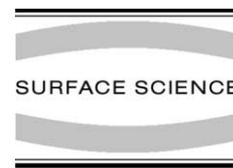




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Surface Science 513 (2002) L391–L396



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Surface Science Letters

Fe deposition on Pt(1 1 1): a route to Fe-containing Pt–Fe alloy surfaces

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Received 13 August 2001; accepted for publication 10 December 2001

Abstract

Bimetallic surfaces formed by the evaporation of Fe onto a Pt(1 1 1) single crystal at 350 K in ultrahigh vacuum were examined by X-ray electron spectroscopy, low energy electron diffraction (LEED), and low energy ion scattering. Some alloying occurs upon deposition, but heating thick Fe films to 600–850 K causes diffusion of Fe into the near-surface region and forms an alloy layer at the surface which contains 0.5-ML Fe. Annealing to 750 K orders the alloy and results in formation of a diffuse 2×2 LEED pattern. This procedure produces Fe-containing alloy surfaces that are more thermally stable against Pt surface segregation than expected from the behavior of $\text{Pt}_{80}\text{Fe}_{20}(1\ 1\ 1)$ bulk crystals, and significant amounts of Fe are stabilized in the surface layer until temperatures as high as 950 K. Alloying with Fe causes a +0.40-eV chemical shift in the $\text{Pt}(4f_{7/2})$ peak, but no chemical shift of the $\text{Fe}(3d_{5/2})$ peak in the bulk of the crystal. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Alloys; Iron; Platinum; Metallic surfaces; X-ray photoelectron spectroscopy; Low energy electron diffraction (LEED); Low energy ion scattering (LEIS)

Modification of pure Pt catalysts with transitional metals often results in improved catalytic efficiency in a range of industrially important processes. As an example, the selectivity to form the unsaturated alcohol, which is the desired reaction pathway, in crotonaldehyde hydrogenation is improved by the addition of Fe to supported Pt catalysts [1]. This selectivity improvement of Pt–Fe bimetallic catalysts has been attributed to the formation of partially oxidized Fe centers at the catalyst surface [2]. Such oxidic centers can form

in situ by exposure of bimetallic alloy phases to the reaction media as a result of $\text{Me}^0\text{--Me}^{n+}$ transitions [2]. Surface science studies using single-crystal $\text{Pt}_{80}\text{Fe}_{20}$ bulk alloys as model catalysts have also attempted to provide a basis for understanding these catalysts [3,4]. In these investigations, however, surface analysis of the $\text{Pt}_{80}\text{Fe}_{20}$ alloy revealed that the topmost surface layer was composed of 100% Pt atoms [5], and thus these surfaces may not provide good models for the binary catalyst. Cleaving or sputtering bulk alloys may create surfaces that expose Fe atoms, but these are non-equilibrium surface structures and surface Fe atoms migrate into the bulk upon heating above 600 K [3]. Other methods are needed to prepare

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Fe-containing surface layers and vary the alloy surface composition in order to improve our fundamental understanding of alloy chemistry and enable fine tuning of the alloy surface properties. To this end, in the present study we attempted to prepare such well-defined Pt–Fe alloy surfaces by annealing ultrathin Fe films deposited on a Pt(111) single crystal at 350 K. The thermal stability of these Fe films and the concentration of Fe in the topmost layer was characterized by X-ray electron spectroscopy (XPS) and low energy ion scattering (LEIS). XPS provided evidence for formation of a Pt–Fe alloy upon annealing to 750 K which caused a chemical shift of both Fe(3d) and Pt(4f) core levels.

Preparation of the Fe/Pt(111) surfaces was done in a ultrahigh vacuum chamber [6] equipped with facilities for XPS, LEIS, Auger electron spectroscopy (AES), and low energy electron diffraction (LEED), with a background pressure of 2×10^{-10} Torr. The Pt(111) surface was cleaned by cycles of Ar⁺ ion bombardment at 2 keV (3 μ A, 5 min) at 350 K and subsequent annealing in vacuum to 1150 K. Surface cleanliness was monitored routinely by XPS, and no impurities above 0.5 at.% were detected in either XPS or AES. Fe was evaporated onto the Pt(111) surface by resistively heating a 0.5-mm tungsten wire that was wrapped with iron wire (0.5-mm diameter, 4 N purity, Puratronic). During Fe evaporation, the background pressure rose to 9×10^{-10} Torr, but experiments were only carried out when C, O, and S impurities in the film were below the detection levels of 0.03, 0.01, and 0.02 monolayer (ML), respectively, using XPS.

XPS spectra were taken with a Mg K α source (300 W, 15 kV) using an analyzer pass energy of 29.35 eV for Pt and Fe and 46.95 eV for C and O, with scan times of a few minutes. The angle between the surface normal and analyzer in XPS was 45°. Binding energies are referenced to the Pt(4f_{7/2}) peak at 71.0 eV BE for clean Pt(111). LEIS utilized 1-keV He⁺ incident ions at a beam current of 10 nA, rastered across the 8-mm diameter crystal surface, using an analyzer pass energy of 1127.1 eV and a scan time of 40 s. Ions were incident at 43° from the surface plane and the scattering angle was 100°.

LEIS was used to determine the surface Fe coverage according to

$$\Theta_{\text{Fe}} = \frac{I_{\text{Fe}}/I_{\text{Fe}}^{\infty}}{I_{\text{Fe}}/I_{\text{Fe}}^{\infty} + I_{\text{Pt}}/I_{\text{Pt}}^{\infty}} \quad (1)$$

where I_{Fe} and I_{Pt} are LEIS intensities (peak heights) measured for the surface under examination, and I_{Fe}^{∞} and I_{Pt}^{∞} are the intensities measured for a thick Fe film and a clean Pt(111) surface, respectively.

The deposition of the Fe film on Pt(111) at 350 K was monitored routinely with XPS by using the Fe(3d) and Pt(4f) core level intensities (peak areas). Because alloying can occur during deposition, we established a reference point for the Fe deposition by calculating an Fe(3d)/Pt(4f) XPS ratio of 0.13 that would be expected for a 1-ML Fe film. This calculation assumed layer-by-layer growth and used values for mean free paths in an Fe film for Fe(3d) and Pt(4f) photoelectrons of 10 and 16 Å, respectively, calculated as described in [7], and bulk intensities for Pt and Fe measured from the clean Pt(111) surface and a thick Fe film (Pt intensity \sim 5% of the clean Pt intensity). The Fe deposition time required to produce an XPS ratio of 0.13 was denoted as a dose unit (DU) and multiples of this deposition time were used to characterize the deposition of the Fe films.

The deposition of Fe on Pt(111) at 350 K was followed by LEIS and the data is shown in Fig. 1. The Pt and Fe LEIS intensities initially change

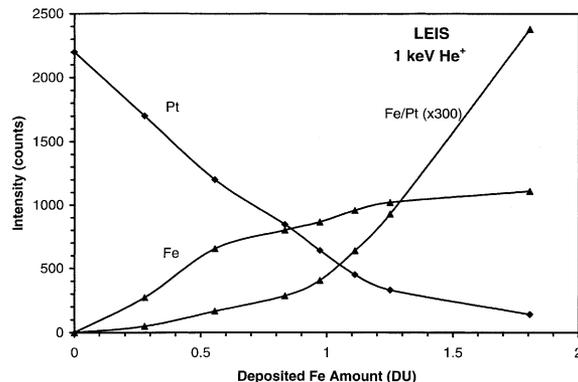


Fig. 1. He⁺ LEIS data for Fe deposition on a Pt(111) surface at 350 K. The Pt and Fe signals, along with the Fe/Pt ratio are shown, as deduced from the peak heights.

linearly with the amount of deposited Fe or Fe deposition time. The changes in the curves near 0.65 DU are attributed to the formation of an alloy layer upon Fe deposition. A shift of the XPS Pt(4f) core level, as discussed below, provides an additional argument for alloy formation at 350 K. The Fe/Pt LEIS ratio exhibits a clear change in slope near 1 DU, which as explained above, corresponds to an XPS ratio expected for a 1-ML Fe film. Thus, 1 DU produces a nearly complete Fe film on top of a Pt–Fe alloy surface, with all of the deposited Fe in the near-surface region.

Annealing a 1.5-DU Fe film causes a decrease in the concentration of Fe at the surface, as shown in Fig. 2. In these experiments, the film was sequentially annealed to 1000 K in 50 K increments, with a 10-s pause at each temperature. The initial decrease in the Fe signal that occurs between 330

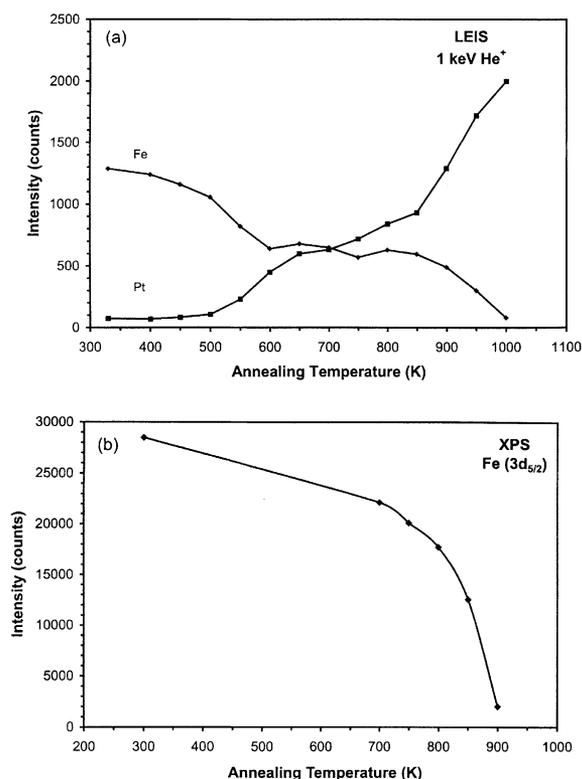


Fig. 2. Studies of the influence of annealing on a 1.5-DU Fe film on Pt(111): (a) He⁺ LEIS and (b) Fe(3d_{5/2}) core level in XPS. The annealing time was 20 s at each temperature.

and 600 K in Fig. 2a is attributed to diffusion of Fe into Pt to form an alloy. However, the Fe LEIS intensity, and thus the surface Fe concentration, is nearly constant over a temperature range of 600–850 K and indicates the formation of an alloy surface layer that has a constant Fe composition. Within this temperature region, the Pt LEIS signal increased by about 50%, and we attribute this to ordering of the alloy surface because of the changes seen in LEED, as described below. Eq. (1) can be used to calculate that the Fe coverage in this temperature range was 0.5 ML. This layer could correspond to a γ_2 phase in the bulk Pt–Fe phase diagram [8] which has 55% Pt and 45% Fe. At temperatures higher than 850 K, the Fe concentration in the surface layer quickly decreases and the surface Pt concentration quickly increases, indicating Fe diffusion into the crystal. After the final annealing to a temperature of 1000 K, the Fe intensity had decreased to about 5% of the initial value for the Fe film prior to annealing.

We also performed XPS measurements of the Fe(3d) peak, following the intensity during the above annealing sequence, and these results are shown in Fig. 2b. Since the mean free path of these electrons is more than 10 Å, this data is sensitive to the changes in the composition of the near-surface region, and this provides additional information. The Fe(3d) signal does not decrease sharply until temperatures above 750 K, which indicates that the decrease in the Fe LEIS signals at lower temperatures mostly occurs due to Fe diffusion into the near-surface region and not deep into the Pt crystal. However, Fe migrates deep into the bulk of the Pt crystal at temperatures above 750 K, and this causes sharp decreases in the Fe signals in LEIS and XPS. We propose that an alloy is formed in the near surface region of the Pt(111) crystal at temperatures of 600–850 K with a relatively high concentration of 45% Fe which stabilizes a concentration of 45% Fe in the topmost layer.

This situation is quite different from that reported for the (111) face of the Pt₈₀Fe₂₀ bulk alloy. Annealing the Pt₈₀Fe₂₀ bulk alloy at 700 K for 5 min resulted in complete disappearance of the Fe LEIS signal [3]. The data in Fig. 2a clearly show the presence of Fe in the surface layer of our alloy film at much higher temperatures of 950 K.

In results not shown here, we carried out additional experiments that allow a more direct comparison in which we monitored the Fe LEIS signal after a 1.5-DU Fe film was annealed at 700 K for increasing amounts of time. We still find an Fe coverage of 0.4 ML after annealing our surface to 700 K for 5 min. This result indicates that the surface Fe is stabilized by this preparation method over that obtained for the Pt₈₀Fe₂₀(1 1 1) bulk alloy surface.

XPS spectra taken for different Fe films are shown in Figs. 3 and 4. Fig. 3 shows results for the Pt(4f) core levels. The clean Pt(1 1 1) surface gave a Pt(4f_{7/2}) core-level peak at 71.0 eV BE with a full-width-at-half-maximum of 1.50 eV. Following deposition of Fe, this peak could be decomposed into two peaks at 71.0 and 71.4 eV BE, as depicted by the dashed lines, assuming a constant line width

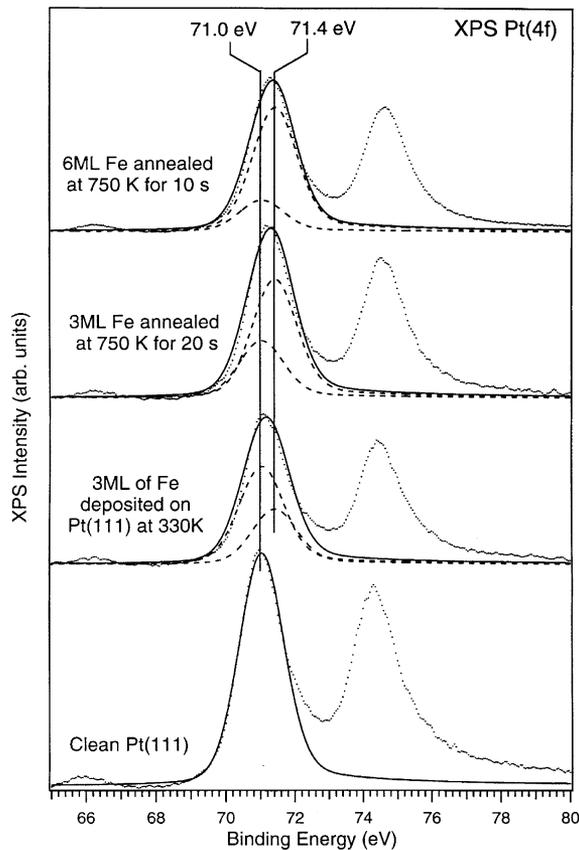


Fig. 3. Pt(4f) core levels in XPS for several Fe films on Pt(1 1 1).

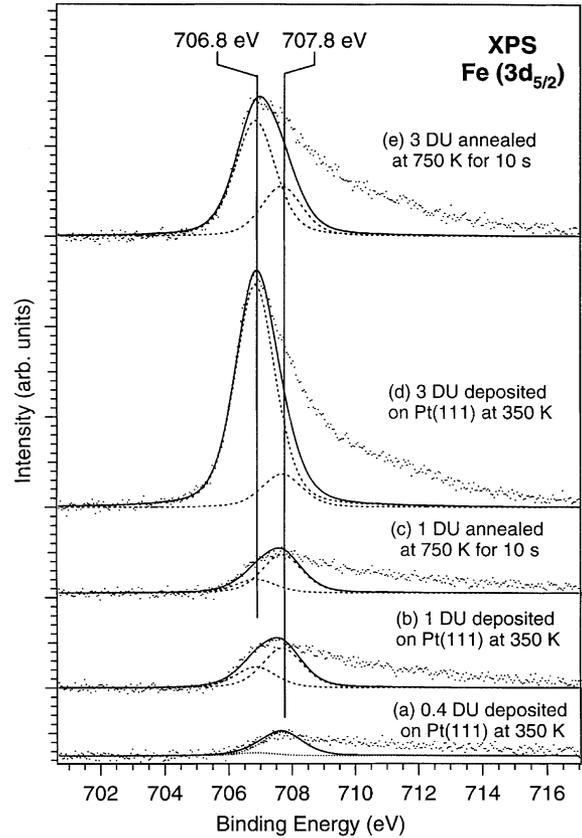


Fig. 4. Fe(3d_{5/2}) core levels in XPS for several Fe films on Pt(1 1 1).

and line shape. The solid line shows the sum of these two peaks. We assign the peak shifted to 0.4 eV higher binding energy to Pt atoms bonded to Fe in a Pt–Fe alloy. This observation is consistent with a shift of Pt core levels to higher binding energy in bulk Pt–Fe alloys, but the 0.4-eV chemical shift observed in our experiments was twice as large as the 0.2-eV shift reported by Berret et al. [9] for a Pt₈₀Fe₂₀ bulk alloy. This chemical shift is evidence for alloy formation, and the size of the shift supports an assignment of the alloy composition to have more Fe than in Pt₈₀Fe₂₀. The fraction of the Pt signal in the chemically shifted peak at 71.4 eV could be as large as 85% (top curve of Fig. 3d) for the annealed 6-DU Fe film.

Fig. 4 shows that the Fe(3d_{5/2}) core-level peak following deposition of 0.4 or 1-DU Fe on Pt(1 1 1) at 350 K, in curves (a) and (b), occurs near

707.8 eV BE. This can be compared to the peak after deposition of a 3-DU Fe film on Pt(1 1 1), in curve (d), which is assigned to be due primarily to a peak at 706.8 eV BE that arises from unalloyed, metallic Fe. Spectra obtained after annealing to 750 K could be decomposed into two Fe peaks at 706.8 and 707.8 eV BE, assuming a constant width of 1.5 eV and nonchanging line shape. These individual components are depicted by dashed lines, and the sum of these two peaks is given by the solid line. The peak at 706.8 BE must be assigned to metallic Fe in the as-deposited film and alloyed Fe in the bulk of the crystal, because the Pt(4f) spectra and the LEIS data both indicate that most of the Fe present is alloyed with Pt in the sub-surface region after annealing a 3-DU Fe film to 750 K. A theoretical calculation has predicted a near-zero value for this core level shift between Fe metal and a Pt₈₀Fe₂₀ bulk alloy [9]. The high-energy Fe peak at 707.8 eV BE can only be assigned to Fe present in the topmost, surface layer, with a surface core-level shift of 1.0 eV. No carbon nor oxygen contamination was detected by XPS, and the size of this peak did not change significantly with the amount of Fe deposited prior to annealing (in a 1–6 DU range) or as a result of the annealing treatment. This strongly supports formation of a Pt–Fe alloy, and is an important argument against the possibility that the Fe is simply clustering into small, 3-D particles.

During the annealing experiments shown in Fig. 2, we also examined the surface with LEED after each annealing step. In the region from 750 to 850 K where the Fe signal did not change significantly, a diffuse (2×2) LEED pattern was observed as shown in Fig. 5. Observation of a (2×2) LEED pattern was also reported for the Pt₈₀Fe₂₀(1 1 1) bulk alloy surface [5] and explained by the existence of two kinds of Pt atoms in the topmost layer. It was proposed that those Pt atoms have different neighbors in the second layer and this causes formation of 2×2 structure comprised of only Pt atoms. We cannot rule out this possibility in our case as well without further studies, but clearly the (2×2) LEED pattern could also result from formation of an ordered Pt–Fe alloy at the surface containing 0.5-ML Fe. The broad spots and high background intensity observed for this (2×2) pattern compared to the (1×1) pattern for the clean Pt(1 1 1) surface indicates that the alloyed surface is not as well ordered as the original Pt(1 1 1) surface. A (2×2) LEED pattern has been observed that arises from a p(2×2)-Sn/Pt(1 1 1) surface alloy formed by annealing a Sn film deposited on Pt(1 1 1), but this surface has 0.25-ML Sn [10].

In summary, we show evidence that Pt–Fe alloy surfaces that expose Fe in the first layer can be prepared by annealing Fe films deposited onto a Pt(1 1 1) surface. Annealing a 1.5-DU Fe film to 600–850 K causes alloying, with much of the Fe

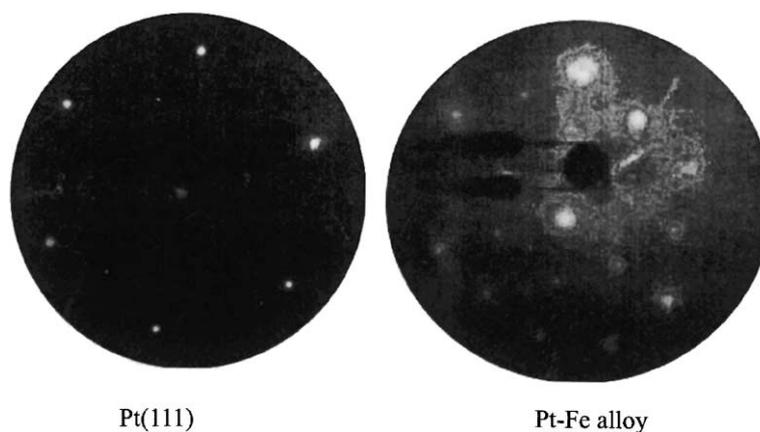


Fig. 5. LEED patterns obtained (left) for clean Pt(1 1 1) and (right) after annealing a 1.5-DU Fe film on Pt(1 1 1) for 1 min at 750 K. Incident beam energy $E_p = 60.0$ eV for both images.

remaining in the near-surface region. The Fe concentration in the surface layer was nearly constant at 0.5 ML. This surface displayed a (2×2) LEED pattern after annealing to 750–850 K. This procedure produces Fe-containing alloy surfaces that are more thermally stable against Pt surface segregation than expected from the behavior of $\text{Pt}_{80}\text{-Fe}_{20}(111)$ bulk crystals, and significant amounts of Fe are stabilized in the surface layer until temperatures as high as 950 K.

Acknowledgement

This work was partially supported by the Analytical and Surface Chemistry Program in the Division of Chemistry, National Science Foundation.

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