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An ultra-thin PdMn intermetallic compound on W(1 1 0)

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Abstract

A study of Pd and Mn co-deposited on W(1 1 0) is presented. Using high resolution core level photoelectron spectroscopy and low energy electron diffraction it is shown that heating of a sandwich consisting of 1 ML each of Pd and Mn yields a double-layer PdMn compound with a c(2 × 2) structure. The layers are suggested to be [1 1 0] planes of a PdMn compound with CsCl structure. This relies on the fact that such a phase exists in the bulk, with a lattice parameter nearly identical to that of W. The results demonstrate the feasibility for growth of ultra-thin ordered Pd–Mn films where the stoichiometry and the geometric structure can be controlled. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Manganese; Palladium; Alloys; Surface structure, morphology, roughness, and topography; Single crystal surfaces; Solid phase epitaxy; Synchrotron radiation photoelectron spectroscopy

1. Introduction

Heteroepitaxial metal–metal growth is one way to atomically engineer materials with novel properties. In this respect, 3d metals are particularly interesting since such ultra-thin films may exhibit interesting magnetic properties as a result of the unique geometric structure of the film. The admetal may also mix with the substrate and in favorable cases atomically ordered surface alloys (i.e. ultra-thin intermetallic compounds) can be prepared, providing a most valuable complement to the homogeneous films.

Manganese is a very good candidate for this kind of studies, since it exists in four different crystallographic phases and it offers the prospect of creating new types of magnetic materials by epitaxial growth of films on suitable substrates. Of special interest is also that well ordered and atomically flat surface alloys can be formed by deposition of Mn on the (1 0 0) surfaces of Cu, Ni, Ag and Pd [1–7]. The surface alloys are usually confined to the outermost 1–4 layers and may therefore be considered as two dimensional (2D).

The Pd–Mn alloy formed on Pd(1 0 0) has not been particularly extensively studied in the past. There is one previous investigation in which intensity vs energy analysis of the low energy electron diffraction (LEED) pattern was employed in order to determine the geometrical structure of the Pd(1 0 0)–c(2 × 2)–Mn alloy and the results were interpreted in terms of a four-layer $Pd_3Mn(1\,0\,0)$ alloy [6]. This structure can be schematically described as follows: a surface layer consisting of equal amounts of Pd and Mn forming a checkerboard pattern, a second layer which only consists

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of Pd, the third layer is another Pd–Mn checkerboard, and, finally, a pure Pd interface layer.

In a very recent scanning tunneling microscopy and photoelectron spectroscopy (PES) study of the Mn/Pd(1 0 0) system we verified the presence of a checkerboard surface layer and demonstrated that a 2D c(2×2) alloy covering the whole surface only exists in a rather narrow coverage regime; at coverages below 0.7 ML, Pd(1 0 0) areas are still present, whereas at coverages above 1 ML, a transition from 2D growth to 3D growth takes place [7]. Since there are some uncertainties in the Mn coverage determination in the LEED study [6], we feel that the exact geometric structure of the epitaxial c(2×2) alloy remains to be established. However, it seems clear that only one type of uniform and well-defined Pd–Mn alloy film can be formed when using Pd(1 0 0) as a substrate.

In this paper, we present a first study of Pd and Mn co-deposited on W(1 1 0) undertaken in order to explore new ways of forming ultra-thin Pd–Mn intermetallic compounds. This approach allows for control of the stoichiometry and the geometric structure of the film, which is important when considering the possibility to tune the physical properties. We show that heating of a sandwich consisting of 1 ML each of Pd and Mn yields a double-layer PdMn compound characterized by a c(2×2) LEED structure. When concerning the exact atomic structure of the film, we propose a model in which the layers can be described as [1 1 0] planes of a PdMn compound with CsCl structure.

2. Experimental

High resolution core level photoemission spectra and LEED pictures were taken at beamline D1011 at MAX II, the National Synchrotron Radiation facility in Lund, Sweden [8]. [1] The beamline consists of an SX 700 monochromator with an end station comprising a measurement chamber with a 200 mm radius electron energy analyzer of Scienta type and a preparation chamber equipped with a LEED, evaporators and necessary equipment for sample cleaning.

The presented C 1s and Pd $3d_{5/2}$ spectra were recorded at a photon energy of 400 eV and with total resolutions (photons plus electrons) of 200 meV (C 1s) and 170 meV (Pd $3d_{5/2}$), respectively. The Mn $2p_{3/2}$ spectra were recorded at a photon energy of 750 eV and a total resolution of 500 meV. The W $4f_{7/2}$ spectra were measured at a photon energy of 70 eV and a total resolution of 60 meV. All binding energies (BEs) are referenced to the Fermi level of the W(1 1 0) substrate. The spectra are normalized to the low BE side to facilitate comparisons of absolute intensities.

The W(1 1 0) sample was typically cleaned by first flashing to 2300 K, then one or two oxygen treatments at 1500 K, followed by a final flash to 2300 K, all according to standard procedures [9,10]. No traces of contaminations were observed with PES (the sensitivity level of surface contaminants is well below 1%).

The Mn evaporator consisted of a Mn flake (Goodfellow, purity 99.95%) firmly placed inside a resistively heated W coil. The evaporation rate was typically 0.1–0.2 ML/min. Pd was evaporated by resistive heating of a Pd wire. The evaporators were carefully outgassed prior to deposition.

The base pressure in the experiments was $\sim 2 \times 10^{-10}$ Torr and during evaporations it never exceeded 7×10^{-10} Torr.

3. Results and discussion

3.1. Preparation of the PdMn film

In Fig. 1 we present high-resolution core level photoemission spectra for the most crucial steps in the preparation and initial characterization of the alloy. The first step is to prepare an atomic layer of Pd and it is known that deposition of Pd at 300 K yields a flat pseudomorphic layer [11]. Upon deposition of $\leqslant 1$ ML Pd on W(1 1 0), we observe one Pd $3d_{5/2}$ peak at a BE of 335.66 eV. After completion of the first layer, second layer islands form, manifested in the Pd $3d_{5/2}$ spectrum by the appearance of a component at 334.91 eV. These findings are in excellent agreement with results for

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[1] Beamline D1011 at MAX II is the relocated Beamline 22 at MAX I.

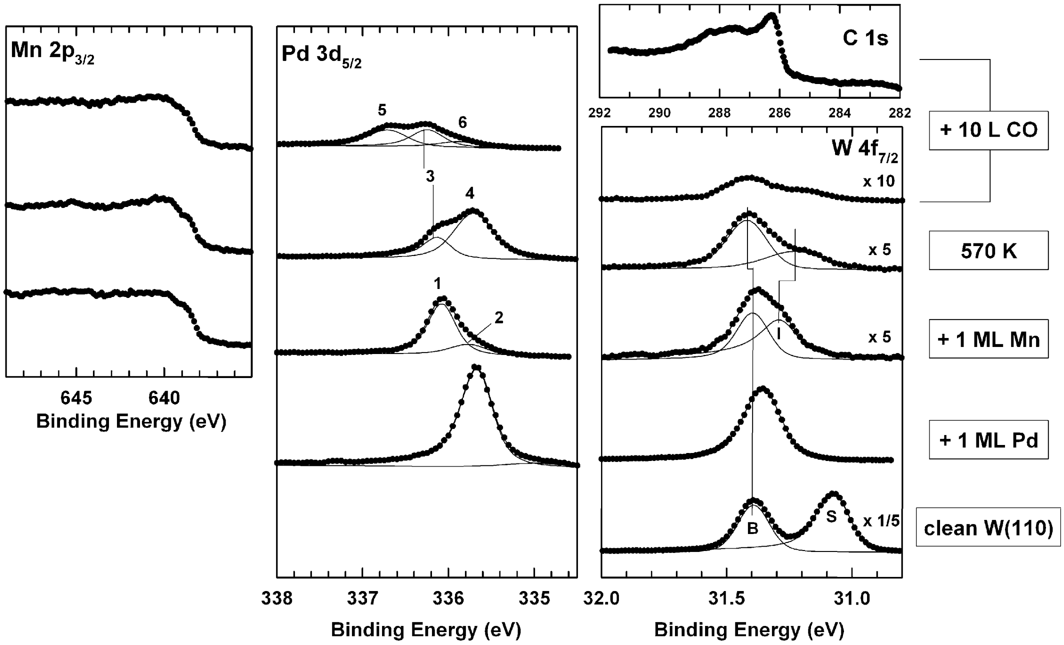

Fig. 1. Mn $2p_{3/2}$, Pd $3d_{5/2}$ and W $4f_{7/2}$ photoemission spectra for the most crucial steps in the preparation of the c(2 × 2) PdMn compound, which is obtained by heating of 1 ML Mn/1 ML Pd/W(1 1 0) to 570 K. At the top, core level photoemission spectra (including C 1s) are shown for 10 L CO adsorbed on the c(2 × 2) compound at 90 K.

Pd/Mo(1 1 0) (see Ref. [12] and Fig. 2). The 1 ML situation, shown in Fig. 1, has a small trace of a second layer peak and the coverage is estimated to about 1.04 ML.

Turning to the W $4f_{7/2}$ spectra, the surface component for clean W(1 1 0) (at a BE of 31.07 eV, labeled S in Fig. 1) vanishes completely upon the formation of the Pd monolayer. Moreover, CO exposure does not induce measurable changes in the W $4f_{7/2}$ spectrum, only a decrease in intensity, which clearly indicates a continuous Pd overlayer. Only one peak is observed, with a BE of 31.35 eV, which is 40 meV lower than the BE of the bulk component in the spectrum for clean W(1 1 0) (BE = 31.39 eV, labeled B). Thus, since the spectrum for 1 ML Pd is expected to contain a bulk component as well as an interface component, the value of 40 meV constitutes an estimate of the interface shift. LEED shows only a (1 × 1) pattern, verifying the pseudomorphic character of the Pd layer. We also note that the attenuation of the total W $4f_{7/2}$ intensity is considerable at this photon energy, about a factor of five.

The next step is to grow 1 ML Mn on top of the Pd layer and the deposition is undertaken at 90 K to prevent intermixing [13,14]. The growth of a Mn layer leads to the emergence of a Pd 3d component at higher BE and at a certain point further Mn deposition does not induce changes in the Pd 3d spectrum. At this coverage, the Pd $3d_{5/2}$ spectrum displays one peak at a BE of 336.08 eV (labeled 1) with a small shoulder at 335.75 eV (2), as shown in Fig. 1.

In the W $4f_{7/2}$ spectrum a doublet with a peak separation of 0.11 eV is seen of which the high BE peak is readily identified as the bulk component (BE = 31.39 eV). The low BE component (BE = 31.28 eV, labeled I) must originate from interface atoms, and it can be concluded that the W(1 1 0)–Pd interface shift has increased upon Mn deposition.

The Mn $2p_{3/2}$ spectrum shows broad features and three components can be discerned. These spectral features are probably due to a main peak and two so-called satellites. The spectral shape is typical for Mn in contact with Pd, and will be discussed in detail in a forthcoming paper [14].

For the coming discussion, it is important to ensure that the Mn coverage at this stage is reasonably close to 1 ML. That the Mn coverage lies in the right regime is supported by the following arguments:

(a) The evolution of a Pd 3d spectrum towards a single well-defined Pd component indicates the completion of an interface.
(b) The reduction of the integrated Pd 3d intensity to a value of about 56% of that of the uncovered monolayer is consistent with the expected damping when a surface layer becomes covered with a single layer, as inferred from Pd growth on Mo(1 1 0) (see Fig. 2, spectrum d).
(c) The integrated Mn $2p_{3/2}$ intensity normalized to the number of scans and beam current agrees within 15% with the intensity for 1 ML Mn/Pd(1 0 0), measured with the same equipment and experimental parameters. [2] The comparison with this system is valuable, since we have observed that a uniform Mn monolayer can be grown on Pd(1 0 0) at 90 K [14], and the absolute Mn coverage was in this case also controlled with a thickness monitor (quartz microbalance).
(d) The W 4f signal has been attuenuated by an additional factor of five, i.e. the same attuenuation observed after deposition of the Pd monolayer.

Thus, we feel confident that the preparation procedure described above leads to a Pd–Mn "sandwich" with a 1:1 stoichiometry. It may also be noted that the small low BE shoulder in the Pd 3d spectrum is most probably due to structural imperfections (cf. below). Only a (1 × 1) pattern was observed with LEED.

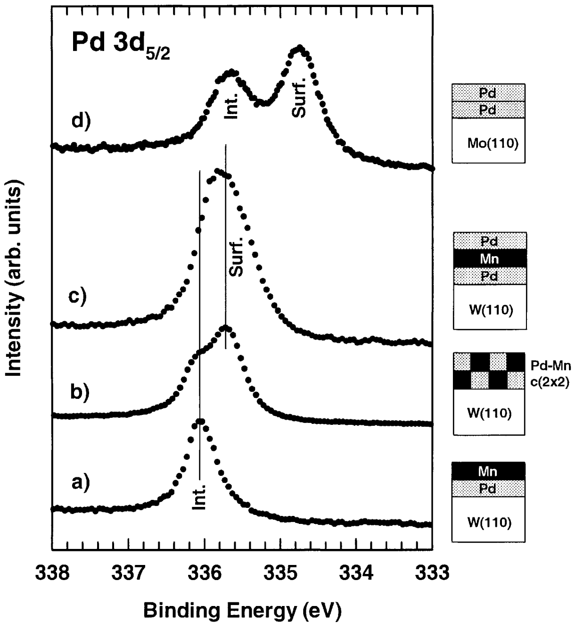

Fig. 2. Pd $3d_{5/2}$ photoemission spectra for four different situations, illustrating how the binding energy depends on the local surroundings. The spectra for the two sandwich preparations gives support to the identification of the doublet seen for the c(2 × 2) compound as due to a surface and an interface component, respectively. The absence of double-layer Pd in the c(2 × 2) film is clearly seen from the comparison with the spectrum for 2 ML Pd/Mo(1 1 0). The spectrum shown in b corresponds to situation a heated to 570 K.

The Pd–Mn double layer on W(1 1 0) is then annealed to 570 K for 3 min, which is the procedure for preparation of a c(2 × 2) Pd–Mn surface alloy on Pd(1 0 0) [6,7,15]. This results in a c(2 × 2) superstructure as observed by LEED (Fig. 3). [3] Substantial changes are observed in both the Pd $3d_{5/2}$ and W $4f_{7/2}$ spectra (Fig. 1): the Pd $3d_{5/2}$ spectrum now features a pronounced doublet structure, with the strongest component (4) at 335.71 eV, i.e. close to the BE observed for 1 ML Pd/W(1 1 0), and a weaker component (3) at 336.11 eV, which is close to the value found for a Pd layer between a Mn layer and the W(1 1 0) substrate. A doublet is also found in the W $4f_{7/2}$ spectrum; a bulk component (B) at 31.41 eV and an interface component (I) at 31.22 eV. It is interesting to note that the interface component is significantly weaker than for the unannealed situation (and at a

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[2] The surface atom density for W(1 1 0) is only about 7% larger than that of Pd(1 0 0), i.e. one layer of Mn, pseudomorphic with respect to the W(1 1 0) surface, contains approximately the same number of atoms as one atomic layer on Pd(1 0 0).

[3] By choosing a different substrate unit cell (with one short and one long base vector), the observed structure can be assigned as (2 × 1). This has no implication on the coverage or the discussed structure models.

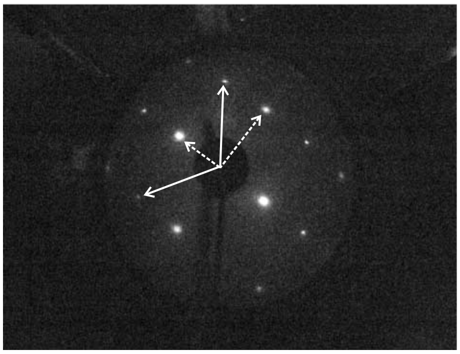

Fig. 3. The observed c(2×2) LEED pattern formed by annealing 1 ML Mn and 1 ML Pd on W(1 1 0). The electron energy was 180 eV, solid arrows corresponds to the 1×1 spots of W(1 1 0) and the dashed arrows to the PdMn overlayer (see also footnote 3).

slightly lower BE). The Mn $2p_{3/2}$ spectrum is largely unaffected by the heating, only a slight sharpening of the features can be seen.

Subsequent dosing of 10 L CO at 90 K causes the low BE Pd $3d_{5/2}$ component to disappear almost completely and a new peak (5) emerges at 336.70 eV. The most straightforward interpretation of this behavior is that the low BE peak in the annealed spectrum originates to a very large extent in Pd atoms situated on the surface, since as a rule the surface Pd $3d_{5/2}$ component shifts towards higher BEs upon CO adsorption [16], i.e. peak 5 is due to Pd atoms at the surface onto which CO is bonded.

It can be observed that the FWHM of the surface peak 4 is 15% broader than FWHM of the surface peak 1. This may imply some disorder in the annealed overlayer. However, the observed broadening of peak 4 is in part due to the existence of peak 6 and consequently the actual width of the annealed surface Pd component is comparable to that of peak 1, i.e. before Mn deposition.

CO adsorption leads to no visible changes in the W $4f_{7/2}$ spectrum, which excludes the presence of free W(1 1 0) surface. In the C 1s spectrum (Fig. 1, top right), we observe a sharp peak at a BE of 286.3 eV with a broad feature on its high BE side, reaching down to about 289 eV. This is not compatible with CO adsorbed on Mn, since CO/Mn gives rise to a C 1s peak at a BE of about 285 eV both in the case of a homogeneous Mn surface and Mn alloyed with Pd [7]. No satellite corresponding to the 289 eV feature is observed for CO/Mn. That CO does not stick to Mn is to some extent supported by the observation of no CO-induced changes in the Mn $2p_{3/2}$ spectrum. The C 1s spectral shape and the BEs of the individual features are instead very similar to those found for CO adsorbed on-top on Pd atoms, a species which has been investigated in detail [7,17]. The pronounced satellite structure is a consequence of the weak coupling between the CO molecule and the Pd atoms in this particular bonding geometry. A flash to RT effectively removes all the CO, as expected since the desorption temperature for CO on-top on Pd is 200–250 K [7,17]. It is interesting to note that the c(2×2) PdMn compound in this respect is similar to the 2D c(2×2) PdMn alloy formed on Pd(1 0 0), onto which CO only adsorbs on-top on the Pd atoms.

The CO coverage was furthermore determined by a calibration against CO on 1 ML Pd/W(1 1 0). Dosing 2 L CO at 90 K on the Pd monolayer yields only CO adsorbed on-top. Consequently, the Pd 3d spectrum only contains two components: one from clean Pd atoms and one from Pd atoms bonded to CO. This behavior is identical to that found for CO/1 ML Pd/Mo(1 1 0) [7,17]. Thus, a determination of the CO coverage is easily obtained by comparing this spectrum with the spectrum for the clean monolayer. By comparing the C 1s intensities, we were then able to estimate the CO coverage on the annealed PdMn layer to 0.50 ± 0.05 ML.

To summarize, we have shown that it is possible to prepare an epitaxial W(1 1 0)–Pd–Mn sandwich structure. Heating to 570 K leads to a considerable atomic rearrangement, evident from the formation of an ordered overlayer with a c(2×2) structure and by the presence of surface Pd atoms.

3.2. The structure of the PdMn film

In this section, we will first show that the c(2×2) Pd–Mn phase can be considered as a homogeneous intermetallic compound and then discuss possible structure models.

That the annealed c(2×2) Pd–Mn film covers the whole W(1 1 0) surface is evident from the CO adsorption experiment discussed above. However, in our study of the growth of Mn on Pd(1 0 0) we found that amounts above 1 ML lead to the agglomeration into 3D alloy islands situated on a single "wetting layer" [7]. Thus, a scenario in which agglomeration occurs upon heating is possible. Such a behavior is however expected to result in an increased substrate signal, but a careful examination shows that this is not the case; the W 4f intensity is largely unaffected.

The presence of a c(2 × 2) LEED pattern is furthermore important; since neither Pd/W(1 1 0) nor Mn/W(1 1 0) form such overlayer structures [11,18], we can exclude the formation of a film made up from separate Pd and Mn islands of mesoscopic size. That the c(2 × 2) structure has a high degree of Pd–Mn mixing can also be inferred by comparing the Pd $3d_{5/2}$ spectra in Fig. 2: the top spectrum (labeled d) is for 2 ML Pd/Mo(1 1 0). The surface and interface peaks are clearly resolved, of which the former has lowest BE. (The peak positions for 2 ML Pd/W(1 1 0) are expected to be very similar.) Spectrum b corresponds to the c(2 × 2) Pd–Mn phase (obtained by heating of situation a to 570 K) and there is no sign of a component due to a pure Pd surface layer on a pure Pd interface layer.

As shown in Fig. 2, we have in addition prepared a situation with a Pd layer deposited on top of the epitaxial Pd–Mn sandwich (situation c). The Pd $3d_{5/2}$ spectrum in this case consists of an interface Pd layer and a Pd surface layer, of which the latter strongly dominates due to the high surface sensitivity. When comparing with spectrum a, which represents the interfacial Pd layer between the Mn layer and the W(1 1 0) substrate, we can conclude that the Pd $3d_{5/2}$ peak due to the surface Pd layer has a lower BE than the interface component. The interface layer a can furthermore be viewed as bulk Pd atoms in a mixed Pd and Mn environment on a W(1 1 0) substrate, whereas the surface layer c can be seen as surface Pd atoms in a mixed Pd and Mn environment. The BEs of the interface layer and the surface layer agree well with the features in the c(2 × 2) spectrum b and that the low BE component in the c(2 × 2) spectrum is due to surface Pd is consistent with the CO adsorption results discussed above. Consequently, this result strongly supports the assumption that a homogeneous mixed phase is formed, consisting of both surface and interface Pd atoms.

The next thing to determine is the distribution of the Pd atoms between the surface and interface layer, respectively. We know that the total amount of Pd is very close to 1 ML. Adsorption of CO yields only molecules bonded on-top on Pd, i.e. each CO molecule requires one surface Pd atom. Thus, the CO saturation coverage gives the minimum coverage of Pd surface atoms, i.e. there cannot be less than 0.5 ML Pd situated in the surface layer.

Moreover, in the Pd $3d_{5/2}$ spectrum for the c(2 × 2) phase, the intensity ratio between the surface and interface component is 2.0 (Figs. 1 and 2). The surface:interface ratio in the Pd $3d_{5/2}$ spectrum for 2 ML Pd/Mo(1 1 0) is 1.5 (Fig. 2). If we assume the same damping factor in the two cases, which is reasonable since the spectra are recorded at the same photon energy, we get that the c(2 × 2) phase has 0.57 ± 0.05 ML Pd in the surface layer and 0.43 ± 0.05 ML Pd in the interface layer.

The composition of the surface and interface layer can also be discussed outgoing from the W $4f_{7/2}$ spectra. However, in order to do so, we have to make the assumption that the W 4f interface peak (I) at 31.22–31.28 eV is solely due to W atoms bonded to Pd atoms, which in turn are directly influenced by Mn atoms. That this assumption is feasible is shown by, firstly, that the resolvable interface peak (I) appears upon deposition of Mn on 1 ML Pd/W(1 1 0) and, secondly, that the relative intensity of peak I decreases upon heating and thus appears to be correlated to the intensity of the Pd $3d_{5/2}$ interface component (compare the intensities of peaks 1 and 3 in Fig. 1 before and after heating to 570 K).

So how much Pd is in contact with both W and Mn before heating? In Fig. 1 we see that the Pd $3d_{5/2}$ component due to Pd sandwiched between the W(1 1 0) substrate and the Mn monolayer is the one at higher BE (1), but there is also a weak component at lower BE (2). The low BE peak is either due to Pd not covered by Mn or due to Pd which has migrated to the surface, i.e. imperfections in the sandwich. The relative intensity of the high BE peak is 75%, meaning that, when taking the damping into account, approximately 0.8 ML Pd is in contact with W(1 1 0), Mn and Pd before heating. The W $4f_{7/2}$ peak labeled I, which is due to W atoms bonded to Pd atoms influenced by Mn, has a relative intensity of 58% before heating and 36% after heating. This yields an interface Pd coverage of $36/58 * 0.8 = 0.5$ ML after heating, in good agreement with the value of 0.43 ML derived from the relative intensities of the Pd $3d_{5/2}$ components.

Thus, in view of the results above it seems clear that half of the Pd monolayer migrates to the surface upon the formation of the c(2 × 2) structure. Consequently, the most straightforward interpretation is that the compound can be described as a two-layer film with a 50–50 distribution of Pd and Mn in both layers. However, the film prepared here is not perfect, which is indicated by the presence of a small trace of a third Pd $3d_{5/2}$ component at low BE after CO adsorption (peak 6 in Fig. 1). In the case of an ideal double layer, there should only be two Pd $3d_{5/2}$ components before as well as after CO adsorption: one due to interface Pd and one due to surface Pd. The reason for the third component could be that the temperature is not ideal and/or that the Pd coverage in this case is slightly above 1 ML. As mentioned earlier, this also has some effect on the width of peak 4 in Fig. 1, corresponding to surface Pd atoms in the annealed Pd–Mn "sandwich".

Since both Mn and Pd grow pseudomorphically on W(1 1 0), it is feasible to assume that the c(2 × 2) compound also adopts a pseudomorphic structure. With this reasoning, we arrive at two possible structure models, schematically shown in Fig. 4. Unfortunately, based on our PES and LEED results we cannot distinguish between these two structures. However, a clue as to the atomic structure is obtained from previous studies of PdMn intermetallic bulk compounds. In the Pd–Mn phase diagram, there are two possible compounds with a 1:1 stoichiometry [19]: the first (β_1), which exists below 600°C, has a tetragonally distorted CsCl structure with lattice parameters $a = 2.89$ Å and $a/c = 1.245$ at room temperature. The second (β) exists above 670°C and has a bcc CsCl structure with a lattice parameter $a = 3.15$ Å. The tendency of the PdMn compound to form structures of CsCl-type supports the structure model shown in Fig. 4a, since this model can be viewed as a CsCl structure cut along the [1 1 0] plane. The lattice parameter for the β-phase is furthermore in very good agreement with the value for W, which is 3.165 Å. That is, the [1 1 0] plane of the β-phase matches the W(1 1 0) surface perfectly. Thus, we propose that the ultra-thin PdMn compound formed on W(1 1 0) outgoing from 1 ML Pd and 1 ML Mn is a two-layer thick PdMn compound with CsCl structure exposing the [1 1 0] plane and with a geometrical structure similar to the bulk β-phase. Provided that this conclusion is correct, this means that it is possible to prepare a thin film of the β-phase on W(1 1 0) which is stable at temperatures much below the transition temperature reported for bulk samples.

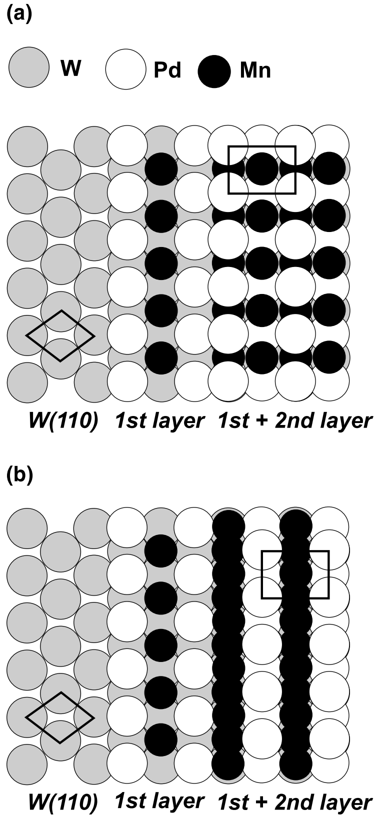

Fig. 4. Suggested real-space atomic structures of the c(2 × 2) PdMn compound. The unit cells of the substrate and the PdMn film are indicated.

4. Summary

A study of Pd and Mn co-deposited on W(1 1 0) is presented. Using high resolution core level photoemission and LEED, it is shown that heating of a sandwich consisting of 1 ML each of Pd and Mn yields a double-layer PdMn compound with a c(2 × 2) structure. The layers are suggested to be [1 1 0] planes of a PdMn compound with CsCl structure. This relies on the fact that such a phase exists in the bulk, with a lattice parameter nearly identical to that of W.

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Acknowledgements

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