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Combined ion scattering, electron diffraction and work function change study on growth, alloying and initial oxygen adsorption of ultrathin Al films in Pd(001)

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Abstract. We have investigated the oxygen-induced lifting of the Pd(001)-(2 × 2)p4g-Al clock reconstruction using low-energy He⁺ ion scattering, low-energy electron diffraction and work function change measurements. The structure was prepared by annealing Al films with initial coverages from 0.5 ML (monolayers) to larger than 1 ML at ~900 K. This surface was determined to consist of a clock-rotated (001) Pd top layer above a mixed c(2 × 2) Al-Pd underlayer. Adsorption of oxygen on the (2 × 2)p4g surface at room temperature induces Al segregation and lifts the reconstruction to yield (1 × 1) phase. Oxygen removal from the (1 × 1) surface by higher-temperature annealing is accompanied by depletion of Al from the surface, recovering the reconstruction. The driving mechanism for the reversible phase transition process is discussed.

1. Introduction

Many surfaces undergo structural transformations under the influence of atoms or molecules. A well studied example for an adsorbate-induced lifting of reconstruction is CO on Pt(001) [1–4]. The driving force of the CO-induced (hex) ↔ (1 × 1) surface phase transition was identified by Thiel *et al* [2] and Behm *et al* [3] from electron diffraction studies to be the higher heat of adsorption of CO on the (1 × 1) phase than on the reconstructed phase. Recently, a new type of surface phase transition induced by the presence of an adsorbate has been reported: oxygen on a (1 × 1) Pt_{0.25}Rh_{0.75}(001) alloy surface [5]. Using scanning tunnelling microscopy Tanaka *et al* [5] observed a (3 × 1) reconstruction of the Pt-Rh(001) surface induced by O adsorption at ~400 K. It has been suggested that the oxygen-induced segregation of Rh atoms from the second layer and the formation of an Rh-O overlayer with a (3 × 1) periodicity are responsible for the phase transition.

In the present study, the oxygen-induced lifting of the Pd(001)-(2 × 2)p4g-Al reconstruction is reported. The main experimental observation of importance here is that a stable (2 × 2)p4g structure was formed when the initial Al coverage (θ_{Al}) deposited at RT (room temperature, 300–325 K) was at least 0.5 ML but may be in excess of 1 ML upon annealing to ~900 K. These results have been interpreted in terms of a surface reconstruction in which a clock-rotated (001) Pd top layer covers an ordered c(2 × 2) Al-Pd underlayer [6]. When the (2 × 2)p4g surface is exposed to oxygen, a remarkable segregation of Al atoms from the second layer occurs at RT and the (2 × 2)p4g reconstruction is lifted to yield the (1 × 1) phase.

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Oxygen removal from the (1×1) surface by higher-temperature annealing is accompanied by depletion of Al from the surface, recovering the reconstruction. This reversible phase transition process of the $(2 \times 2)p4g \rightarrow (1 \times 1)$ by O adsorption at RT and the $(1 \times 1) \rightarrow (2 \times 2)p4g$ by higher-temperature annealing could be observed up to at least five times.

The main experimental technique used was low-energy ion scattering (LEIS) with a combination of low-energy electron diffraction (LEED) and work function change ($\Delta\Phi$) measurements. LEIS is a highly surface sensitive technique, which has been well established as an advantageous approach to study surface, interface and thin-film phenomena [7, 8].

2. Experimental details

Our angle-resolved ion scattering system (VSW Scientific Instruments) and other standard techniques for surface preparation and characterization have been described previously [9, 10]. The base pressure in the UHV chamber was 7×10^{-11} mbar after bakeout, and rose to 4×10^{-10} mbar during evaporation. The scattered ions were energy analysed by a hemispherical electrostatic analyser with a dual multichannel detector (MCD). The use of an MCD allows data collection with small ion doses, typically at a beam current density of $\sim 2 \times 10^{-8}$ A cm $^{-2}$ for the 1 keV He $^{+}$ ions used in this study.

The Pd(001) sample (Technisches Büro) had been used and extensively cleaned in previous examinations [6]. The Al films were produced by physical vapour deposition from a home-built evaporator using resistively heated and collimated crucibles. The Al coverage (θ_{Al}) was determined by a quartz crystal microbalance (Leybold INFLCON XTM), which was calibrated by ion scattering measurements. The source gave constant, reproducible and clean deposition of Al over long periods of time. Oxygen exposure measurements were carried out by back-filling the chamber with 99.999% research pure O $_2$ through a leak valve at a pressure of 1×10^{-8} mbar. The O $_2$ pressure reading of the ion gauge was calibrated using the well established oxygen adsorption kinetics on Pd(001) [11]. All the $(2 \times 2)p4g$ phases presented here were prepared with 1 ML Al deposited at RT followed by annealing to 900 K for 3 min, but in some cases different coverages were also used as described in the text. The substrate was held at RT during O adsorption, LEED study and LEIS measurement.

3. Results

3.1. Growth and thermal annealing of ultrathin Al films on Pd(001)

Low-energy He $^{+}$ ion scattering is an extremely surface-sensitive method with virtually no signal contributed from the second or deeper layers of a surface. This makes it an ideal technique for distinguishing whether the adsorbate initially wets the surface. Figure 1(a) depicts a plot of the Pd intensity normalized to the intensity from a clean surface as a function of Al film thickness. Typical energy spectra for this experiment are shown in the inset from clean Pd(001) and two Al depositions under double-alignment conditions. The Pd intensity in figure 1(a) decreases almost linearly with θ_{Al} up to 1 ML where a distinct breakpoint in the slope is observed. On further increasing θ_{Al} up to about 1.5 ML, the residual Pd signal remains merely a few per cent. This residual Pd signal is probably due to substrate atoms which are not completely covered by the two-dimensional Al film as the second layer starts growing before the completion of the first one. Nevertheless, three-dimensional crystallites or clusters can be totally excluded since in this case one would expect the film to leave large parts of the substrate uncovered [8].

The changes in work function ($\Delta\Phi$) upon deposition are shown in figure 1(b). It is seen that with non-annealed films the $\Delta\Phi$ drops by 1.5 eV from the Pd(001) surface work

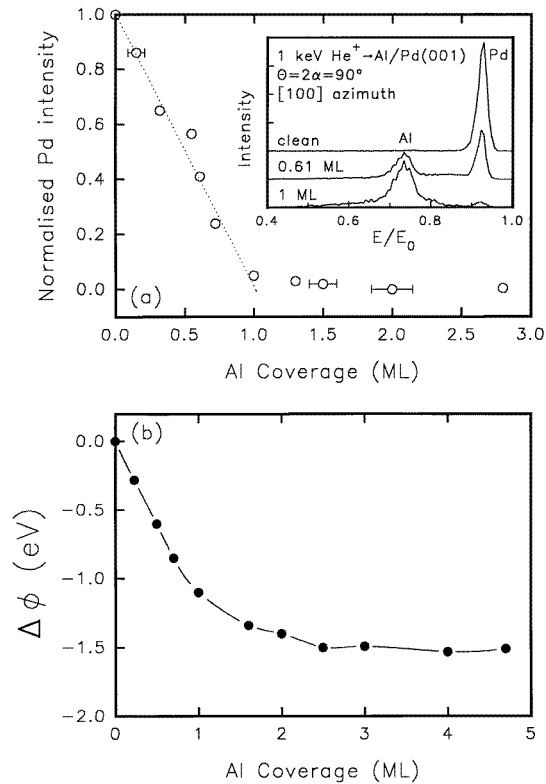


Figure 1. (a) Normalized Pd intensity as a function of the thickness of Al films deposited at RT. The inset shows typical energy spectra from clean Pd(001) and two Al depositions. (b) The $\Delta\Phi$ of Al deposited on Pd(001) at RT as a function of θ_{Al} .

function for $\theta_{Al} \geq 2.5$ ML, and stays almost constant when a thicker layer is deposited on top of it. Taking the $\Delta\Phi$ of the clean Pd(001) surface, 5.65 eV [12], as a reference, with the procedure used the films have a work function of 4.15 eV, in agreement with the published value from metallic aluminium [13].

The effect of thermal annealing on the $\Delta\Phi$ is shown in figure 2. First we stepwise deposited 1 ML Al at RT. The changes in $\Delta\Phi$ with θ_{Al} are displayed in the left panel of figure 2. The curve closely resembles that in figure 1(b). The deviation of 80 meV in the $\Delta\Phi$ value at 1 ML mostly results from the uncertainty in determining θ_{Al} in these experiments. The right panel of figure 2 shows a heating sequence, starting with a 1 ML Al-covered surface at RT and subsequently annealed to successively higher temperatures; after cooling down to RT the resulting work function was recorded. A gradual increase of the work function with increasing annealing temperature is observed, leading to a $\Delta\Phi$ value of -0.20 eV with respect to the clean Pd(001) surface after annealing to 750 K. The $\Delta\Phi$ value remains almost unchanged on further increasing anneal temperatures up to 950 K.

3.2. A reversible structural change of the $(2 \times 2)p4g \leftrightarrow (1 \times 1)$

The ion scattering behaviour for a reversible structure conversion (the first two cycles), the $(2 \times 2)p4g \rightarrow (1 \times 1)$ by O adsorption at RT and the $(1 \times 1) \rightarrow (2 \times 2)p4g$ by higher-

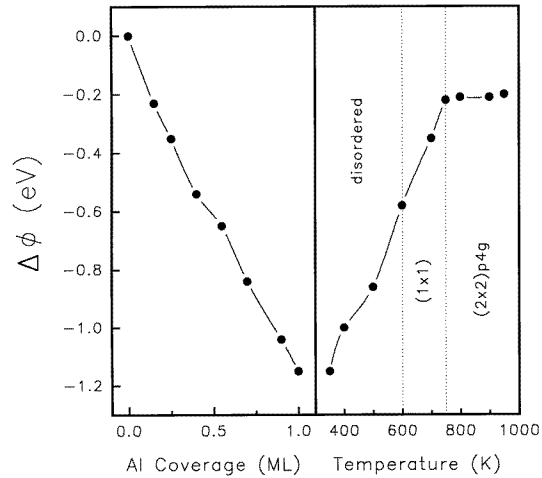


Figure 2. Development of the $\Delta\Phi$ upon annealing. The Al film was stepwise deposited up to 1 ML at RT (left panel); it was subsequently annealed to higher temperatures, held for 3 min and then the $\Delta\Phi$ was recorded after cooling down to RT (right panel). LEED patterns of the process observed were also recorded.

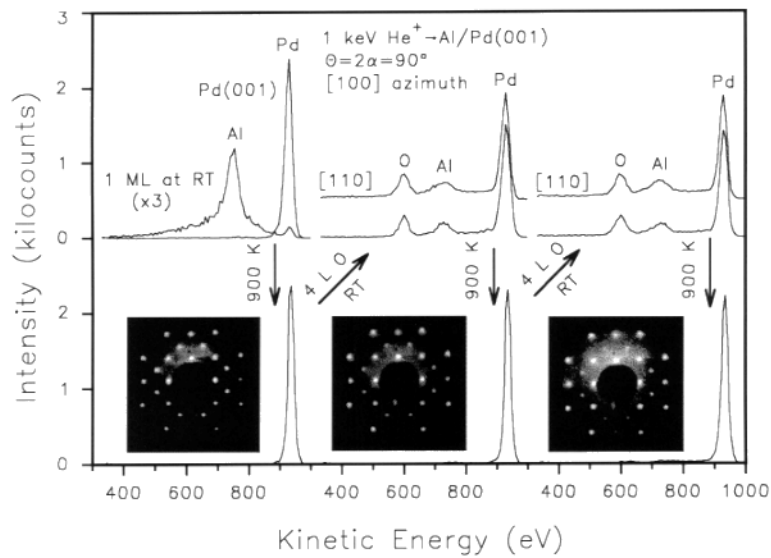


Figure 3. Energy spectra of 1 keV He^+ ions scattered from different surfaces in the [100] azimuth for the first two cycles of structural changes. The corresponding $(2 \times 2)\text{p}4\text{g}$ LEED patterns recorded from the original and after recovering the reconstruction are also shown. Note that spectra shown for the O-covered surfaces are along two different azimuthal directions.

temperature annealing, is summarized in figure 3. In these experiments the ion beam was incident along the [100] azimuth (also along the [110] azimuth for O-covered surfaces) at an incident angle of $\alpha = 45^\circ$ and a scattering angle of $\theta = 90^\circ$. Under these conditions,

the crystallographic surface effects are of minor importance. The corresponding $(2 \times 2)p4g$ LEED patterns recorded after each measurement are also shown in the figure.

The measurement begins with the clean and well ordered Pd(001) surface. The spectrum for the clean surface shows a Pd single-scattering peak at ~ 925 eV. As 1 ML Al is deposited, an intense Al single-scattering peak is observed at ~ 740 eV while the residual Pd signal remains only about 5%. After annealing to 900 K for 3 min, a very pronounced Pd single-scattering peak appears. Simultaneously, the Al single-scattering intensity is no longer detectable. This is due to the fact that annealing the Al film to this temperature provides sufficient atomic mobility for Al atoms to diffuse into the substrate. Our LEED confirmed that the surface is the $(2 \times 2)p4g$ structure (see the original $(2 \times 2)p4g$ LEED pattern). The conclusion from these observations is that the formation of the $(2 \times 2)p4g$ reconstruction is thermally activated requiring higher temperatures to cause the excess Al to diffuse away and to bring about the long-range ordering in the second layer, and then to drive a clock rotation in the top layer [6].

Oxygen adsorption experiments were performed on a clean and well ordered $(2 \times 2)p4g$ surface at RT. As oxygen is adsorbed, the O single-scattering intensity (at ~ 600 eV) increases while the Pd single-scattering intensity decreases. The most interesting feature for this observation is that during O adsorption, the Al single-scattering peak also appears. These observations immediately lead to the conclusion that exposure to oxygen provides a driving force causing segregation of Al from the second layer into the first layer. Although the dynamics of the segregation process that occurs upon O adsorption are not known in detail, it is known that diffusion of Al atoms with lower surface energy across an interface can occur readily by a place exchange with surface Pd atoms with higher surface energy [14]. At O exposure of ~ 4 L ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr s} = 1.33 \times 10^{-4} \text{ Pa s}$), the reconstruction is totally lifted over the whole surface as indicated by the complete loss of the half-order beams and the eventual appearance of the (1×1) LEED pattern (not shown). By annealing the O-covered surface to about 700 K, the O atoms were removed from the surface, which was accompanied by depletion of Al from the surface. However, at this stage the surface is a Pd layer with the (1×1) LEED structure. It was found that a short anneal (about 3 min) at 900 K was sufficient to fully recover the $(2 \times 2)p4g$ reconstruction.

Interestingly we note that re-exposure of this ordered $(2 \times 2)p4g$ surface to oxygen results in the lifting of the reconstruction again. The O, Al (segregated) and Pd intensities in the He^+ energy spectra are found to be identical to those obtained from the first O-covered surface. On re-heating the surface to 900 K, this process is essentially reversed, resulting in the eventual restoration of the reconstruction. We found that, once the $(2 \times 2)p4g$ phase is prepared, its disappearance and reappearance are completely reversible. Experimentally, the reversible transition of the $(2 \times 2)p4g \leftrightarrow (1 \times 1)$ was observed by LEED at least five times, although the final $p4g$ pattern was not as sharp as the original one. We conclude that there was no loss of Al from the surface during higher temperature annealing and O adsorption processes. We would like to point out that upon heating the surface to temperatures above 1100 K the $(2 \times 2)p4g$ pattern changed to a sharp (1×1) pattern of the clean Pd(001) surface due to Al diffusion into the bulk [6].

3.3. Properties of segregated Al and surface remaining Pd atoms

When the transition of the $(2 \times 2)p4g \rightarrow (1 \times 1)$ was completed, the surface Pd and Al atoms were found to be still ordered. This was determined from the ϕ scans of Pd and Al using 1 keV He^+ ions at grazing incidence (figure 4). The evidence is that the Pd ϕ scan is nearly identical in shape compared to the ϕ scan from clean Pd(001). The ϕ scan from the

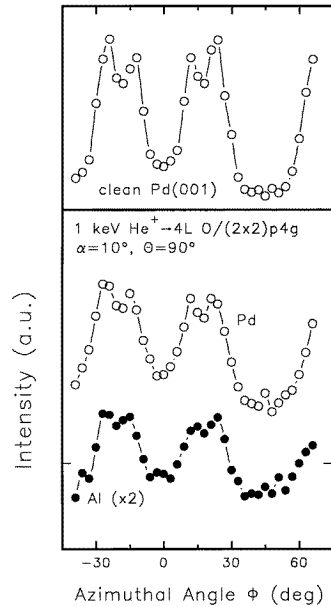


Figure 4. Azimuthal angle ϕ scans of the integrated Al and Pd intensities obtained from the 4 L O-covered $(2 \times 2)p4g$ surface are compared with those for a clean Pd(001) surface using 1 keV He^+ ions at grazing incidence.

segregated Al atoms also exhibits the same shadowing features, which are centred along the [110] and [100] azimuths. This fact suggests that the segregated Al atoms are located in surface fcc Pd sites by a random place exchange with top-layer Pd atoms. In contrast to this, the O intensity does not show any structural features as a function of the azimuthal ϕ angle (not shown). We suggest that the chemisorbed O atoms may be randomly located above the top layer. This interpretation is also consistent with the disappearance of the $(2 \times 2)p4g$ LEED pattern forming a (1×1) pattern with a high background. The observation that an overlayer of oxygen is located above the surface is further supported by the work function change measurement. It was found that 8 L O was sufficient to achieve a saturation coverage of adsorbed O ($\Delta\Phi = 380 \pm 10$ meV). The increase in $\Delta\Phi$ associated with oxygen indicates that the O atoms are located above the surface, and not in subsurface sites.

Detailed information about the segregation of Al induced by O adsorption on the $(2 \times 2)p4g$ surface has been obtained by collecting a series of He^+ energy spectra during O adsorption. Figure 5 shows the O and Al intensities measured as a function of oxygen exposure. As oxygen is adsorbed, the O and Al intensities increase while the Pd intensity decreases. At the initial stage of O adsorption (≤ 2 L) the Al intensity exhibits a near-linear increase with increasing O exposure. With increasing O exposures, the increase rate of the Al intensity observed becomes lower, indicating that the segregated Al atoms may be partially shadowed by O atoms. We suggest that some adsorbed O atoms may directly bond to the Al atoms, causing strong shadowing. This assumption has been confirmed by the experiment, which involved the removal of oxygen by dosing with CO and the dissociation of CO by heating at ~ 450 K (without resulting in onset of the diffusion of Al atoms into the substrate) [15]. At large exposures (≥ 5 L), Al signals detected by ion scattering are almost constant, indicating that the Al diffusion becomes rate limiting.

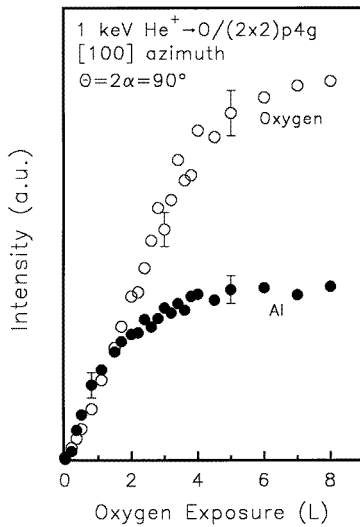


Figure 5. The integrated O and Al intensities as a function of oxygen exposure using 1 keV He⁺ ions along the [100] azimuth at $\theta = 2\alpha = 90^\circ$. The O adsorption experiments were performed on the $(2 \times 2)p4g$ surface at RT.

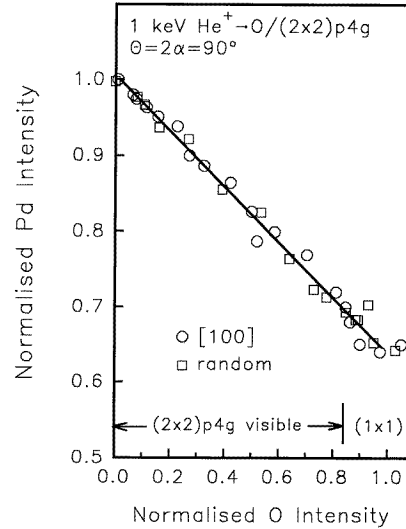


Figure 6. The Pd intensities as a function of the normalized O intensity obtained with 1 keV He⁺ ions in two different scattering directions. The Pd intensities were normalized to the intensity obtained from a clean surface.

Measurement of the number of first-layer Pd atoms remaining visible, and then quantitative determination of the amount of segregated Al atoms during O adsorption, is demonstrated in figure 6, where the Pd intensities measured are plotted as a function of the O intensity. Results are shown for two different scattering conditions chosen to avoid any shadowing effect. Here we define a normalized O intensity of 1.0 as the point of saturation of segregated Al atoms. The Pd intensities were normalized to the intensity obtained from a clean surface, and should be proportional to the coverage of visible, first-layer Pd atoms, providing quantitative determination of the segregated Al atoms. The assumption made in the following analysis is that the reduction in the Pd intensity is solely due to place exchange between first-layer Pd atoms and second-layer Al atoms, and that the charge fraction of scattered He⁺ ions from the substrate Pd atoms remains constant. Based on Hagstrum's model [16], the main neutralization mechanism for noble gas ion scattering is an Auger process. An electron tunnels from the Pd(4d) conduction band into the He ground state. The energy gain for this transition is about 20 eV so that a work function change of about 0.4 eV should be no remarkable influence on the probability of the Auger transition.

Both scattering conditions yield comparable, linear decline with increasing O intensity. It is seen that at saturation of Al segregation (~ 5 L), about 65% of the first-layer Pd atoms remain visible, implying that the majority of Al atoms (about 0.35 ML) originally located in the 50% Al–50% Pd underlayer have segregated onto the top layer to replace the Pd atoms. This is supported by data not shown here, where a mixed Al–Pd top layer could be obtained with the careful removal of the oxygen by hydrogen or CO [15]. Finally, from these LEIS measurements we conclude that if there is any change of the specific neutralization of the He⁺ ions with the surface Pd atoms, this change is negligibly small. The linear dependence of the normalized Pd intensity on the normalized O intensity has been confirmed using three different beam energies (0.5, 1.0 and 1.5 keV) after repeated O adsorption on the

freshly prepared $(2 \times 2)p4g$ surfaces over many days. The results were reproducible within ± 10 – 15% . Although the depth distributions of Al for the $(2 \times 2)p4g$ phase are unknown, further measurements indicate that the excess Al at the subsurface has very little effect on the amount of segregated Al atoms during O adsorption.

4. Discussion

The thermodynamical criterion based upon the surface energies of the substrate (γ_s) and film overlayers (γ_f) and upon the interfacial energy (γ_{int}) has been traditionally established for predicting the growth mode [17]. If the system minimizes the surface free energy, then for $\Delta\gamma = \gamma_f + \gamma_{int} - \gamma_s > 0$ three-dimensional island growth is expected, while for $\Delta\gamma \leq 0$, layer-by-layer growth is expected. It has been argued that in highly strained systems with $\Delta\gamma < 0$, partial layer-by-layer growth followed by 3D growth in subsequent layers. Based upon this criterion, the large negative surface energy difference between aluminium and palladium ($\gamma_{Al} - \gamma_{Pd} < 0$) should favour a layer-by-layer growth for Al on Pd(001) at RT. This is in agreement with our LEIS observations, although it is impossible to distinguish between the layer-by-layer or layer-by-layer followed by 3D growth mode by the LEIS experiment. In a previous study of this system by AES [18], a layer-by-layer growth at RT was found up to several monolayers.

The annealing used in this present investigation presumably serves only to activate atom diffusion, place exchange and structure conversion. In the normal case, the lower surface energy of Al should favour its remaining at the surface. However, by annealing at ~ 900 K a clock-rotated (001) Pd layer above an ordered $c(2 \times 2)$ Al–Pd underlayer is formed with exclusion of Al by diffusion of Al into Pd. Our LEED and LEIS results strongly indicate that the formation of the $(2 \times 2)p4g$ phase is an activated process [6]. We believe that thermally induced interfacial mixing and ordering may serve to stabilize the clock-rotated structure in the top layer. Moran-Lopez and Falicov [19] have shown in a model calculation including pairwise interactions that the surface composition of strongly ordered intermetallic phases might be determined by ordering effects rather than by segregation alone.

The most important finding in this study is that the oxygen adsorbs on the $(2 \times 2)p4g$ reconstructed surface at RT and directly lifts the reconstruction under easily accessible and reproducible conditions. When the reconstruction is lifted, the majority of Al atoms in the second layer segregate onto the top layer. Our LEED data indicate that initial O adsorption does not lift the reconstruction immediately. Only after a critical amount of oxygen on the surface has been reached resulting in extracting enough Al from the Al–Pd underlayer, does the subsequent lifting of the reconstruction occur. In other words, if the loss of Al in the underlayer is locally increased above a certain level, then a $(2 \times 2)p4g$ reconstruction is fully lifted. This critical amount was measured to be about 0.3 ML. The fact that the oxygen induces Al segregation and then lifts the reconstruction is predicted from thermochemical data. From thermodynamic considerations the formation of an AlO_x (Al_2O_3) oxide is energetically strongly favoured over the formation of an PdO overlayer because the heat of formation for Al_2O_3 (-1678.2 kJ mol $^{-1}$) is much larger than the corresponding value for PdO (-112.6 kJ mol $^{-1}$) [20]. Such a place exchange is favoured by the more stable Al–O bonding. However, under the experimental conditions, there is no oxide present, since all oxygen is removed above ~ 700 K although some of the oxygen may dissolve into the bulk. The residual O is therefore in a chemisorbed state and the place exchange is favoured by the more stable Al–O bonding. After the Al diffusion becomes rate limiting, the O may start to react with Pd. Further experiments for investigating this reaction are under way in a separate XPS/AES UHV chamber in our surface science laboratory.

Clearly, for the transition process studied here involving a small portion of the O adatoms and segregated Al atoms, AES may not be sensitive enough to detect such subtle but important segregation processes. The main advantage for analysing the segregation process by LEIS with He⁺ ions is that He⁺ ions are almost 100% neutralized for ions penetrating into the second or deeper atomic layers. Therefore, low-energy He⁺ ion scattering has an extremely high sensitivity during scattering events, ensuring that the detected segregated Al signals mainly come from the outermost layer. However, due to the unknown neutralization probability for O adsorbed systems, the influence of the shadowing effect on surface-segregated Al atoms induced by O adsorption is difficult to assess quantitatively.

5. Conclusion

We have provided first experimental evidence that adsorption of oxygen on the Pd(001)–(2 × 2)p4g surface at RT induces Al segregation and lifts the reconstruction. Three conclusions are strongly supported by the results. Firstly, a large amount of Al (about 0.35 ML at 5 L O exposure) originally located in the 50% Al–50% Pd second layer segregates into the first layer to replace the Pd atoms. This segregation process lifts the reconstruction. Secondly, the O atoms chemisorbed are transferred to segregated Al atoms and remaining Pd atoms are left unaffected. However, not all the Al atoms are covered by O atoms. Thirdly, oxygen removal from the (1 × 1) surface by higher-temperature anneal was accompanied by depletion of Al from the surface, recovering the reconstruction. Once the (2 × 2)p4g phase is formed, a structural change, (2 × 2)p4g → (1 × 1) by O adsorption at RT and (1 × 1) → (2 × 2)p4g by higher-temperature annealing, occurs reversibly.

Acknowledgments

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