Combined STM, LEED and DFT study of Ag(100) exposed to oxygen near atmospheric pressures

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Abstract

We have investigated the interaction of molecular oxygen with the Ag(100) surface in a temperature range from 130 K to 470 K and an oxygen partial pressure ranging up to 10 mbar by scanning tunneling microscopy, low electron energy diffraction, Auger electron spectroscopy and ab initio density functional calculations. We find that at 130 K, following oxygen exposures of 6000 Langmuirs O₂, the individual oxygen atoms are randomly distributed on the surface. When the sample is exposed to 10 mbar O₂ at room temperature, small, p(2×2) reconstructed patches are formed on the surface. After oxidation at ≈470 K and 10 mbar O₂ pressure the surface undergoes a c(4×6) reconstruction coexisting with a (6×6) superstructure. By ab initio thermodynamic calculations it is shown that the c(4×6) reconstruction is an oxygen adsorption induced superstructure which is thermodynamically stable for an intermediate range of oxygen chemical potential.

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Silver plays an important role as an oxidation catalyst in the partial oxidation of ethylene to ethylene-oxide and methanol to formaldehyde. This has created a special attention to the interaction of oxygen with Ag surfaces, which has been the subject of many experimental [1–19] and theoretical studies [20–23]. The chemisorption process is an essential step of the catalytic process, and the microscopic identification of chemisorbed species is a prerequisite to understand the catalytic cycle. The identification of the catalytically active oxygen species on silver surfaces was the subject of numerous studies [2,16,17]. Four oxygen species were observed following the oxygen exposure of various silver surfaces [24,25]. Apart from the physisorbed O₂, two other molecular oxygen species were identified [26]. One of them is the superoxo-like molecular species (O₂⁻) which was observed during non-thermal O₂⁺ adsorption on Ag(111) [26]. The other molecular oxygen species is peroxy-like (O₂'). Its appearance was evidenced experimentally on Ag(110) [27] and was explained by electron transfer from the metal to the O₂ antibonding π* orbital of the O₂ molecule which is the precursor state for its dissociation [18,24]. The fourth oxygen species present on silver surfaces is chemisorbed atomic oxygen. For this state, density functional theory (DFT) calculations of O on Ag(110) have shown a strong hybridization between the d band of Ag and the p subshell of the O atom which is almost completely filled, indicating an O²⁻ charged state [28].

Recently it has been shown that silver oxide clusters [29] and silver oxide thin films [30] could be potential...
candidates for optical memories. The conversion from n to p-type semiconductor with varying oxygen stoichiometry in thin Ag₂O films [30] again shows the importance of the understanding of the oxidation process itself.

The very low dissociative sticking coefficient (10⁻⁵–10⁻⁶) of oxygen on silver is the main experimental difficulty to study ordered superstructures under near-UHV (near ultrahigh vacuum) conditions [15]. Several ways to increase the amount of atomic oxygen on Ag surfaces were reported in literature: Bao et al. exposed the Ag surface to O₂ at high temperature and atmospheric pressure. Rocca et al. [6] used a supersonic molecular O₂ beam in order to obtain a higher sticking coefficient (S=0.7). Bare et al. have used NO₂ as a source of atomic oxygen [15].

On the Ag(100) surface the following detailed reaction scheme of O₂ and surface structures were derived from existing X-ray photoelectron spectroscopy (XPS), high resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron diffraction (XPD), scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) studies [6,14]: dosing O₂ at low temperature (T≤120 K) leads to molecular absorption with O₂ molecules in hollow sites, forming a c(2×4) structure [6,14]. Further heating leads to the dissociation of oxygen molecules (already at ≈130 K), and at around 190 K a c(2×2) LEED pattern is reported to appear [6]. Based on XPD a missing-row p(2√2×√2)R45° structure with the oxygen atoms forming a c(2×2) structure was proposed [1,6]. In-situ surface X-ray diffraction experiments demonstrate that the missing-row structure is locally present at elevated temperatures and near atmospheric pressures [31]. This is confirmed by DFT calculations which have shown that the missing-row reconstructed p(2√2×√2)R45° structure is thermodynamically more stable than the c(2×2) adatom structure [22]. It is reported that by heating this structure above 320 K the reconstruction is lifted and only a p(1×1) LEED pattern can be observed [6].

Our study is motivated by the lack of a systematic experimental and theoretical investigation of the oxygen coverage dependent formation of superstructures on Ag(100) surfaces. It will be shown that O/Ag(100) exhibits an up to now unknown variety of surface structures, which are controlled by the amount of oxygen on the surface. In the present investigation oxygen on Ag(100) was prepared in two different ways: (a) relatively low oxygen partial pressure and low temperature; (b) high oxygen partial pressure and room temperature or elevated temperatures. In both cases a higher coverage than after room temperature adsorption at UHV-compatible pressures is expected, but all measurements were performed in UHV and at ≈80 K. New c(4×6) and p(6×6) reconstructions were observed, previously not reported.

1. Experimental

The experiments were performed in a UHV system with an Omicron low temperature STM (LT STM) operated at liquid nitrogen temperature. In addition to the LT-STM chamber, the UHV system consists of a preparation chamber equipped with LEED optics, an Auger electron spectroscopy (AES) system with hemispherical analyzer and an ion sputter gun for sample surface cleaning. AES was performed with a hemispherical analyzer using a 3 keV electron beam to determine the cleanliness of the sample and to estimate the relative amount of oxygen. The LEED experiments were performed at room temperature at normal incidence of the primary electron beam. The LEED images were acquired as eight-bit images at various energies and analyzed after subtraction of a background image. The Ag(100) single crystal surface was cleaned by cycles of Ar⁺ sputtering (1 keV, approx. 20 min at 4–10 μA) and annealing (700 K) before each experiment until no trace of contaminants was observed in the AES spectrum. Prior to oxygen dosing, the LEED pattern exhibits

Fig. 1. (a) STM constant current topograph (100×100 nm², Vsample = −0.9 V, It = 1 nA) of the clean Ag (100) surface. Inset: atomically resolved image (9×9 nm², −0.1 V, 2 nA); (b) STM image (taken in UHV at 80 K) after exposure to 6000 L O₂ at 130 K (−0.2 V, 1 nA).
a sharp (1 × 1) structure. The STM image in Fig. 1a shows a large area scan of the clean Ag(100) surface with large terraces and monoatomic steps. In the inset an atomically resolved image of the clean surface is shown. The crystallographic bulk directions sketched in the inset are used as a reference.

2. Experimental results

First, we performed oxygen adsorption experiments at low temperature (≈130 K) by dosing O_2 in the preparation chamber at a partial pressure of oxygen of 5 × 10⁻⁶ mbar. Fig. 1b shows the STM constant current topograph of the Ag(100) surface after exposure to 6000 L O_2 (1 L (Langmuir) = 10⁻⁶ Torr s) at 130–140 K. At this temperature oxygen molecules adsorb dissociatively. The individual oxygen atoms are randomly distributed over the surface. At a tip-sample voltage of 0.2 V they appear as bright protrusions with dark wings along the \(h_{110}\) directions. A similar appearance of atomic oxygen on Ag(100) was observed in Ref. [4]. The authors interpreted the apparent shape of the oxygen atoms based on calculations with a Green's function method as being located in a hollow site. A similar shape was observed by Hahn et al. [32] following the adsorption of oxygen on Ag(110). The shape was theoretically simulated by Olsson et al. [28] based on density functional theory (DFT) and the Tersoff–Hamann theory (TH) approximation for tunneling. From the calculated local density of states (LDOS) they have found only a wide depression for atomically adsorbed oxygen and no protrusions as for molecular oxygen on Ag(110) at low tip-sample distances. The depletion of electron density in the vicinity of oxygen was explained by a decrease in the free-like density of metal states associated with two main effects: (a) electron transfer from free-like states into the p state of O and (b) the screening of the negative charge transferred into the adsorbed state by the free-electron like metal state. Comparing these results to the experiment makes it obvious that an accurate interpretation of the shape of the oxygen atoms observed in Fig. 1b must go beyond the TH model and must include tip-surface interaction.

In order to obtain a higher oxygen surface coverage, we have performed oxidation in a small load lock chamber pumped to UHV before oxidation. We have used an oxygen pressure of 0 mbar for 30 min with the crystal maintained at room temperature or at ≈470 K. Prior to pumping down to UHV, the sample was cooled to 300 K in the same oxygen atmosphere in order to prevent oxygen desorption. Then the load lock chamber was evacuated, and the sample was transferred within 5 min into the LT-STM analysis chamber where it was cooled down to 80 K. It cannot be excluded that during this procedure partial oxygen desorption and restructuring of the surface takes place.

Fig. 2 shows the surface of Ag(100) after exposure for 30 min to 10 mbar O_2 at room temperature, i.e., after applying a gas dose of ≈10¹⁰ L. Small islands showing a \(p(2 \times 2)\) reconstruction are observed. The LEED pattern (not shown) showed essentially a \(p(1 \times 1)\) structure, with very weak and broad \(p(2 \times 2)\) spots. This observation agrees with the fact that the \(p(2 \times 2)\) domains seen by STM are very small and cover only a limited fraction of the surface. The immediate conclusion is that at room temperature the sticking coefficient is very low. The \(p(2 \times 2)\) structure has been predicted theoretically as a stable structure for low oxygen coverage [22] in agreement with the experimental findings described here.

Fig. 3a shows the LEED pattern of the Ag(100) surface after exposure to 10 mbar O_2 for 30 min at ≈470 K. The spots corresponding to a \(c(4 \times 6)\) reconstruction are clearly visible. Fig. 3b shows the schematic LEED pattern for two rotational domains of a \(c(4 \times 6)\) reconstruction. The LEED pattern was reproducible for repeated experiments. The superstructure spots were strong and as sharp as the integer spots, indicating a high surface coverage and large areas of this superstructure without domain boundaries. However, the LEED observations show a specific peculiarity. The superstructure spots became very weak after an exposure of a few minutes to the electron beam. Since the LEED measurements were performed at room temperature, after the low temperature STM measurements, we attribute the disappearance of the LEED spots to the low stability of
the reconstruction at this temperature and/or to electron induced desorption of oxygen. The Auger peak-to-peak intensity measured prior to the LEED experiments of \(O_{\text{KVV}}(511\,\text{eV})\) is in this case \(9\%\) of \(Ag_{\text{MNN}}(356\,\text{eV})\) peak-to-peak intensity, a value which points to a higher coverage of the surface as compared to adsorption at room temperature for the same time at the same partial pressure of oxygen \((O(511)/Ag(356) = 2\%)\). This gives evidence that the adsorption process is thermally activated, as was pointed out in [12].

Fig. 4a shows an STM image of the \(c(4\times6)\) reconstructed Ag(100) surface. In order to get a better view of the main features of the STM image, a zoomed region was filtered in the Fourier domain and it is shown in the inset. The unit cell of the \(c(4\times6)\) structure is also sketched. The primitive cell of the \(c(4\times6)\) reconstruction exhibits four maxima (bright in the STM image). These maxima are arranged in squares with a distance between the maxima of \(\approx4.1\,\text{Å}\) along the \([010]\) and \([001]\) directions, corresponding to \(\sqrt{2}\) times the surface interatomic distance of Ag or also the bulk lattice constant of silver \((a_{Ag} = 4.09\,\text{Å})\).

However, from these STM images it is difficult to derive the structure of the reconstruction itself. The difficulties related to the interpretation of STM images for oxygen adsorbed on Ag(110) and Ag(111) were already discussed in the literature [28,33,34]. In addition to electronic effects discussed there, tip–sample interaction may modify the contrast in the STM image, thus the oxygen atoms may appear as protrusions or depressions.

Fig. 4b shows a schematic representation of the \(c(4\times6)\) reconstruction, assuming the most simple structure model conceivable, an adatom structure, in which the protrusions in the STM image correspond to the O atoms. We do not have direct experimental evidence for this structure model.
and we cannot exclude a more complicated structure, but the ab initio calculations described below support this simple model.

In addition to the already described $c(4 \times 6)$ structure another pattern was identified by STM on the surface. The morphology of the second superstructure is shown in Fig. 5a–d. Fig. 5a shows a large area scan with two terraces. On these terraces we find two areas (“islands”) with an apparent height of ≈0.5 Å above the rest of the surface (line scan). The island located on the lower terrace seems to start from the step edge. A similar behavior was observed during the oxidation of Ag(111) surface [34]. The author considered in this case the step acting as nucleation center due to the lower coordination of silver atoms compared to

![Fig. 5. STM images of the oxygen-induced $p(6 \times 6)$ reconstruction of Ag(100) following exposure to 10 mbar O$_2$ at $\approx$470 K for 30 min. (a) Wide area scan showing two terraces with $p(6 \times 6)$ areas appearing ≈0.5 Å higher than their surroundings (500 × 500 nm$^2$, +1.728 V, 0.04 nA). (b) Zoomed region of one superstructure domain (50 nm wide, +1 V, 0.04 nA). The 17.3 Å periodicity corresponding to the $p(6 \times 6)$ reconstruction is visible in the line scan. Panels (c) and (d) show the same surface with higher resolution (20 nm wide; tunneling conditions: (c) +1.8 V, 0.69 nA; (d) +1 V, 0.28 nA).](image-url)
those within the terrace. Scanning a smaller area, the periodicity of these islands is revealed. It shows a square shape, centered around a deep depression (Fig. 5b). The line scan along the [011] direction shows a periodicity of 17.3 Å, and a corrugation of ≈1 Å (Fig. 5b). Such a large corrugation was already observed after oxidation of a Ag(111) surface under similar conditions, and it was attributed to the influence of local electronic effects rather than to a real topography of the surface [35]. The observed structure has a periodicity of 17.3 Å and corresponds to a p(6 × 6) reconstruction. The structure was further resolved as can be seen in Fig. 5c and d. Fig. 5c and d shows the same structure for two different tip–sample voltages. Image 5c, taken at higher tip–sample voltage (i.e larger tip–sample distance) appears like a “negative” of the image 5d, acquired at smaller voltage. The change of the apex of the STM tip could be also a reason for the change in the contrast of the STM image. Fig. 5d shows the best resolution we could obtain on this surface. The protrusions in the side of the square have a distance of ≈4.1 Å; the distance between each of these protrusions and the smaller protrusions located at the corner of the square is ≈6.6 Å. The protrusions in the corner of the square appear ≈0.2 Å lower than the protrusions in the sides. The distances between the protrusions indicate that the p(6 × 6) structure is not a simple O adatom structure with O atoms in fourfold hollow sites. Since the inner region of the square is not resolved in our STM images we could not obtain more structural details. The atomic structure of the p(6 × 6) therefore remains unresolved.

3. DFT calculations

To get more insight into the atomistic structure of the c(4 × 6) reconstruction DFT calculations have been per-
formed. The ab initio calculations presented in this study are performed using the plane-wave density functional framework implemented in the Vienna Ab initio Simulation Package (VASP) [36], which employs projector-augmented wave (PAW) potentials [37,38]. For exchange and correlation the functional proposed by Perdew and Zunger [39] is used, adding (non-local) generalized gradient corrections (GGAs) of PW91 flavor [40]. The energy cut-off was set to $E_{\text{cut}} = 400$ eV. A Gamma-centered $k$-point mesh of $(24 \times 24 \times 1)$ was used for the $(1 \times 1)$ cell and equivalent meshes for larger structures (e.g. $(8 \times 8 \times 1)$ for the $(3 \times 3)$ cell). For the detailed definitions of adsorption energy $E_{\text{ads}}$ and generalized surface energy we refer to our previous ab initio study [22]. The Tersoff–Hamann approach [41] is applied to simulate STM images from the ab initio calculation. The STM image is approximated by the charge density around the Fermi level ($\pm 50$ meV).

For the determination of the stability of various structures, in addition to the above mentioned $p(2 \times 2)$ and $c(4 \times 6)$ oxygen adatom structures we have included the $c(2 \times 2)$ and missing-row $p(2 \sqrt{2} \times \sqrt{2})$ structures. Fig. 6 presents the generalized surface energy with respect to the amount of oxygen on the silver surface. It describes the stability of the structural phases by different sloping lines depending on coverage as a function of varying chemical potential. The stable structures are represented by the minimum of all generalized surface energies $\gamma$. These structures and the $c(2 \times 2)$ structure, which is not thermodynamically stable according to our calculations, are schematically represented at the bottom of Fig. 6.

In spite of the more accurate computational setup, much denser $k$-point mesh and higher cut-off energy, the energetic properties of the calculated structures are only marginally different compared to our previous article [22]. Compared to our previous study a slightly lower value for the clean Ag(100) surface energy is calculated (change from $0.80$ J/m$^2$ to $0.79$ J/m$^2$) and the maximal difference between the adsorption energies is around 60 meV for the $p(2 \times 2)$ surface structure (change from $E_{\text{ads},p (2 \times 2)} = -0.80$ eV in the previous study to $-0.86$ eV). However, the previously highly stable $p(2 \times 2)$ structure is now affected by including the $c(4 \times 6)$ structure into the phase diagram. The stability range of the $p(2 \times 2)$ structure shrinks to a few meV. Considering the effects of entropy, this nicely agrees with the experimental observation of broad spots in the LEED pattern and very small domain sizes in the STM images. Moreover, the phase diagram shows that the $c(4 \times 6)$ structure is thermodynamically stable which was previously not calculated due to missing experimental evidence and limited computer resources. The wide range of stability suggests that the LEED pattern of the structure should be clearly visible. According to Fig. 6, the $c(4 \times 6)$ structure should be stable at somewhat lower oxygen pressures than applied experimentally. This indicates that thermodynamic equilibrium has not been reached after 30 min, probably due to the low sticking probability of O$_2$.

In addition to the structures and phase diagram, a calculated STM image of the $c(4 \times 6)$ structure is presented in Fig. 7, which shows a high similarity to the experimental STM image (see inset in Fig. 4). In contrast to previous studies of structures with low oxygen coverage, we find that the O atoms appear as protrusions, even in the simple Tersoff–Hamann approximation. Thus, both the phase diagram and the simulated STM image strongly indicate that the $c(4 \times 6)$ structure observed experimentally is a simple oxygen adatom structure with a coverage of $\theta = 1/3$.

4. Summary

We have used STM, LEED and DFT calculations to study the structure of the Ag(100) surface after exposure to oxygen at various temperatures and partial pressures. After exposing the surface to 6000 L O$_2$ at a temperature of 130 K, individual oxygen atoms are observed on the surface. After dosing oxygen at room temperature for 30 min at a partial pressure of 10 mbar O$_2$ (gas dose $\approx 10^{10}$ L), small islands displaying a $p(2 \times 2)$ structure can be identified in STM images.

Exposure of the Ag(100) surface at $\approx 470$ K to 10 mbar O$_2$ for 30 min results in a $c(4 \times 6)$ superstructure. This structure, which was previously not reported for oxygen on Ag(100), was observed both by LEED and STM. DFT calculations indicate that this $c(4 \times 6)$ structure is
an adatom structure with a coverage of $\theta = 1/3$. The structure is stable in the calculated phase diagram and its appearance in STM images is in agreement with the Tersoff–Hamann approximation. In addition to the $(4 \times 6)$ superstructure, islands showing a $p(6 \times 6)$ pattern were found by STM. At the experimental conditions applied, only a small fraction of the surface is covered with islands possessing the $p(6 \times 6)$ structure. We argue that this structure is not a simple adatom structure with oxygen in fourfold hollow sites. Further measurements and theoretical studies are needed in order to get a deeper understanding of this oxygen-induced structure.

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References