Scanning tunneling microscopy (STM) was used to study the adsorption of oxygen on the PdAg(111) surface. Oxygen appears as dark holes of ca 40 pm depth, whereas palladium atoms appear as bright spots. By comparing consecutive STM images, oxygen was found to occupy only palladium sites: the oxygen was found to travel exclusively to and from the palladium atoms. The surface concentration of oxygen was low under all the experimental conditions used, as indicated by STM as well as Auger electron spectroscopy. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption; Alloys; Low-index single crystal surfaces; Oxygen; Palladium; Scanning tunneling microscopy; Silver

1. Introduction

Over recent years, scanning tunneling microscopy (STM) has developed to a technique that can be used in the chemical identification of species at surfaces. There is for instance a lot of interest in the discrimination of the constituent elements at the surface of binary metal alloys. For the PtRh(100) surface it has been shown that rhodium atoms appear in the STM image with an apparent height 22 pm greater than platinum atoms [1]. The basis of this discrimination is the difference in local density of states (LDOS) near the Fermi level between platinum and rhodium at the alloy surface [2]. On the PtNi(111) surface, the STM images nickel atoms with an apparent height 30 pm greater than platinum atoms [3]. Here the basis of the discrimination is the element-specific interaction of the substrate metal atoms with an adsorbate at the tip. Imaging adsorbates at metal surfaces is a different story: adsorbates mostly induce greater apparent height variations, although at the same time they may be mobile and easily removed or displaced by the tip. They are often difficult to identify because their adsorption mode determines the way they appear in the STM image. Nevertheless, STM is a powerful tool in imaging adsorbates and even their surface reactions as recently shown, for instance, for CO + O/Pt(111) [4], O/PtRh(100) [5], CO + O/Cu(110) [6] or CO/Pt/Ru(0001) [7]. In this paper, some STM observations of oxygen on the Pd$_{67}$Ag$_{33}$(111) surface are presented.
2. Experimental

Prior to adsorption or STM measurements, the surface was extensively cleaned in vacuum by sputtering (2 keV Ar\(^+\)) and annealing (770–820 K). Using Auger electron spectroscopy (AES) the surface was checked for the presence of contaminants and adsorbates; this was complicated by the fact that the S 152 eV peak coincides with one of the minor Pd peaks. By using low energy ion scattering (LEISS), we did not find any indication of sulphur contamination. The LEISS measurements were obtained with a 1 keV He\(^+\) beam and a hemispherical analyser. A comparable problem concerns the C peak that is located in the flank of the Pd 279 eV peak. No indication of carbon build-up (usually visible as dark patches in atomically resolved images (see e.g. Ref. [8]) was observed during the STM measurements.

The vacuum system consisted of two chambers: a preparation chamber with a base pressure of \(1 \times 10^{-10}\) mbar in which all annealing, sputtering and adsorption procedures took place and a STM/AES chamber in which the pressure during measurements was ca 8 \(\times 10^{-11}\) mbar. The scanning tunneling microscope used in this study was a commercial Omicron micro-STM which has been provided with additional vibration damping: the STM head itself was supported by a viton stack and the entire vacuum system was suspended in a combined spring-elastomer system as is described in Ref. [9]. A tungsten tip was used and the sample bias was always negative. The AES data were all recorded at an electron energy of 3 keV and with a cylindrical mirror analyser. The peak-to-peak height ratios were calculated from the differentiated spectra.

3. Results and discussion

In Fig. 1 a 100 \(\times\) 100 Å\(^2\) STM image of a clean PdAg(111) surface is shown. The spots with larger apparent height are the palladium atoms. The low concentration of palladium atoms (ca 5.2\%) indicates strong surface segregation of silver, based on the large difference in the surface energy between palladium and silver. In another paper we go deeper into the matter of imaging the clean PdAg(111) surface [10].

When adsorbing 100 Langmuir O\(_2\) (1 L \(= 1.3 \times 10^{-5}\) mbar s) of oxygen, a small amount of black spots appears in the STM images as can be seen in Fig. 2(a). Fig. 2 illustrates what such a hole looks like in a line profile. This example represents the appearance of most of these features at these tunneling conditions. The average apparent depth of the depressions in Fig. 2a is determined to be 0.41 Å. This value compares reasonably well with the 0.35 Å calculated in Ref. [11] for O on Pt(111). Earlier, Lang also found out that oxygen atoms on transition metal surfaces would appear as depressions [12].

In the work of Stipe et al. [13], the oxygen atoms are also imaged as depressions, although the authors were not specific on the point of the apparent depth. Oxygen atoms have also been imaged as depressions on Pt(111) [14] and on Ru(0001) [15]. Kopatski and Behm imaged oxygen on Ni(100) as depressions of ca 0.3 Å deep [16]. These considerations independently lead to the confirmation that the depressions indeed repre-
images in Fig. 2a to a 100 × 100 Å² image with atomic resolution we do not observe the large dark patches caused by the reduction in the apparent height of the substrate atoms around the adsorbed carbon atom that are usually found [8] for carbon on transition metal surfaces.

2. This relatively high degree of mobility (see below) has not been reported for adsorbed carbon atoms before.

3. Sautet [11] predicted a shallow depression (0.1 Å) with a small bump in the middle for CO, a structure that is not observed in our images. Furthermore, experimental results from the literature indicate that CO is generally imaged as a protrusion, as in the case of CO on Pt(111) and (100) [17] or the case of CO on Cu(110) [6] or Co(1012) [18]. In some cases CO appears as a depression [19], but such cases are rare.

The percentage of depressions in Fig. 2a is 6.6% relative to the amount of palladium atoms, assuming that the depressions each cover one palladium atom, an assumption that will be justified later in this paper. The image in Fig. 2a shows the oxygen and palladium atoms without atomic resolution of the metal surface. We used the calibration of atomically resolved images from earlier and later in the session in order to determine the oxygen coverage relative to the metal substrate. This results in a 0.0029 ML oxygen coverage with respect to the substrate. The AES data for 100 L O₂ on Pd₆₇Ag₃₃(111) give an O/Pd ratio of 1.4% after correction for relative sensitivity. This translates into a O/Pd ratio of 3.5% after correction for relative sensitivity. This value is lower than the O/Pd ratio in the first atomic layer due to the contribution of Pd in deeper layers to the Auger signal. The low concentration of oxygen atoms on the surface is caused by two factors.

1. When we ‘zoom in’ from the 300 × 300 Å² sent oxygen atoms. The concentration of the dark spots is very low and therefore it is difficult to identify them by AES. In principle the dark spots could be species of a different chemical identity, having contaminated the sample during oxygen adsorption. The two adsorbates possibly relevant for our case are carbon and CO. However, there are three points against this possibility:

(a) STM image (300 × 300 Å²) of the PdAg(111) surface after exposure to 100 L O₂ at room temperature. A low concentration of depressions is present. The palladium atoms appear with a larger apparent height, \( V_{\text{tunnel}} = 1.2 \text{ V}, I_{\text{tunnel}} = 1.3 \text{ nA} \).

(b) Example of a line profile of a depression; the depth is ca 0.4 Å. The arrow in (a) indicates where the line profile is taken.

Fig. 2. (a) STM image (300 × 300 Å²) of the PdAg(111) surface after exposure to 100 L O₂ at room temperature. A low concentration of depressions is present. The palladium atoms appear with a larger apparent height, \( V_{\text{tunnel}} = 1.2 \text{ V}, I_{\text{tunnel}} = 1.3 \text{ nA} \).

Example of a line profile of a depression; the depth is ca 0.4 Å. The arrow in (a) indicates where the line profile is taken.

1. When we ‘zoom in’ from the 300 × 300 Å² images in Fig. 2a to a 100 × 100 Å² image with atomic resolution we do not observe the large dark patches caused by the reduction in the apparent height of the substrate atoms around the adsorbed carbon atom that are usually found [8] for carbon on transition metal surfaces.

2. This relatively high degree of mobility (see below) has not been reported for adsorbed carbon atoms before.

3. Sautet [11] predicted a shallow depression (0.1 Å) with a small bump in the middle for CO, a structure that is not observed in our images. Furthermore, experimental results from the literature indicate that CO is generally imaged as a protrusion, as in the case of CO on Pt(111) and (100) [17] or the case of CO on Cu(110) [6] or Co(1012) [18]. In some cases CO appears as a depression [19], but such cases are rare.

The percentage of depressions in Fig. 2a is 6.6% relative to the amount of palladium atoms, assuming that the depressions each cover one palladium atom, an assumption that will be justified later in this paper. The image in Fig. 2a shows the oxygen and palladium atoms without atomic resolution of the metal surface. We used the calibration of atomically resolved images from earlier and later in the session in order to determine the oxygen coverage relative to the metal substrate. This results in a 0.0029 ML oxygen coverage with respect to the substrate. The AES data for 100 L O₂ on Pd₆₇Ag₃₃(111) give an O/Pd ratio of 1.4%. This translates into a O/Pd ratio of 3.5% after correction for relative sensitivity. This value is lower than the O/Pd ratio in the first atomic layer due to the contribution of Pd in deeper layers to the Auger signal. The low concentration of oxygen atoms on the surface is caused by two factors.

1. The probability of O₂ dissociation at room temperature is extremely low for Ag(111) under our experimental conditions [20,21]. Butler et al. [21] found that the dissociative sticking probability of O₂ on Ag(111) is highly dependent on the incidence energy of the O₂ molecule and that this dissociative sticking probability is practically zero at room temperature of the
oxygen gas. It has to be mentioned here that the molecular sticking probability at 165 K is ca $10^{-5}$–$10^{-4}$ for low incidence energies and incidence angles close to the surface normal.

2. On this PdAg alloy surface there is a low concentration of sites with two neighbouring palladium atoms. Based on the current knowledge of the dissociation behaviour of CO, NO and O$_2$ on transition metal surfaces [22] it is reasonable to say that an ensemble of neighbouring palladium atoms is conditional in making O$_2$ dissociation possible on PdAg(111). The presence of certain palladium ensembles on this surface is elaborately analysed in our paper about the clean surface of PdAg(111) [10]. So in spite of the fact that the initial dissociative sticking coefficient for O$_2$ on Pd(111) is ca 0.3 as was found by Conrad et al. [23], the dissociation of O$_2$ on PdAg(111) is limited because of the small amount of dissociation sites. The dissociation process will be such that O$_2$ adsorbs and dissociates on a site with two neighbouring palladium atoms. After this, the mutual repulsion of the two O atoms causes at least one of them to diffuse away from the dissociation site, leaving only single O atoms.

The apparent height of the palladium atoms as observed by the STM is on average 0.34 Å, a value that is comparable to the 0.25–0.30 Å apparent height difference that was found for palladium relative to silver in atomically resolved PdAg(111) images [10].

The migration of the depressions can be observed by analysing a series of consecutive images, as shown in Fig. 3. The six images (ca 20 s per scan) cover about the same area and the black features are observed to appear and disappear from one image to another. When this migration behaviour is studied more closely, it turns out that from under a disappearing depression a bright spot always appears. Likewise, if a depression appears in an image, it will always cover a bright spot. The migration distance is at least of the order of several tens of Ångströms within the period of one scan (ca 20 s). This means that from one scan to the other an oxygen atom may disappear from one location and either appear again at a location in the same scan frame or cross the borders of the scan frame and not reappear. These observations allow the estimate of the minimum value of the migration distance. The two major migration mechanisms are diffusion and tip-induced migration. We see no direct evidence of tip-induced motion, such as O atoms disappearing or appearing between successive scan lines. There is also no significant dependence of mobility on tunneling voltage (between $-0.1$ and $-1$ V). This indicates that the diffusion of the O atoms is not severely influenced by the tip.

Fig. 4 is the STM image of an area with a monoatomic step edge. None of the depressions are present directly at the step nor is there a significant dependence of mobility on tunneling voltage (between $-0.1$ and $-1$ V). This indicates that the diffusion of the O atoms is not severely influenced by the tip.
Fig. 3. Series of subsequent images (300 × 300 Å²) as in Fig. 2a. The numbers under each image indicate how many depressions have appeared (+) and disappeared (−) relative to the previous image. The white boxes indicate the corresponding areas of two images where the black depressions are appearing or disappearing. \( V_{\text{tunnel}} = 1.2 \text{ V}, I_{\text{tunnel}} = 1.3 \text{ nA} \).
as described in Ref. [10]. The reason why the chemical methods do not lead to an increase in palladium in the first layer could be thermodynamic as well as kinetic. From a thermodynamic point of view, the differences in energy of O adsorption on Ag and Pd are too small to overcome the large difference in the surface energy between the (111) surfaces of palladium and silver. Kinetically, the atom mobility in the top layers of the crystal is too low at room temperature.

4. Conclusions

Oxygen atoms on the PdAg(111) surface have been found to selectively adsorb on palladium atoms which are mainly isolated in a matrix of silver atoms. The surface coverage of oxygen after exposure to up to 1000 L O$_2$ remains as low as 0.0029 ML, pointing at an extremely low sticking coefficient. This result is in agreement with the expectation that an ensemble of neighbouring palladium atoms is required for dissociation. There is a certain migration of these oxygen atoms between the palladium atoms, which are the exclusive O adsorption sites. The migration distance varies from several Ångstroms to several tens of Ångstroms within the period of one scan (ca 20 s). The adsorption of oxygen does not lead to a measurable change in the surface composition of the alloy.

Acknowledgements

This project was supported by the Fonds zur Förderung der wissenschaftlichen Forschung (Austrian Science Foundation) and the Nederlandse Organisatie voor Wetenschappelijk Onderzoek [Netherlands Organisation for Scientific Research (NWO)] under Stipendium No. SIR 13-4239.

References