after 3 h.

It is interesting to consider the dynamics of the site-specific formation of hydride. Generally a mechanistic description of gas surface interactions consists of decomposing the overall reaction into a sequence of elementary steps, including the following: (1) adsorption of reactant from the gas phase, characterized by a sticking probability; (2) surface reactions that may involve only a surface-adsorbed intermediate [Langmuir–Hinschelwood (LH) mechanism] or that may be the result of direct interaction of an incident gaseous reactant with a surface specie or specific site [Eley–Rideal (ER) mechanism]; and (3) transport of surface species to microscopic surface sites which facilitate reaction.

The sticking probability of hydrogen on a U surface that is constantly bombarded with argon ions to keep it clean (and is therefore amorphous) is $\sim 4 \times 10^{-2}$ [1]. For ordered U, this probability has not been measured yet. If this probability is low for flat and ordered surfaces of U, then the chance of formation of hydride will also be low for the LH-type.

The purpose of this investigation was to determine whether a metal with high sticking probability deposited on the U surface could serve as a source of hydrogen

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atoms and thus lead to a local enhancement of hydriding. A similar idea was implemented to accelerate the gasification of carbon using Pt as a catalyst to dissociate di-hydrogen [2]. In the present work, the resulting site-specific hydriding was monitored, in situ, by STM, showing that the contribution of the ER mechanism is insignificant. We observe in this investigation that the mechanism for hydride formation is dissociation of hydrogen on Pt, diffusion of adsorbed H through Pt and UH_3 toward the interface with uranium. Recombination and desorption of hydrogen as di-hydrogen can simultaneously occur.

2. Experimental procedure

To investigate the initial hydriding process using STM with nanometer-scale resolution, it is essential to start with a high purity, atomically flat U substrate. Polishing does not achieve this, since a U surface oxidizes very rapidly in a laboratory atmosphere; consequently, electron tunneling cannot be established under the STM tip. This difficulty was overcome using laser ablation of a U target, resulting in deposition of the ablated U onto highly oriented pyrolytic graphite (HOPG) in an ultra high vacuum (UHV) system with a base pressure of 6×10^{-9} Pa. HOPG with an atomically flat surface acts as an ideal substrate.

The sample substrate used in these experiments was the basal plane orientation of HOPG supplied by Dr. Arthur Moore at Union Carbide. The samples ($1\ \mathrm{cm}^2 \times 1$ mm thick) were cleaved in laboratory air by pealing off layers of graphite using scotch tape. Once a mirror-like surface was obtained by cleaving, the sample was mounted onto a holder which could then be transferred into the UHV chamber through a load-lock. The sample was then heated to 1200 K for approximately 1 min prior to the deposition of U to out-gas the sample and remove any adsorbed surface contaminants.

A UHV system was used with a stainless-steel surface analysis chamber, a 300 l/s ion pump, and a top vacuum level in the mid 10^{-9} Pa range. Because of uranium's high reactivity with water vapor, oxygen, and other gases, it was necessary to keep the chamber below a maximum pressure of 1×10^{-8} Pa to maintain a clean uncontaminated U surface for the duration of these experiments. The chamber's pressure was also affected by the experiment itself. For example, heating the sample to 1100 K for 2 min raised the pressure to 8×10^{-8} Pa. In addition, the laser pulses that created a plume of U used for deposition also momentarily increased the pressure to around the 10^{-6} Pa range for $\lesssim 1$ s. The pressure then decreased quickly to the 2×10^{-8} Pa range. This effect from the ablation process took several minutes to be completely pumped away. The surface contamination resulting from this pressure burst was estimated to be $\lesssim 1/100$ of a monolayer. Deposition of U was accomplished by ablating a highly pure U target by a high-power pulsed laser [HCl and Xe gas excimer (308 nm and 20 ns)]. A shutter in front of the ablated material was used to block the laser-created plume while the U target was cleaned with repeated laser pulses. A power density of about $4 \times 10^8\ \mathrm{W/cm}^2$ was incident on the U target for film growth.

Platinum was deposited by evaporation. The sample was then annealed to create clusters with different sizes.

The main focus of this experiment was to measure the site-specific hydriding rate, using the high spatial resolution of an STM (Mc Alister Technical Services, Coeur d'Arlene, ID). The STM contained a cylindrical piezoelectric crystal that facilitated x, y, and z tip motion, ranging from 1.4 μm for x and y and 0.4 μm for z. Constant-current-mode images were used with the bias voltage set to 500 mV (sample positive) and the tunneling current at 0.6 nA.

3. Results

3.1. Uranium deposition on HOPG and characterization

3.1.1. Low coverage

The surface morphology of the initial deposition of U onto HOPG as seen by in situ STM showed U clusters of varying sizes, yet with a uniform number density (number of clusters per unit area) across the sample. The images of clusters as deposited on the graphite did not change over time if the samples were left at room temperature. In previous work [3], the kinetics of the U deposit was investigated by annealing the samples to different temperatures (typically 2 to 4 min at 800–1200 K) and analyzing them with STM after they cooled down. The annealing affected the morphology of the U clusters on the surface. The as-deposited U surface with low coverage showed clusters of varying sizes with a uniform number density across the surface. In this context, the meaning of low coverage referred to an amount of U less than, or approximately equal to, one monolayer as measured by X-ray photoelectron spectroscopy (XPS). Annealing caused the average size of the clusters to increase (in both the lateral and vertical dimensions) and the number density of clusters to decrease appreciably.

3.1.2. High coverage

High coverages of U were considered to be those with more than one monolayer of U. Once annealed at similar time and temperature ranges, these films behaved quite differently than the low-coverage samples. Initially, these high coverage depositions appeared to have a higher number density of small clusters than those seen for low coverages. Yet upon annealing, the surface morphology of these high-coverage samples changed from small clusters to platelets that had planar tops and uniform stepped edges with step heights of about 0.55 nm (Fig. 1). Some samples showed as many as three steps in the U deposit. The value

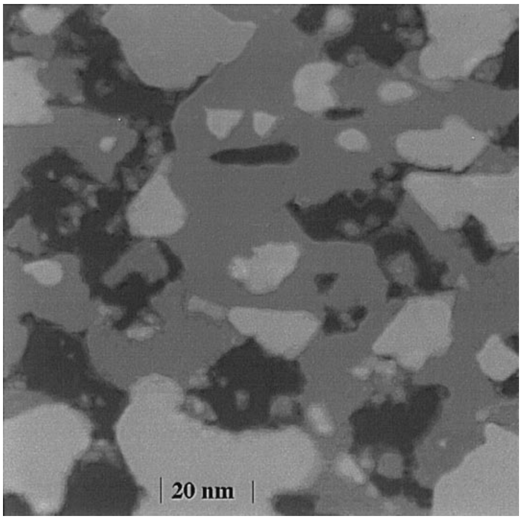

Fig. 1. STM image of uranium film obtained by laser deposition and subsequent anneal. The z elevation is displayed as increasing brightness, thus, the bright platelets represent the top U layer.

of 0.55 nm is close to the c_0 lattice constant (0.5656 nm) of the β-phase of U crystals [4].

3.2. Platinum on uranium

Fig. 2 shows a STM image of Pt deposited on the U film that is produced by high coverage deposition and annealing of U onto HOPG. To improve resolution, the scanned area was reduced but kept within the border of Fig. 1. The deposition is equivalent to a coverage of 0.8 monolayer, as measured by the quartz oscillator technique. Annealing to 900 K for 5 min resulted in clusters of Pt formed almost uniformly on the surface of the U film. Fig. 3 shows the size distribution of the clusters (most probably at ~ 1 nm^2 area). However, clusters as small as 0.25 nm^2 and as large as 3 nm^2 could be detected as well. Note that the actual diameters were smaller than the measured STM diameters due to convolution of the tip and sample.

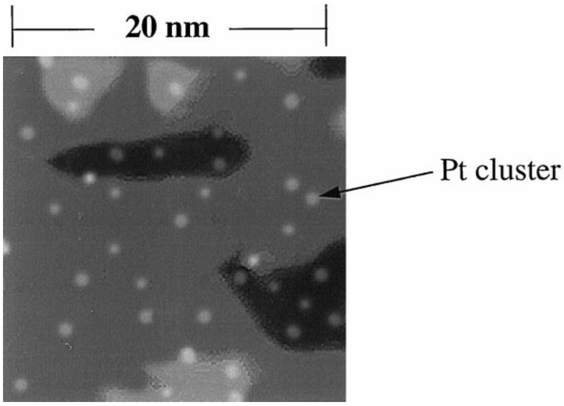

Fig. 2. STM image of Pt clusters formed on uranium film by evaporation and anneal. The z elevation is displayed as increasing brightness.

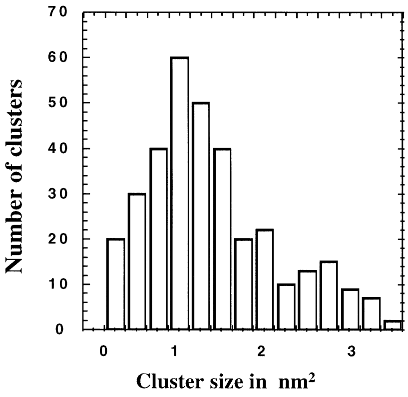

Fig. 3. Pt cluster area-size distribution as a result of evaporation and anneal. Same area as shown in Fig. 2.

3.3. Reaction with di-hydrogen

The kinetics of hydriding were studied by exposing the sample to pure di-hydrogen at a pressure of 1.3×10^{-3} Pa up to 20 min. No in-situ imaging was performed during hydrogen exposure to avoid possible arcing (a high voltage is applied to the piezo-electric tube during the scan). Once the di-H was pumped out, the same area was monitored by STM and the procedure was repeated.

The interaction of di-H with a pure U film was first considered, as shown in Fig. 1. The film consists of platelets of U of different heights. No noticeable hydride formation was observed. This suggests that the sticking probability of di-hydrogen on this surface is either extremely low or that adsorbed H prefer to recombine and desorb rather than form hydride. In addition, the ER mechanism discussed earlier can be eliminated as a possible mechanism since in this mechanism, one expects the direct collision and interaction with edges to produce hydride.

Fig. 4 shows the results of exposures on samples with Pt (at 5 and 20 min), indicating expansion of the clusters due to hydrogen exposure. However, the expansion cannot be due to coalescence of clusters since the exposure was at room temperature, giving no chance for Pt diffusion, and in addition, each cluster could be identified by its location in the field of view of the STM. Therefore, the apparent expansion must be due to reaction of hydrogen with U in the vicinity of the perimeter of clusters. Since there is an

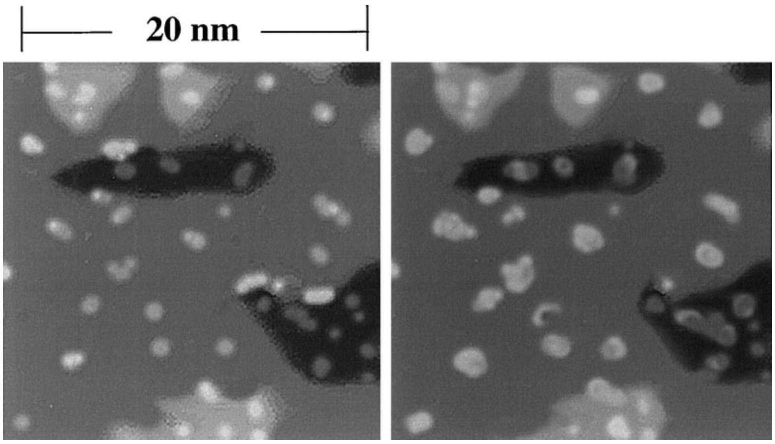

Fig. 4. STM images of Pt-catalyzed uranium hydriding after exposure to hydrogen at 1.3×10^{-3} Pa, (a) after 5 min and (b) after 20 min. The z elevation is displayed as increasing brightness. Same area as shown in Fig. 2Fig. 3.

increase in volume due to the conversion of U to its hydride, it is reasonable to assume that hydride rings are being created and expand around the clusters. By scanning over the area many times, the clusters disappeared and were replaced by disk-shaped pits with a depth of 0.55 nm (Fig. 5). Since UH_3 did not form epitaxially on HOPG, it can easily be swept away by the STM tip, thus, only the unreacted U is imaged after many cycles of scanning the area.

Fig. 6 shows the radial expansion of hydride around a Pt cluster as a function of time, normalized to the radius of the Pt cluster $[R(t)/r_{\mathrm{Pt}}]$. The expansion is nonlinear with time. To obtain the catalytic strength of Pt to convert U to its hydride, the hydriding probability was defined as the ratio of the hydrogen uptake to form hydride in the vicinity of the most probable Pt cluster size to twice the number of di-hydrogen striking at the cluster during the exposure. The number of U atoms swept away during multiple scans can be calculated from the size of the pit. The hydrogen uptake is three times this number. The number of di-hydrogen striking at the cluster during the exposure can also be easily calculated by the kinetic theory of gases. The hydriding probability ε can then be expressed as

$$\varepsilon = 0.277 \frac{\left(\frac{R}{r_{\mathrm{Pt}}}\right)^2 - 1}{t}, \tag{1}$$

where t is measured in seconds. Fig. 6 shows the result of the calculation vs. time. The hydriding probability appears to be independent of time within the experimental accuracy.

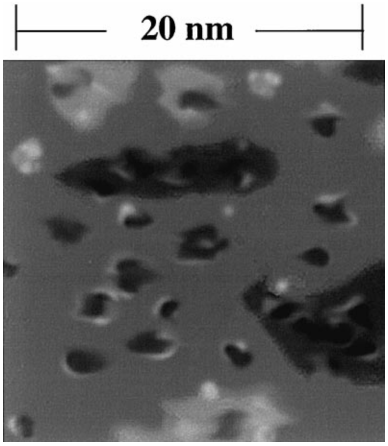

Fig. 5. STM image of the area shown in Fig. 4 after many scans. The z elevation is displayed as increasing brightness. Same area as shown in Fig. 2Fig. 3Fig. 4.

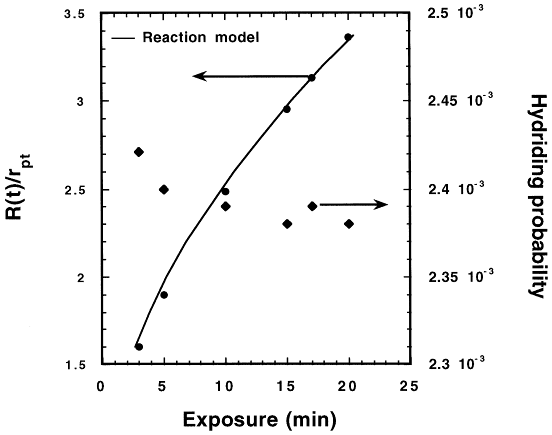

Fig. 6. Normalized radial expansion of hydride around a Pt cluster and calculated hydriding probability as a function of exposure at a hydrogen pressure of 1.3×10^{-3} Pa. The line represents the edge reaction model.

3.4. Reaction model

A unit cell consists of a Pt cluster and a UH_3 ring enclosed by U metal. We assume that the Pt cluster is the sole supplier of atomic hydrogen to the adjacent UH_3 surface and the UH_3/U interface. The hydride formation is assumed to be reaction limited at the edge of the UH_3 front. The basic idea of the mechanism is simple: incident H_2 is dissociatively adsorbed on the Pt cluster but merely scatters from the U and UH_3 parts of the surface. Some of the H atoms chemisorbed on the Pt cluster recombine and are re-emitted to the gas phase as H_2. The remainder of the chemisorbed H spills over onto the adjacent UH_3 and proceeds to diffuse along the surface toward the UH_3/U interface. A first-order reaction is assumed for hydride formation at the interface. For simplicity the diffusion is considered to be fast and the spill-over of H atoms from Pt to UH_3 is treated as an interfacial equilibrium.

The H atom balance for the unit cell is

$$2\eta I = k_d^{Pt}\left(n_H^{Pt}\right)^2 + k_d^{UH_3}\left(\frac{R^2}{r_{Pt}^2} - 1\right)\left(n_H^{UH_3}\right)^2 + 2\frac{R}{r_{Pt}^2} \times k\left(n_H^{UH_3}\right) \qquad (2)$$

and

$$n_H^{Pt} = k_s\left(n_H^{UH_3}\right), \qquad (3)$$

where: $I = H_2$ flux at the Pt surface, molecules/cm^{2}s; n_H^{Pt} and $n_H^{UH_3}$ = surface concentration of H on Pt and UH_3, respectively, atoms/cm^2; η = sticking probability of H_2 on Pt; k_d^{Pt} = rate constant for H atom recombination and desorption as H_2 on Pt, cm^2/s; $k_d^{UH_3}$ = rate constant for H atom recombination and desorption as H_2 on UH_3, cm^2/s; k_s = H distribution coefficient between Pt and UH_3; k = rate constant for UH_3 production, cm/s.

The first and second terms on the right side of Eq. (2) represent desorption of H_2 from Pt and UH_3 as a result of recombination, respectively. The last term represents the formation of hydride at the UH_3/U interface.

The rate of growth of hydride, dR/dt can then be expressed as

$$\frac{dR}{dt} = \frac{M_u k}{3N_A \rho b}\left(n_H^{UH_3}\right), \qquad (4)$$

where M_u and ρ are the atomic weight and density of U, respectively, and b is the step height of the U platelet.

The values of the rate constant for H atom recombination and desorption (6.9×10^{-18} cm^2/s) and of the initial sticking probability on Pt (0.05) reported by Engstrom et al. [5], using temperature programmed desorption were used. In addition, the H distribution coefficient between Pt and UH_3 was assumed to be unity. Using a minimization routine, the experimental radius expansion of the hydride with time was fitted to Eqs. (3) and (4). The solid line in Fig. 6 represents the best fit to the experimental results with $k = 2.5 \times 10^{-10}$ cm/s and $k_d^{UH_3} = 6.9 \times 10^{-18}$ cm^2/s.

4. Discussion

STM is a powerful technique for obtaining insight into site-specific reaction kinetics. The hydriding probability of di-hydrogen on well-ordered and flat surfaces of U were found to be extremely low ($\lesssim 10^{-6}$) since no detectable changes were noticed in topography on areas scanned by STM after the sample had been exposed to di-hydrogen at a pressure of 1.3×10^{-2} Pa for many minutes. The prerequisite for hydride formation appears to be dissociative adsorption of hydrogen on the surface. The results imply that either the recombination probability of adsorbed H is extremely high or the sticking probability (dissociative adsorption probability) is extremely low. In addition, the ER mechanism can be ruled out since no hydride was formed at the edges of platelets during these experiments.

Previous experiments determined the sticking probability of di-hydrogen on Pt. Christmann and Ertl [6] determined initial sticking probability values of 0.35 and 0.08 for Pt(997) and Pt(111) surfaces, respectively. The values decreased with coverage. Shern [7] then reported a value of 0.5 at coverage of about 0.1 for Pt(110), which decreased with coverage as well. The structure and orientation of the Pt clusters used in the present work have not been determined. However, based on these reported values, the sticking probability of hydrogen on the clusters is estimated to be between 5×10^{-2} to 1×10^{-1}, higher than for amorphous U reported earlier [1]. Pt can therefore act as a catalyst to dissociate hydrogen and thus provides adsorbed atomic H to the surrounding U. Hydride formation starts at the Pt–U boundary and expands from then on at the UH_3/U interface. The existence of flat-bottom pits and the fact that no attack occurs on U terraces suggest that hydride formation on an ordered U surface is low as compared with steps or defects. In addition, the lack of formation of hydride on pure U strongly suggests that the limiting step in hydride formation is the dissociative adsorption of di-hydrogen.

It has been reported that for polycrystalline samples, the hydride expansion rate is constant at the early stages of hydriding [8]. The constant rate is explained by assuming that the hydride forms as a hemisphere into U and that di-hydrogen dissociatively adsorbs on the hydride and diffuses fast to the interface to form hydride. The present finding is different in the sense that the rate of hydride production is constant and essentially two dimensional. This strongly suggests that the sticking probability of hydrogen on Pt is considerably higher than on UH_3. As a result, adsorbed hydrogen is mainly provided by Pt rather than by the hydride itself. This in turn suggests that the mechanism of UH_3 expansion in the present experiment differs from what is observed in previous work.

It is interesting to point out that on a macro scale, uranium can be readily hydrided at room temperature while the present work suggests the reaction does not proceed easily on the microscale. This is due to the fact that bulk uranium can not be easily produced as a single crystal and with ultra high purity. In addition, uranium oxidizes readily. The oxide scale often cracks and therefore provides passages to the underlying uranium which could be under appreciable amount of local stress. Local stress, impurities and defects such as grain boundaries and dislocations are favourite sites for dissociation of incoming hydrogen and, therefore, hydride formation. In the present and previous work [1], considerable efforts have been made to single out such sites for detailed understanding.

5. Summary

The interaction of di-hydrogen with a clean and well-ordered U surface is weak. However, the presence of Pt clusters deposited on U increases the hydride formation appreciably. The hydride forms as a ring around the Pt clusters and expands over time. Early experiments of pure U exposed to hydrogen at the early stage of interaction reported the average radial growth velocity of hydride to be constant [8]. The experiment discussed in this paper shows this velocity to be time dependent. A simple model based on adsorption of hydrogen only on Pt, recombination and desorption from Pt and UH_3, and first order reaction at the U/UH_3 edge explains the experimental results fairly well.

Acknowledgements

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