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The Interaction of N_2 with Iron on W(110), Pd(111) and Rh(111)

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Dedicated to Gerhard Ertl on the occasion of his 60th birthday

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We have studied the interaction of molecular nitrogen with thin iron films on W(110), Pd(111) and Rh(111) using angular resolved spectroscopy (ARUPS). Iron layers on W(110) with thicknesses of up to 2 layers are strained thereby acquiring the lattice constant of the substrate. Also a moire like superstructure has been studied. In contrast to results obtained for Fe(110) we find molecular adsorption at low temperatures as well as dissociation of nitrogen molecules on strained Fe/W(110). In agreement with calculations we find an upward shift of the iron 3*d* band density which might be the reason for the enhanced reactivity of Fe/W(110) as compared to Fe(110). In order to study the influence of the substrate on the interaction with nitrogen we have investigated films with different thickness.

Iron layers on Pd(111) and Rh(111) have been studied since the strain of pseudomorphic iron films on these substrates is intermediate between that of Fe/W(110) and unstrained Fe(110). We find the formation of surface compounds and iron diffusion into the substrate at elevated temperatures. The chemical activity of the compound films is intermediate between those of pseudomorphic Fe on W(110) and Fe(110).

Wir haben die Wechselwirkung von molekularem Stickstoff mit dünnen Eisenfilmen auf W(110), Pd(111) und Rh(111) mit winkelaufgelöster Photoelektronenspektroskopie untersucht. Auf W(110) können pseudomorphe Eisenfilme mit Schichtdicken von bis zu zwei Lagen präpariert werden. Die Gitterkonstante der Filme entspricht der des W(110)-Substrates. Weiterhin werden Daten für einen Film mit Moire-artiger Struktur präsentiert. Während die Fe(110)-Oberfläche bezüglich Wechselwirkung mit N_2 inaktiv ist, beobachten wir für die pseudomorphen Filme sowohl molekulare Adsorption bei tiefen Temperaturen als auch Dissoziation der N_2-Moleküle. In Übereinstimmung mit Rechnungen finden wir eine Verschiebung der Fe 3*d*-Bänder zu höherer Energie, was möglicherweise die Ursache für die erhöhte chemische Aktivität der pseudomorphen Filme ist. Um den Einfluß des W(110)-Substrates auf die chemische Aktivität der Filme zu studieren, wurden Adsorptionsuntersuchungen an Filmen mit verschiedenen Dicken durchgeführt.

Die berechneten Gitteraufweitungen von pseudomorphen Filmen auf Pd(111) und Rh(111) sind kleiner als die von Fe/W(110). Für dünne Eisenfilme auf diesen Substraten finden wir sowohl die Bildung von Legierungen als auch Diffusion der Eisenatome in das Volumen des Substrates. Die chemische Aktivität der Filme liegt zwischen denen von Fe/W(110) und Fe(110).

Introduction

Due to the industrial importance of ammonia synthesis nitrogen adsorbates on iron ingle crystal surfaces belong to the most studied systems in surface science [1–20]. In particular Gerhard Ertl has performed pioneering work in this field. The active component of the Haber-Bosch catalyst for NH_3 synthesis is finely dispersed iron which dissociates the N_2 molecules. Previous studies have shown that this is the rate determining step in the catalytic process [1–3].

In studies of iron single crystals with different surface orientations Somorjai and coworkers [20] have shown that the NH_3 formation rate depends strongly on the structure of the respective iron surface. They found that Fe(111) exhibits the highest reactivity whereas the flat and closely packed Fe(110) surface does not show any reactivity at all, i.e. the N_2 dissociation rate is strongly structure sensitive. From the results of Somorjai *et al.* [20] one may conclude that for the N_2 dissociation to occur an open structured surface is needed.

In a previous study of nitrogen adsorption on Fe(111) it has been shown that dissociation occurs via a chemisorbed precursor state of N_2 which is π-bonded to the surface [15, 17]. This species is strongly inclined with respect to the surface normal [17] and dissociates upon warming up to $T \cong 140$ K. The inclined form of N_2 is stabilized in the hollow sites of the (111) surface which may be viewed as an indication that an open surface structure is a prerequisite for the dissociation process due to steric reasons. However, of course also the electronic structure of the surface which goes hand in hand with its geometric structure has to be considered.

In order to study the influence of the geometric structure on the interaction of nitrogen with iron surface we have performed adsorption studies on strained iron films prepared on various substrates. On W(110) pseudomorphic Fe films may be grown, i.e. films that acquire the lattice constant of the substrate. According to our data and in agreement with literature data [23–27] pseudomorphic films may be prepared with thickness of up to 2 layers. The structures of the films are similar to that of Fe(110) in that they are quasi hexagonal. They differ from Fe(110) in that their lattice constant is enlarged.

One important aspect for the present study is the interaction of the iron films with an absorbate. This modifies the electronic structure of the layer and thereby its interaction with the substrate. It has been shown by Wurth and coworkers [22] that this effect influences the interaction of CO with a monolayer of Ni on W(110) considerably. In order to minimize this effect we have studied mostly doublelayer films on the respective substrates. However, also data for a monolayer film and non pseudomorphic thicker will be presented.

The adsorption properties of iron films on Pd(111) and Rh(111) have been studied for comparison since the strain of pseudomorphic films is smaller on these substrates as compared to Fe/W(110). However, we found that compound formation and iron diffusion takes place so that the results may not be appropriate for a direct comparison to results for Fe(110) and Fe/W(110).

Experimental

The experiments have been performed in a UHV system equipped with facilities for angular resolved photoelectron spectroscopy using an analyser rotable in two orthogonal planes, residual gas analysis, thermal desorption spectroscopy with a quadrupole mass spectrometer and LEED. Photoelectron spectra were excited with light from the TGM3 beamline at the BESSY synchrotron radiation center in Berlin.

The samples could be cooled down to temperatures of about 90 K and heating was possible to about 3000 K electron impact. For W(110) the only contaminant found was carbon. It was removed by cycles of annealing in an oxygen atmosphere with subsequent flashing to 2000 K. The Pd(111) and Rh(111) substrates were cleaned by prolonged and annealing cycles.

Iron was sublimated from an iron block which was heated by electron impact. During evaporation the pressure was in the 10^{-10} mbar range. We determined the evaporation rate of the Knudsen cell with a quartz microbalance and calculated the deposition time needed to prepare an iron film with a specified thickness from this value.

Results and discussion

a) Fe/W(110)

Iron on W(110) is an often studied system [23–29] since it represents a model system for the study of magnetic properties of thin films [26–29]. Therefore data on the structure of iron layers on W(110) are readily available in literature [23–26]. Pseudomorphic iron films may be grown with thicknesses of up to two layers. Coverages higher than two layers lead to the formation of a mosaic structure with a (10×10) LEED pattern [23–25] with decreasing intensity of the superstructure spots when the coverage is increased. At thicknesses of some 10 layers a LEED pattern is observed which is indistinguishable from that of Fe(110). We have studied pseudomorphic mono and doublelayers films as well as the (10×10) mosaic struc-

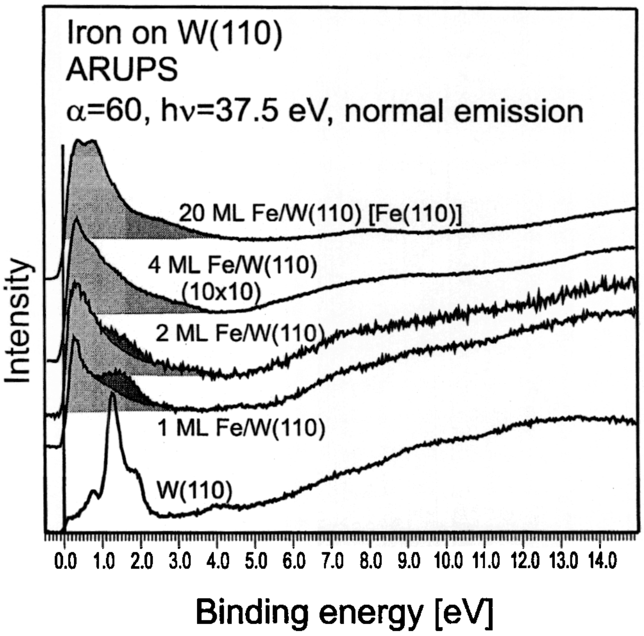

Fig. 1. ARUPS spectra of different iron films on W(110) in comparison with a spectrum of uncovered W(110). Gray shaded region: Fe3*d*; dark gray region: remaining W5*d* intensity.

ture and films with a thickness of 20 layers which have the same structure as Fe(110). An overview of photoemission data for the uncovered films is given in Fig. 1. In Fig. 2 corresponding data for a molecular nitrogen adsorbate at T = 80 K are shown. It is obvious from these data that a film with a thickness of 20 layers does not adsorb any nitrogen at this temperature. This is as expected since the structure of this film is equal to that of Fe(110) which is inactive with respect to nitrogen adsorption. The pseudomorphic mono- and doblelayer films on the other hand show strong nitrogen signals whereas the (10 × 10) structure exhibits a somewhat weaker signal. From these data it may be concluded that the expanded lattices of the thin films lead to a situation which enhances the activity of the films towards molecular adsorption of N_2. For the (10 × 10) structure the situation is somewhat intermediate which is likely due its moire like structure. In this film regions with different lattice extensions are expected to coexist on the surface and therefore part of the surface may not adsorb molecular N_2.

Fig. 3 shows what happens when molecular nitrogen on a monolayer iron films is warmed up. At about 90 K the signal of molecular N_2 is not visible any more and a new feature is observed at about 6 eV. The latter is

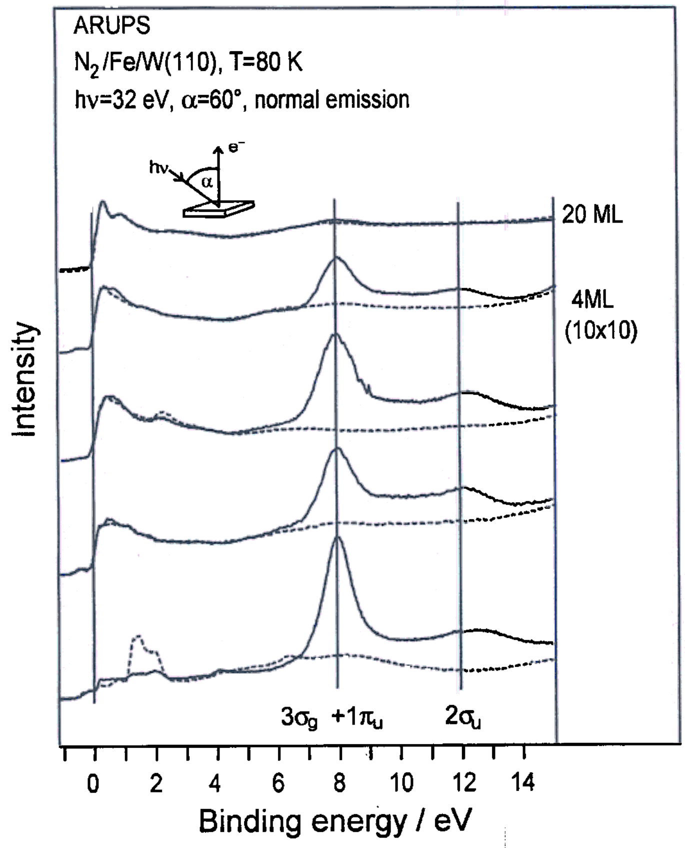

Fig. 2. ARUPS spectra of molecular nitrogen on different iron films on W(110).

attributed to atomic nitrogen, indicating that N_2 dissociates on the thin film. TDS data (see Ref. [21]) show that another part of the adsorbed N_2 desorbs from the surface. After several TDS cycles the film shows signs of nitride formation leading to a (2×3) superstructure in the LEED pattern [21]. A molecular precursor state for dissociation, as observed on Fe(111) [17] could not be found. Nitrogen dissociation is also found for a doublelayer film whereas a film consisting of 20 layers is inactive.

The formation of atomic nitrogen can also be observed when an iron film is exposed to N_2 at elevated temperature (Fig. 4). After dosing about 10000 L of N_2 at room temperature clearly a signal of atomic nitrogen is observed at 6 eV binding energy. A similar result has been obtained for

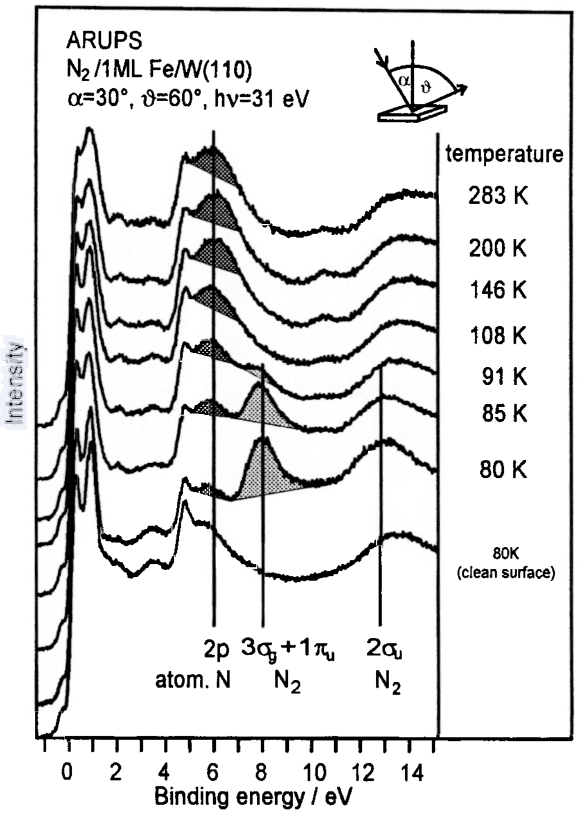

Fig. 3. ARUPS spectra of N_2 on a monolayer of iron on W(110) taken at different temperatures in comparison with a spectrum of the uncovered film.

nitrogen at $T = 600$ K [21]. The film with a thickness of 20 layers film is again inactive at both temperatures.

In the case of Ni/W(110) a considerable influence of the substrate on the adsorption properties of the nickel film with respect to CO has been deduced [22] using theoretical calculations and experiment. The data point towards a charge transfer from the nickel to the tungsten substrate which in turn influences the CO adsorption properties. To investigate the effect of the W(110) substrate onto the adsorption properties of the iron layers we compare the adsorption properties of films with different thicknesses. We find N_2 dissociation and absorption at low temperature on a monolayer film, a doublelayer film and also on the mosaic (10×10) structure with a thickness of 4 layers. For the thicker films the modification of the electronic structure at the surface due to the underlying tungsten substrate will be

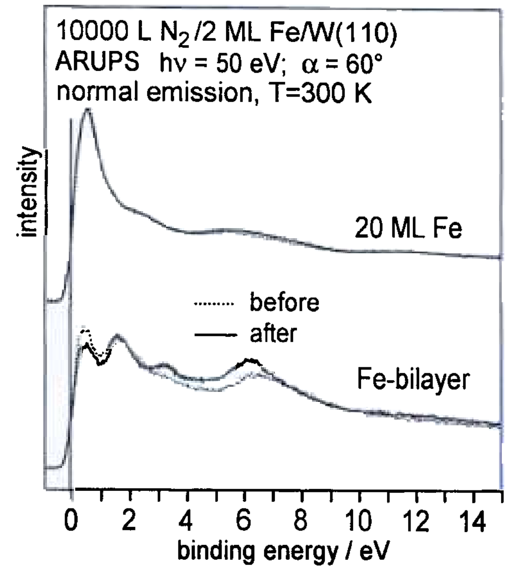

Fig. 4. ARUPS spectra of a film with a thickness of 20 layers and an iron doublelayer on W(110) recorded before and after dosing of 10000 L of N_2 at room temperature.

small so that it may be concluded that the strain of the iron lattice (and the resulting electronic effects) will be the main reasons for the modified adsorption properties whereas the underlying substrate does, most likely, not play a significant role.

The reasons for the enhanced chemical activity of the strained iron films still need to be adressed. For strained iron mono and doublelayers supported on W(110) Nørskov and coworkers [30] have calculated an upward shift of the Fe 3*d*-band density by 0.40 eV and 0.46 eV, respectively. Our data are qualitatively in agreement with this result (see Fig. 1) although it is not easily possible to evaluate the upward shift quantitatively. For CO on metals theoretical and experimental studies show that an upward shift leads to an increased CO-substrate binding energy [31]. The mechanism responsible for this result is the enhanced π-backbonding which results from the decreased energetical π-d spacing. As indicated by Nørskov and coworkers [30] this could also be the case for a nitrogen adsorbate with the increased N_2-iron binding energy leading to a lowered dissociation barrier. Of course, also steric reasons may play a significant role for the enhanced reactivity of the films. However, this seems to be unlikely for the discussed films since the lattice constant is strained only by about 10% in each direction.

For N_2/Fe(111) a molecular dissociation precursor was observed which was stable on the surface for temperatures of up to about 140 K. It could

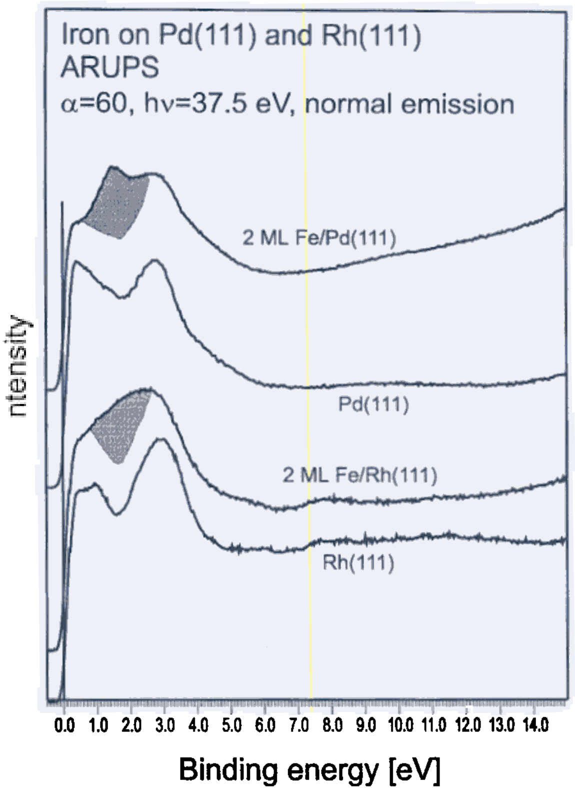

Fig. 5. ARUPS spectra of doublelayer of Fe on Pd(111) and Rh(111) in comparison with spectra of the uncovered surfaces. Gray shaded areas indicate emission due to the Fe 3*d* bands.

not be observed for any of the studied systems discussed in this paper although we tried to isolate this state spectroscopically. This does not necessarily mean that the dissociation of N_2 on the strained films proceeds in a considerably different way as compared to Fe(111). It may be the case that the precursor exists only at temperatures where the molecular nitrogen is also on the surface so that its emissions may be hidden by the emissions of the undisturbed molecules. On Fe/W(110) dissociation occurs already at $T = 80$ K when the molecular N_2 is still on the surface (see Fig. 2) so that the emissions of a possibly existing precursor may be hidden. Of course, it may also be the case that the molecular potential as a function of the reaction coordinate does not have a minimum or only a small minimum for the precursor state on the strained films so that it would be invisible due to a short lifetime.

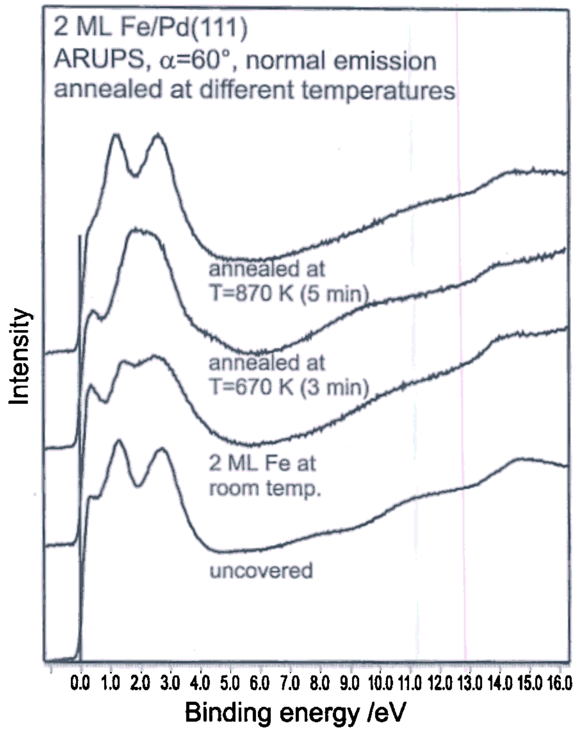

Fig. 6. ARUPS spectra of doublelayer iron on Pd(111) subjected to annealing at different temperatures in comparison with a spectrum of the uncovered substrate and a spectrum taken directly after preparation of the layer at room temperature.

b) Fe/Pd(111) and Fe/Rh(111)

Pseudomorphic iron films on W(110) represent strongly strained layers with significantly altered N_2 adsorption properties as compared to unstrained Fe(110). Therefore it was near at hand to study adsorption on iron films with intermediate strain. For pseudomorphic iron films on Pd(111) and Rh(111) the calculated area per surface iron atom is larger by 12.7% and 7.8%, respectively, as the value for the Fe(110) surface. The respective value for iron on W(110) is 21.5% so that the strain for pseudomorphic iron films on Pd(111) and Rh(111) is about half way between the values for pseudomorphic layers on W(110) and the unstrained Fe(110) surface.

About the structure of iron films on Pd(111) and Rh(111) much less is known than for Fe/W(110). Begley *et al.* studied the Fe/Pd(111) system with LEED [32]. They found that iron films may be grown pseudomorphically with thicknesses of up to 5 layers at $T = 473$ K. However, it was

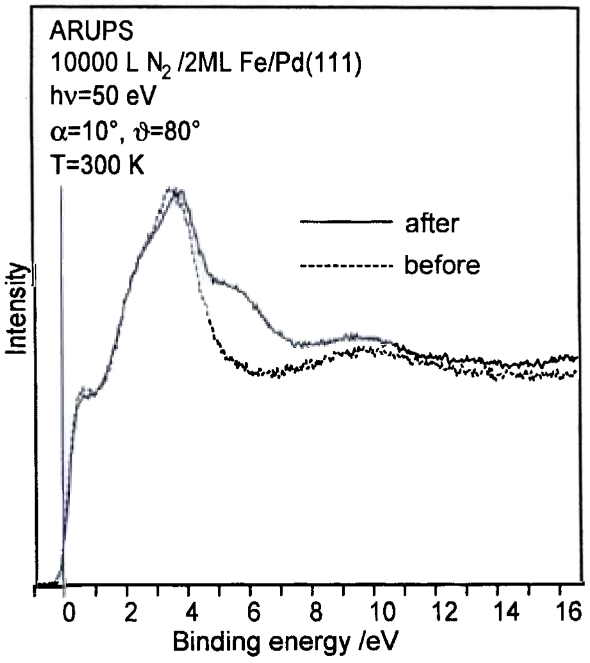

Fig. 7. Interaction of N_2 with 2 ML Fe/Pd(111) at room temperature. Spectra are shown for the surface before and after dosing of 10000 L of N_2.

also stated that the authors were not able to exclude the formation of a Fe/Pd compound at monolayer coverage. For iron on Rh(111) no structural information was available.

A set of ARUPS spectra of a doublelayer of iron on Pd(111) and Rh(111) is compared with data for the respective uncovered substrates in Fig. 5. The iron films have been evaporated at room temperature with subsequent annealing at $T = 500$ K. No extra spots were visible in the LEED pattern. However, a comparison of the data presented in Fig. 5 with the data in Fig. 1 shows that the suppression of the substrate emission is much stronger for a doublelayer iron on W(110) than for Pd(111) and Rh(111). The strong suppression of the substrate emission intensity as observed for Fe/W(110) is as expected, since the mean free path of the valence band electrons in Figs. 1 and 5 should be small. The high remaining emission intensity of substrate 4*d* bands for Fe on Pd(111) and Rh(111) in Fig. 5 is as a strong indication that compound formation and diffusion of iron atoms into the substrate take place at these surfaces. This still holds when the photoemission cross sections of the W 5*d*, Pd 4*d* and Rh 4*d* bands are considered since they are not too much different [33]. Also, the observed

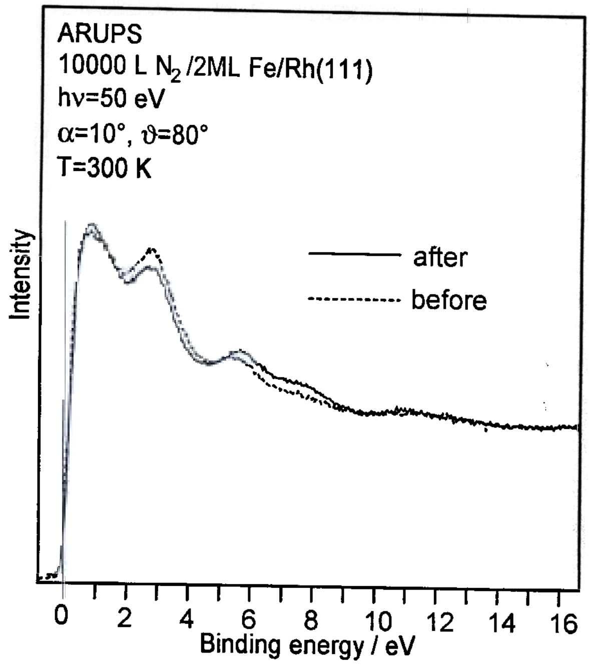

Fig. 8. Interaction of N_2 with 2 ML Fe/Rh(111) at room temperature. Spectra are shown for the surface before and after dosing of 10000 L of N_2.

Fe 3*d* binding energies are higher than expected. Nørskov and coworkers have calculated an upward shift for the Fe 3*d* density of states for iron films on Pd(111) and Rh(111) [30] whereas a downward shift is observed in the experimental data. This may also be explained by compound formation.

The high tendency of the Fe/Pd system for compound formation and iron diffusion is also documented by a set of ARUPS spectra of a double layer film which has been subjected to annealing at different temperatures (Fig. 6). At highest temperature most of the iron has disappeared from the surface so that the spectrum resembles that of the uncovered substrate. Interestingly an enhanced emission is observed directly at the Fermi level in the spectrum of the unannealed iron film in Fig. 6. This may be an indication that on the surface atoms exist which are not part of a Fe/Pd compound since this intensity is in an energy region where emission from pure iron has to be expected according to Ref. [30].

The N_2 adsorption properties of the compound films have also been studied. The deposited amount of iron corresponded to a doublelayer in both cases. Neither for Fe/Pd(111) nor for Fe/Rh(111) molecular N_2 adsorption at $T = 80$ K could be observed. Prolonged dosing at room temperature on the other hand leads to signs of nitride formation as indicated by a signal at about 6 eV binding energy in the ARUPS spectra. This is quite obvious for the Pd(111) substrate (Fig. 7) whereas for Fe/Rh(111) the signal is rather weak (Fig. 8). In principle the adsorption properties would fit into a model where the activity of the films with respect to N_2 adsorption and dissociation depends on the lattice strain. However, since compound formation is likely this conclusion must be taken with care.

Summary

In this paper we have reported on results of N_2 adsorption studies on strained iron films on W(110). We find that the chemical activity of the films is significantly increased with respect to that of Fe(110) since on the strained layers we observe molecular adsorption at $T = 80$ K as well as dissociation at room temperature and 600 K. Our data indicate that the interaction with the tungsten substrate is not the determining factor for the enhanced activity of the films.

In qualitative agreement with our data calculations by Nørskov and coworkers [30] show that the iron valence band density for the strained double- and monolayer films on W(110) should shift upwards by 0.46 and 0.40 eV, respectively. This leads to an enhanced bonding strength and results in an increased N_2 dissociation probability as observed for the strained Fe/W(110) films.

A molecular dissociation precursor as has been found for N_2 on Fe(111) [17] could not be observed for nitrogen on the strained films.

For iron on Pd(111) and Rh(111) compound formation at the surface is observed at $T = 500$ K. At higher temperatures the iron diffuses into the volume of the substrate. The chemical acivity of the compound films with respect to the interaction with N_2 is intermediate between those of Fe/W(110) and Fe(110) in that no molecular adsorption at $T = 80$ K is observed whereas dosing of 10000 L of N_2 at room temperature leads to the formation of atomic nitrogen in both cases.

Acknowledgements

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