N_2 adsorption and dissociation on thin iron films on W(110)

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Abstract

Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS), thermal desorption spectroscopy (TDS) and low energy electron diffraction (LEED) have been utilized to study molecularly adsorbed N_2 on thin (110) oriented Fe layers grown on W(110). Layers with thicknesses of up to 2 monolayers acquire the lattice constant of the substrate which is by 10.4% larger than that of iron. These strained layers show different properties than the bulk Fe(110) surface. To our knowledge no molecularly adsorbed N_2 species on bulk Fe(110) is reported in the literature at $T \geq 80$ K, whereas on the pseudomorphically grown iron layers on W(110) we observe a molecularly adsorbed species which stands upright on the surface.

Pseudomorphically grown Fe layers on W(110) show a strongly enhanced dissociation probability for adsorbed N_2 which we attribute to the open structure of the strained surface. For comparison also results for thick Fe(110) layers, which resemble the structure of an unstrained Fe(110) surface, are reported.

1. Introduction

Ammonia synthesis by heterogeneous catalysis is the most important process in industrial chemistry for the utilization of atmospherical nitrogen, making it available for the production of all kinds of different chemicals.

Due to the importance of this process many investigations have been performed in order to understand the reaction steps of this catalytic reaction [1–24]. Iron is the catalytically active component in all commercial catalysts and the decomposition of the molecularly adsorbed N_2 on Fe into atomic nitrogen is known to be the rate limiting step [8,13]. One of the results of the many studies performed in the past is that the rate of nitrogen dissociation is dependent on the surface structure of the iron [5,13,16]. By monitoring the NH_3 formation rate [18] it has been found that surfaces which offer C_7 sites like Fe(111) (see Fig. 1) are the most reactive ones, while Fe(100) and Fe(210) surfaces which offer C_4, C_6 and C_8 sites exhibit a NH_3 formation rate which is smaller by a factor of five. On Fe(110) which only offers C_6 sites no NH_3 formation is found [18]. Similar results have been obtained for Re single crystals [25]. The open structured Re(11$\bar{2}$1) surface, offering C_{11} and C_{10} sites, is by a factor of 1000 more reactive than the close-packed Re(0001) surface.

The N_2 dissociation rate can also be influenced by changing the lattice constant of a given active material. For strained chromium overlayers on W(110) it has been found that N_2 dissociates already at 80 K [26–29] whereas on unstrained Cr(110) N_2 dissociation is not observed at temperatures below 100 K [27].

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In this paper we present data for N_2 adsorption on strained and unstrained Fe(110) layers on W(110). As shown by Böheim et al. [19] unstrained Fe(110) is rather unreactive with respect to N_2 dissociation. Using Auger electron spectroscopy they concluded that the upper limit of dissociative sticking probability should be below 1×10^{-5} at elevated crystal temperature. Strained Fe(110) on W(110) on the other hand is quite reactive with respect to N_2 dissociation. Even at low temperature nitrogen dissociation in considerable amounts is observed.

We prepared strained Fe(110) as films with thicknesses of up to 2 monolayers on W(110) [30,31]. Since these films acquire the lattice constant of the substrate their lattice constant is enlarged by 10.4% with respect to that of bulk iron ($a_W = 1.104\,a_{Fe}$) [32,33].

2. Experimental

The experiments have been performed in an ultra-high vacuum system which contains facilities for LEED, AES, TPD, and ARUPS. TPD data were taken with a quadrupole mass spectrometer equipped with a so-called Feulner cup [34]. An electrostatic electron analyser with an angular acceptance of two degrees mounted on a double-axis goniometer allows for angular-resolved electron detection in two orthogonal planes. Electrons were excited with light from the TGM3 monochromator at the BESSY synchrotron radiation center in Berlin. The base presure of the UHV system was below 1×10^{-10} mbar.

The sample was spotwelded to two tungsten wires which were attached to two tungsten rods. These rods were pressed into two holes in a sapphire block which was connected to a liquid nitrogen reservoir. With this setup temperatures as low as about 80 K could be reached. For heating purposes a tungsten filament was mounted behind the crystal which could be used for heating via electron bombardment or radiation. With a tungsten/rhenium thermocouple (5%Re/26%Re) the temperature was monitored.

The W(110) crystal was cleaned by repeated cycles of oxidation at 1800 K in 6×10^{-6} mbar of O_2 to remove carbon. After this procedure the crystal was annealed at 2300 K in order to remove tungsten oxide.

The Fe layers were then prepared according to procedures given by Gradmann and Waller [30] and by Berlowitz et al. [31]. During Fe evaporation the crystal was kept at a temperature of 600 K in order to avoid an unordered growth of the film. The iron flux could be monitored by a quartz microbalance.
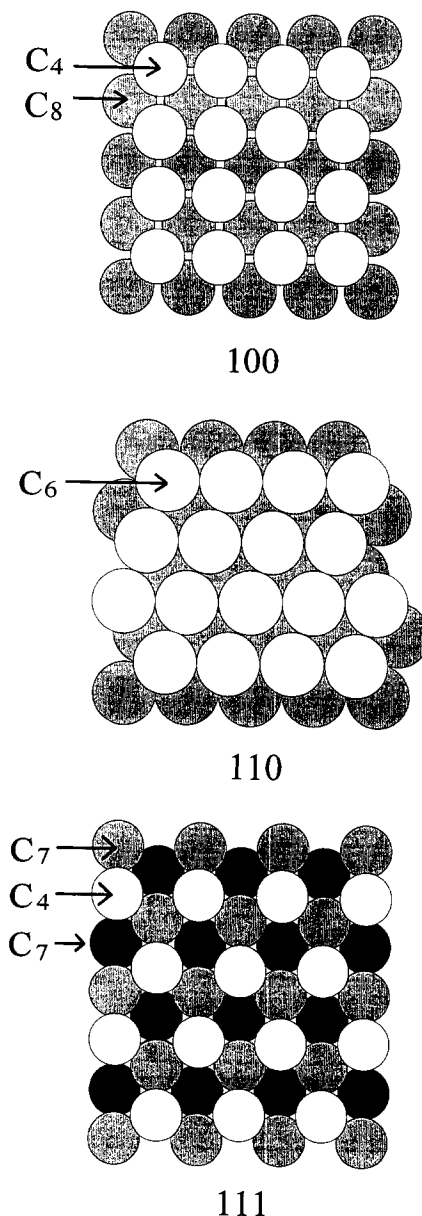

Fig. 1. Schematic diagram showing the arrangement of atoms on three different surfaces of a bcc crystal. The types of the sites (C_4, C_6, C_7, and C_8) are indicated.

Since molecularly adsorbed N_2 is dissociated/desorbed by synchrotron radiation it was necessary to keep a background pressure of 1×10^{-8} mbar of N_2 while recording the ARUPS data.

Iron films on W(110) are known to be very sensitive towards oxygen contamination [35]. According to Ref. [35] a dose of only 0.1 L of oxygen leads to a (2×2) superstructure in the LEED pattern

of a monolayer of Fe on W(110). We did not observe this superstructure so that most likely no notable oxygen contamination did exist.

Concerning the structure of the thin films, only a limited amount of data is to be found in the literature. For an iron monolayer it has been shown using STM that this film forms a nearly perfect monolayer [36]. For the thicker films structural data are still
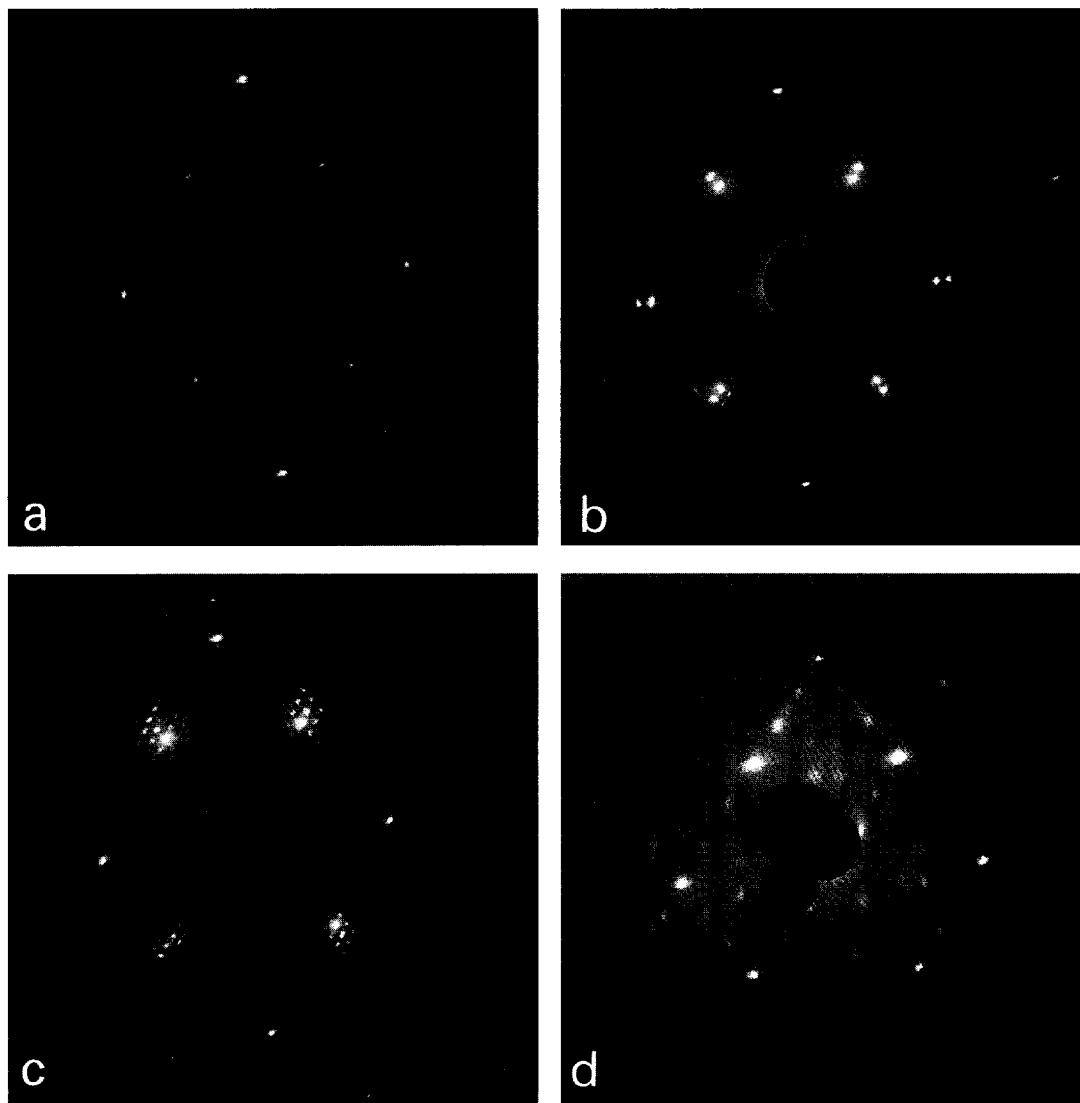

Fig. 2. Photographs of LEED patterns. (a) Clean W(110); (b) iron clusters on W(110) prepared by flashing an iron film with a thickness of 20 ML to 1000 K; (c) (10×10)Fe/W(110) prepared by evaporating 3 ML of iron at a sample temperature of 550 K; (d) nitrided Fe/W(110) obtained after taking two TDS spectra of nitrogen on a bilayer of iron. Two domains of a (2×3) superstructure are visible.

missing. Only photographs of LEED patterns exist [30,31] which agree with the data presented in this paper.

3. Results and discussion

Depending on the preparation procedure different iron superstructures can be produced [30,31]. Fig. 2a displays the LEED pattern of the clean W(110) surface. Deposition of iron films with thicknesses in excess of a monolayer at temperatures above 750 K leads to the formation of iron clusters. These iron clusters grow with the lattice constant of iron which is by 9.4% smaller than the lattice constant of the substrate [32,33]. In the LEED pattern a superposition of the reciprocal lattices of the clusters and the substrate is observed which leads to doublet spots (Fig. 2b). For thick iron layers prepared at temperatures above 750 K only the Fe(110) spots are observed which points towards a tungsten surface which is densely covered with an unstrained Fe(110) film. Iron layers prepared at temperatures below 750 K with thicknesses of more than two monolayers lead to a (10×10) LEED pattern which is due to the mismatch between the W and the Fe lattice (Fig. 2c). The finding that this LEED pattern is not observed for iron doses less than those corresponding to two monolayers may be viewed as an indication that the third layer does not start to grow before the second one is completed.

Fig. 3 shows a series of ARUPS spectra of N_2 on W(110) and Fe/W(110) for different iron coverages. For comparison also á spectrum of CO on a strained bilayer is shown. The nitrogen coverages on W(110) and Fe/W(110) may be compared directly using the ARUPS intensities of the N_2 levels on the respective surfaces since N_2 on Fe/W(110) is standing upright on the surface as will be discussed later so that its differential photoionization cross section should be similar to that of N_2 on W(110) where the N_2 molecules adsorb in the same geometry [37]. From these data it is obvious that the N_2 coverage on the strained layers with thicknesses of up to 2 ML is rather high, similar to the coverage of N_2 on W(110) whereas nearly no molecular nitrogen is detectable on the thick unstrained Fe(110) film. For the iron film which shows a (10×10) structure somewhat
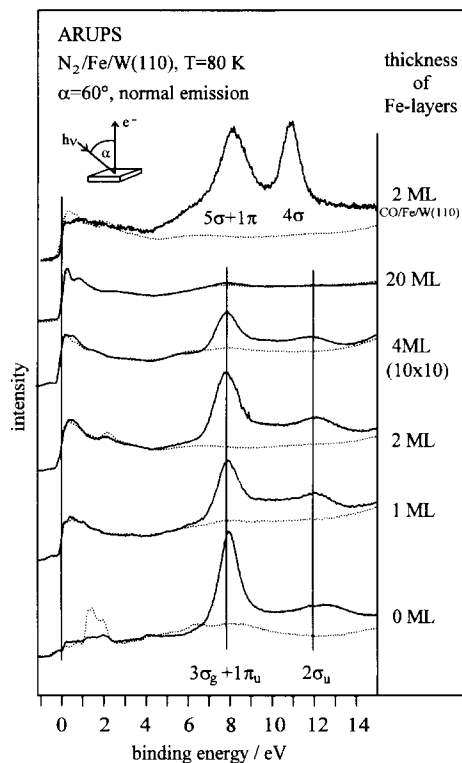

Fig. 3. ARUPS spectra of N_2 and CO on W(110) and Fe/W(110) as a function of the iron coverage. For comparison in each case also a spectrum of an uncovered iron film is shown (dotted line).

smaller nitrogen signals are visible. The result for the thick film is as expected since the structure of this film is the same as that of massive iron crystals exposing the (110) face to the vacuum as concluded from the LEED pattern (see Fig. 2b). For Fe(110) no reports about molecular N_2 adsorption are found in the literature which means that the adsorption properties of the thick film on W(110) are most likely similar to those of Fe(110).

The situation is different for the pseudomorphically grown films. For these layers the spectra in Fig. 3 show strong emissions, characteristic for molecular nitrogen. The $3\sigma_g$ and $1\pi_u$ levels show up as a broad structure at about 8 eV whereas the $2\sigma_u$ level is found at about 12 eV. There seems to be also some intensity between these peaks that we attribute to shake-up excitations which have also been observed for N_2/Ni(110) [38]. Such excitations are not uncommon for weakly bound adsorbates on metals [39]. The strong signals of N_2 on the strained films
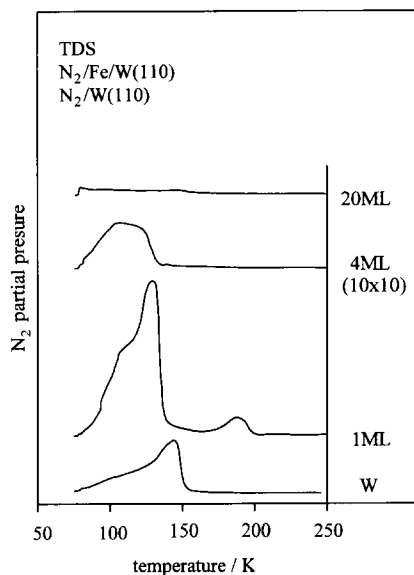
Fig. 4. Thermal desorption spectra of N_2 on W(110) and Fe/W(110).

indicate that their adsorption properties must be different from those of massive Fe(110). This is not surprising since it is well known that the electronic properties of the strained films differ drastically from the properties of bulk Fe [40]. For (10×10)Fe/W(110) the situation is somewhat intermediate. Here only comparably weak signals of molecular nitrogen are found. This is as expected since this iron film is most likely partly strained. The (10×10) structure is a coincidence structure with a unit cell of (11×11) iron atoms on (10×10) tungsten atoms [30,31].

The difference between the strained Fe(110) films and unstrained Fe(110) is also manifested in TDS data. Fig. 4 exhibits TDS spectra of saturation coverages of N_2 on W(110) and Fe layers with different thicknesses. For all Fe layers the maximum of N_2 desorption occurs between 100 and 120 K. The doublet structure of the desorption peaks may indicate that two adsorption states are occupied on the surfaces of the films. However, also lateral interactions of the adsorbed molecules may play a role.

The spectra displayed in Fig. 4 are a strong indication that the iron layers wet the surface since otherwise one would also find a desorption signal at about 150 K in the spectra. This is the temperature where desorption from W(110) occurs (see Fig. 4).

In the spectrum of the iron multilayer a weak structure is found at this temperature but in view of the thickness of the film it seems to be unlikely that this signal is to be attributed to desorption from W(110). The origin of the structure at about 190 K in the spectrum of N_2 on the iron monolayer is not known yet. It is most likely not due to CO since desorption of CO occurs at higher temperature (data not shown). Here it may be possible that the W(110) substrate plays a certain role since for the monolayer the exact iron dose plays a critical role.

All in all, the data displayed in Fig. 4 are in line with the ARUPS data shown in Fig. 3: strong desorption signals from strained Fe(110), weak signal from thick films and a somewhat intermediate signal intensity from (10×10)Fe/W(110).

The orientation of the molecular nitrogen species has been studied by monitoring the intensity of the $3\sigma_g$ level as a function of photon energy in two different experimental geometries. It is well known that the photoemission intensity of the $3\sigma_g$ level exhibits a maximum at about 31 eV when the electrons are detected along the molecular axis and the electric field of the light contains a component parallel to the molecular axis [41]. This intensity resonance is the so-called σ resonance. It is due to an excitation into the unoccupied $3\sigma_u$ level [41,38]. Figs. 5 and 6 display series of ARUPS data of N_2 on a strained iron bilayer on W(110) as a function of the photon energy. The data in Fig. 5 have been taken with light predominantly polarized perpendicular to the surface plane, detecting the electrons in normal emission whereas the data in Fig. 6 were recorded for nearly perpendicular light incidence, detecting the electrons at a grazing angle. These sets of data differ in that in Fig. 5 an intensity maximum of the $3\sigma_g$ emission is found at a photon energy of 32 eV whereas in Fig. 6 the intensity is more or less independent of the photon energy. Since the σ resonance is only observed when the electrons are detected along the molecular axis it must be concluded from Figs. 5 and 6 that the molecules are standing upright on the surface. The absence of an intensity maximum in Fig. 6 shows that no N_2 molecules or only a negligible number of molecules lie flat on the surface.

The properties of strained Fe(110) on W(110) do not only differ with respect to the adsorption of

molecular N_2 from those of unstrained Fe(110); also the N_2 dissociation probabilities differ drastically. According to Böheim et al. [19] the probability of N_2 dissociation on Fe(110) at elevated sample temperature is below 10^{-5} [19]. For low temperatures the dissociation probability is not known, but it will likely be smaller. As will be shown in the following, N_2 dissociates on the strained layers even at 80 K in considerable amounts.

In TPD spectra (Fig. 7) a drastic reduction in molecular nitrogen uptake is noticed after the first exposition and heating the sample to 300 K. This means that the number of available adsorption sites must have decreased considerably. After recording two TPD spectra a LEED pattern caused by (2×3) domains was found (Fig. 2d). The same pattern was observed for a Fe(110) surface covered with atomic nitrogen [6]. However, contrary to the case of unstrained Fe(110), for the strained layer only two
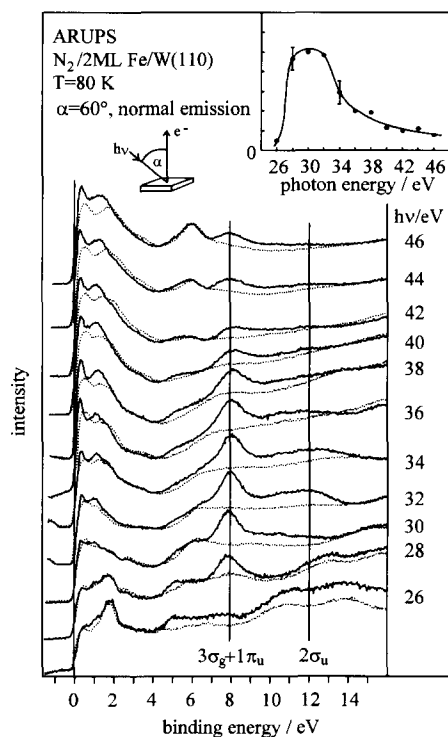

Fig. 5. ARUPS spectra of N_2 on 2 ML Fe/W(110) recorded with mainly z-polarized light for normal electron emission as a function of the photon energy. In the inset the dependence of the intensity of the $3\sigma_g / 1\pi_u$ level on the photon energy is displayed. The spectra of the uncovered surfaces are shown as dotted lines.
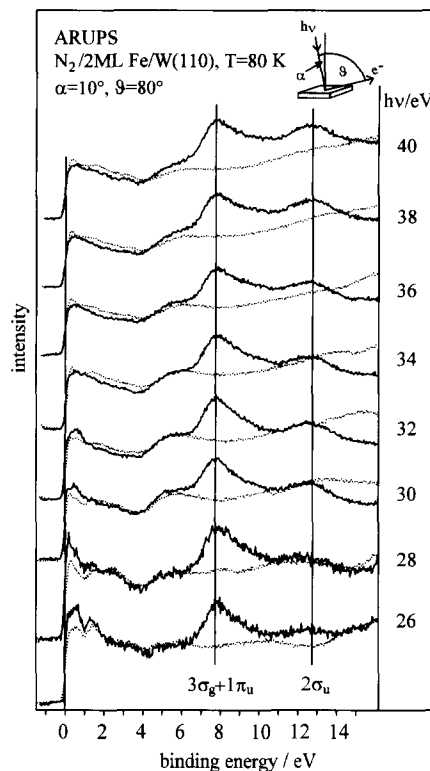

Fig. 6. ARUPS spectra of N_2 on 2 ML Fe/W(110) recorded for grazing electron emission and near perpendicular light incidence as a function of the photon energy. The spectra of the clean surfaces are shown as dotted lines.

cycles of annealing of a saturated layer of N_2 were needed to produce a nitrided surface with a (2×3) superstructure in the LEED pattern, which points towards a high probability for N_2 dissociation. At $T \approx 800$ K a N_2 desorption peak is observed from a nitrided surface which we attribute to the recombination of nitrogen atoms (see inset in Fig. 7). An enhanced nitridation activity was also found for strained Cr layers [27]. The chromium layers could also be nitrided already at 80 K.

As shown by the spectra displayed in Fig. 8 the dissociation of the N_2 molecules on a strained Fe(110) bilayer takes place already at 80 K. This figure displays a series of spectra of adsorbed nitrogen as a function of temperature. At about 108 K the molecular nitrogen is desorbed. A comparison with the spectrum of the clean surface (bottom on Fig. 8) shows that some additional intensity remains at a

binding energy of 6 eV which is to be attributed to atomic nitrogen. This peak seems to show up already at 80 K while the molecular nitrogen is still on the surface, indicating that dissociation takes place already at this temperature.

The data displayed in Fig. 8 and all the other data presented so far do not show any evidence for the existence of a molecular precursor to dissociation as it has been observed for Fe(111) [21,22]. On Fe(111) this precursor forms a π-bond to the surface with a strongly inclined molecular axis with respect to the surface normal. It could be isolated on the surface by desorbing the weakly chemisorbed molecular nitrogen species. On strained Fe(110) on W(110) no molecular species could be detected after desorption of the weakly chemisorbed molecular N_2 so that we tried to detect a signal of a molecular precursor state while the weakly chemisorbed N_2 was still on the surface. We did this by recording a series of spectra of N_2 on a bilayer of iron at low temperature, varying the light incidence angle from 80° to 10° with respect to the surface normal in 10° steps, always detecting the electrons along the direction of electric field vector (spectra not shown here) so that
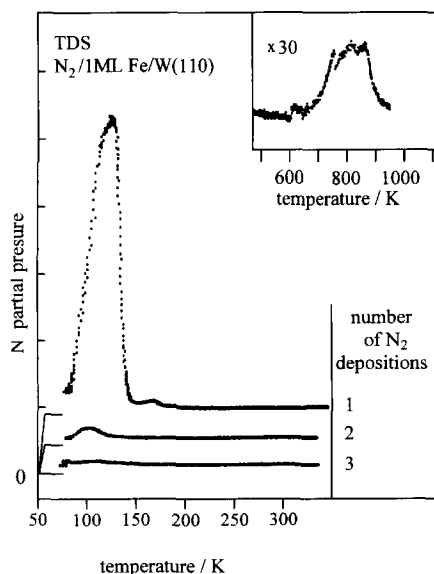

Fig. 8. ARUPS spectra of N_2 on 2 ML Fe/W(110) taken while annealing at different temperatures in a nitrogen atmosphere of 10^{-6}. The nitrided bilayer films were prepared by annealing the sample for 5.5 h at 300 K and then for 2 h at 650 K. For the multilayer two different films were annealed for 5.5 h at 300 and 650 K, respectively.

at least in one of the spectra the σ levels of a possibly inclined chemisorbed precursor species should exhibit high emission intensities. However, we could not find any feature in the spectra which could be attributed to a precursor state. It is possible that the emissions of the precursor – if any precursor with a sufficiently high lifetime does exist – are hidden by the emissions of the unperturbed molecular nitrogen species. According to Fig. 8 nitridation of the surface occurs already at about 80 K. The amount of atomic nitrogen does not change very much when going to higher temperature so that the precursor should already be dissociated to a large extent at this temperature. If there is any stable precursor at this temperature or lower then its emissions will likely be hidden under the strong features due to the unperturbed molecular nitrogen species.

In Fig. 9 photoemission spectra of a Fe bilayer and a multilayer film heated in a N_2 atmosphere of

Fig. 7. Thermal desorption spectra of N_2 on 1 ML Fe/W(110). The spectra have been taken consecutively from the same iron film. In the inset a part of a spectrum taken at higher temperatures is displayed.
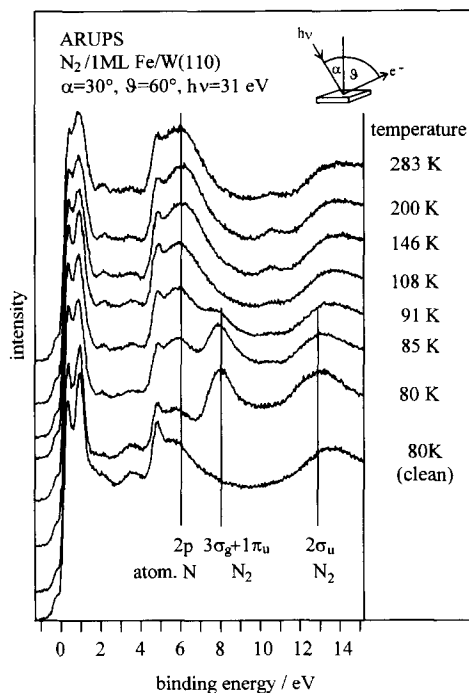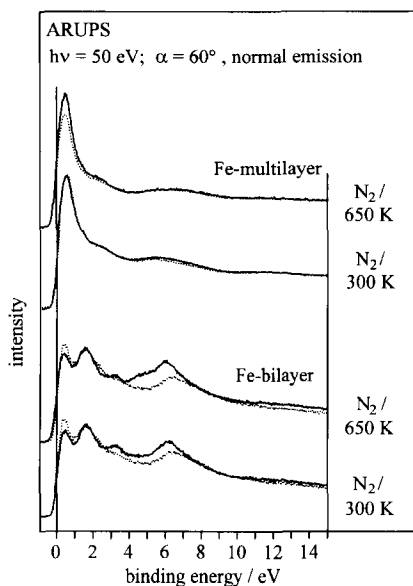
Fig. 9. ARUPS spectra taken after dosing iron films on W(110) with 10^{-8} mbar of N_2 at different temperatures. The spectra of the clean surfaces are shown as dotted lines.

1×10^{-6} mbar are compared. At the right side of the figure the annealing temperatures are given. The corresponding spectra of the clean surfaces are shown as dotted lines. While the spectra taken from the Fe bilayer show considerable intensity due to nitride formation in the range of the d-band emissions and at 6 eV after annealing the sample in a N_2 atmosphere, there are only small changes in the spectra of the thick unstrained film. The feature at 6 eV binding energy is due to the 2p electrons of atomic nitrogen whereas the emissions in the range of the d-band are most likely to be attributed to Fe 3d–N 2p hybrid states. According to the findings of Boszo et al. [6] a Fe(110) surface can by nitrided by exposing it to some 10 000 L of N_2 at a temperature of 683 K.

In our case at 650 K nearly no nitride formation is observed. Only the d-band intensity seems to be somewhat attenuated. This may be due to different qualities of the surfaces which could also be the reason for the experimental result that annealing at 300 K leads to a more pronounced nitride formation than annealing at 650 K.

The data obtained for a strained iron bilayer do not differ very much from data for a strained monolayer. This means that the reactivity on the iron films is most likely due to the enlarged lattice constant and not to the interaction with the substrate. Otherwise the adsorption properties of the monolayer and the bilayer should differ significantly. This is in line with observations made for different iron surfaces where it was found that N_2 is more easily dissociated on open faces [18].

From the (2×3) LEED pattern observed for a nitrided Fe(110) single crystal surface Boszo et al. [7] concluded that the geometry of the surface nitride should be similar to that of the (111) surface of Fe_4N. For the strained Fe(110) layers on W(110) we obtained the same LEED pattern after nitridation so that geometric structures of the nitrides on Fe(110) and strained Fe(110)/W(110) may be similar.

4. Summary

We have shown that the N_2 adsorption properties of Fe(110) films on W(110) with an enlarged lattice constant differ drastically from those of a Fe(110) single crystal surface. In contrast to a Fe(110) single crystal, on the strained films molecular adsorption is observed at temperatures above 80 K and dissociation already takes place in considerable amounts at this temperature. An enhanced dissociation probability is observed also at elevated temperatures. Obviously the strained Fe(110) layers on W(110) are considerably more reactive than Fe(110) single crystals with respect to N_2 adsorption and dissociation.

Due to the similarity of the spectra from the iron monolayer and the bilayer and in line with the observation that N_2 is more easily dissociated on open surfaces [18] we attribute the enhanced reactivity to the enlarged lattice constant of the thin films and not to the interaction of the films with the substrate.

A molecular precursor for dissociation could not be found. If there is any stable precursor then its emissions are most likely hidden by the emissions of the unperturbed molecular nitrogen species since the dissociation of N_2 occurs already at 80 K or lower temperature while the unperturbed species is still on the surface.

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