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Adatom extraction from pristine terraces by dissociative oxygen adsorption at metal surfaces: Combined STM and DFT investigation of O/Ag(110)

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Abstract

The reconstruction and modification of metal surfaces upon O₂ adsorption plays an important role in oxidation processes and in gauging their catalytic activity. Here, we show by employing scanning tunneling microscopy and *ab-initio* density functional theory that Ag atoms are extracted from pristine (110) terraces upon O₂ dissociation, resulting in vacancies and in Ag-O complexes. The substrate roughening generates under-coordinated atoms and opens pathways to the Ag subsurface layer. With increasing O coverage, multiple vacancies give rise to remarkable structures. The mechanism is expected to be very general depending on the delicate interplay of energy and entropy, so that it may be active for other materials at different temperatures.

Most metallic surfaces reconstruct upon dissociative O₂ adsorption. Such rearrangements of the surface, bearing an enormous importance in determining the catalytic activity in oxidative environments, consist most often in the formation of added-rows of oxygen and metal atoms. The source of substrate atoms needed for the reconstruction has been heavily debated. The currently accepted mechanism is that they are released from pre-existing step edges and diffuse eventually to the terraces, where they react with oxygen atoms generated by dissociation of O₂ impinging from the gas-phase [1-3]. Evidence for this mechanism comes from the retraction of step edges of the substrate terraces upon oxidation, observed under controlled ultra-high vacuum conditions e.g. for Cu [2-5]. At odds with this explanation, Scanning Tunneling Microscopy (STM) investigations show also added rows located in the middle of terraces [6,7], far away from atomic steps. Oxidation induces, moreover, surface roughening with the formation of pits, as reported both for Ag [8,9] and Cu [10]. For the latter case, excavation of the substrate to produce the adatoms needed for the reconstruction was suggested to dominate when the supply from steps is inhibited, albeit without unravelling the mechanism.

We show here that Ag atom excavation occurs on Ag(110) already at a sample temperature $T < 200$ K, leading to single vacancy formation or to more complex structures depending on atomic oxygen coverage, Θ_{O} . Density functional theory (DFT) based calculations allow to describe the detailed mechanisms involved in the extraction process.

Silver bears a special importance in this context since it is a unique catalyst for industrially relevant but not completely understood reactions [11-16]. Thus, oxygen adsorption on Ag surfaces continues to be the subject of thorough investigations and a paradigm for understanding the initial stages of oxidation. The tremendous complexity of an apparently simple system led to conflicting results (see e.g. the debate about the surface oxide vs chemisorbed nature of Ag(111)-(4x4) O [17,18]). Eventually, it became clear that the O atoms may end up in a variety of super- and sub-surface sites [19-23], induce various types of substrate reconstructions and cause the nucleation of different surface oxide phases [24]. In addition, the ease by which oxygen penetrates into the Ag subsurface region already at low T is puzzling. Not surprisingly, the role of subsurface O was invoked in catalytic processes at Ag surfaces [16,21,22]. Segregation and dissolution were monitored by photoemission

spectroscopy for different Ag surfaces [25-26]. In particular, for O₂/Ag(110) some observations remained so far unexplained:

a) The outermost Ag(110) plane is known to undergo disordering upon thermal O₂ dissociation (occurring at 150 K) as evidenced by a severe drop in the elastic reflectivity of the low energy electron beam used in High Resolution Electron Energy Loss Spectroscopy (HREELS) [27]. Broad EEL peaks, extending from 30 to 40 meV, indicate a strong surface inhomogeneity and the presence of several oxygen species. Two of them were shown to be reactive to CO dosed by supersonic molecular beam (SMB) in titration experiments, while others must be unreactive since not all surface O is removed in the reaction [28,29]. The electron reflectivity recovers to normal values only at T~200 K, when substrate mobility sets in and the added-row reconstruction forms [27].

b) At the nanoscale, STM investigations [30,31] evidenced a variety of O-related features for 150 K <T<190 K, i.e. in the temperature realm between O₂ dissociation and added row nucleation. The relative abundance of these features depends much on the surface preparation procedure. In the low coverage limit slight rhombus shaped (lozenges) and deep circular indentations (black holes) [30,31] are predominant. If O₂ is dosed directly at 175 K, as in Ref. [31], additional mobile sombrero-shaped objects, are present, identical to those formed when O₂ dissociation is induced at 11 K by electron injection through the STM tip [32,33]. Similarly, sombrero-shaped O adatoms were observed also on Ag(001) upon brief O₂ exposure at 200 K [34] and assigned by STM image simulation.

In the present study the O₂ uptakes have been performed either by backfilling or by SMB. With the latter technology, already applied in Refs. [23,28,35], the O₂ sticking probability is increased due to the hyperthermal energy, so that clean experiments at coverages precluded in backfilling conditions are possible [35,36]. Details about the experimental protocol and the DFT calculations for the energetics and simulation of STM images can be found in the Supporting Online Material (SOM). A description of the experimental set up is reported in Ref. [37].

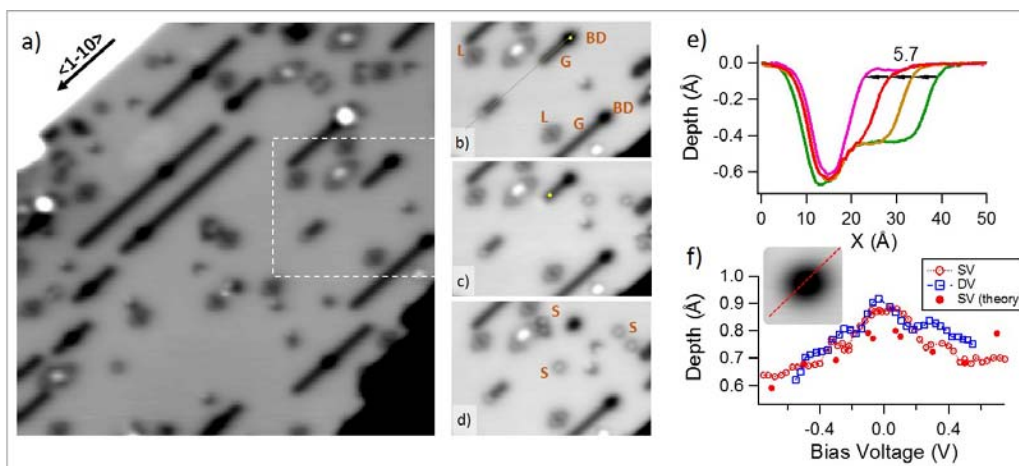


Fig. 1 a): STM image ($250 \text{ \AA} \times 250 \text{ \AA}$) recorded after exposure of 19 L of O_2 on $\text{Ag}(110)$ at 175 K by backfilling. Different structures are present, among which the lozenges (L), black dots (BD) and grey tails (G) marked in panel b). (b-d) Images of the area delimited by the rectangle in panel a). Size ($120 \text{ \AA} \times 82 \text{ \AA}$). The sequence shows the effect of vertical manipulation on the grey lines: voltage pulses (at the yellow dot positions) lead to the production of two sombreros (S) and the corresponding shortening of the structure by two lattice spacing (STM images were recorded at 6 K, $V=70 \text{ mV}$). e) Line profiles of BD and G cut along $[1\bar{1}0]$ (dotted line in panel b) recorded at different stages of the manipulation process. f) Apparent depth vs bias voltage for BD corresponding to a single vacancy (SV) or a double vacancy (DV). For SV, comparison with the values predicted by simulated STM images is shown, too. Inset enlargement of a BD with line scans used to determine the depth. The depth inferred from the line scan in panel e) is slightly lower than the value reported in panel f) at the same bias. This is due to a less sharp tip in this set of measurements than in those of panel f).

Fig. 1a shows a typical STM overview of the $\text{Ag}(110)$ surface after a short O_2 exposure at 175 K. The coverage, evaluated a posteriori by counting the O-containing objects present in several images, is $\sim 0.02 \text{ ML}$, so that all features are well isolated. Lozenges (marked L in Fig. 1b), grey tails (G), and black dots (BD) are visible as depressions 0.25 \AA , 0.4 \AA and $0.6\text{-}0.8 \text{ \AA}$ deep, respectively, at a bias $V=70 \text{ mV}$. BD and G structures are located on top of Ag rows by taking as reference atomically resolved added rows coexisting on the surface (see Fig. S1 of SOM). Though other

structures can be identified in Fig. 1a, *they are not relevant for the message of this paper* and will be described in a future publication.

Grey features are imaged only at low tip voltage (+70 mV) and their bias dependence indicates that they contain O atoms. Most of them are arranged in segments aligned along $[1\bar{1}0]$ starting from a black dot. When a low voltage pulse (70mV, 200 msec, 1 nA) is applied either to the black dot or to its tail (sequence b-d), the latter shortens from its free end by $\sim 5.7 \text{ \AA}$ (see line scans in panel e), i.e. by two lattice spacing along $[1\bar{1}0]$. Simultaneously, two sombrero-shaped objects are generated (marked S in panel d and located in long bridge sites). Also sombreros are imaged only at low bias (± 70 mV). In accord with literature, we ascribe them to O adatoms [30-33].

The elongated grey structure could be completely destroyed by repeated vertical manipulation, until an isolated BD is retrieved. In this case the structure is perfectly round, with a highly symmetric depth profile (pink trace in panel e) centred at an Ag lattice site. Sometimes, on the contrary, BDs have a prolate shape and are centred on short bridge sites. In both cases there is little bias dependence (see Fig. 1f), which suggests that they are single (SV) and double (DV) Ag vacancies, respectively, and not O containing features.

The statistical relevance of the dissociation process is demonstrated by its absolute reproducibility, tested over five grey rows. Overall, 22 sombreros were generated in a controlled way from the grey rows by short voltage pulses. By subsequent voltage pulses, the so generated sombreros could be displaced, merged into grey or black and white features and separated again.

These experimental evidences are corroborated by simulated STM images (Fig. 2d-f), corresponding to the DFT optimized geometries shown in Fig. 2a-c. Oxygen at a long bridge (LB) site (Fig. 2a,d,g) appears as a sombrero-shaped depression of 0.25 \AA in the STM image simulated for 70 mV, confirming our empirical assignment of this object. Its apparent depth becomes shallower at $\pm 0.7 \text{ V}$ (not shown), in agreement with experiment [31]. The single Ag vacancy (Fig. 2b,e,h) appears as a depression of $\sim 0.8 \text{ \AA}$, corresponding to a black dot in the STM images simulated for 70mV and 700mV. O-adatoms in three fold hollows (TFH - Fig. 2c,f,i) appear as depression of $\sim 0.4 \text{ \AA}$ in the STM image simulated for 70 mV; they form zig-zag chains at the opposite side of a vertically displaced Ag row. This structure is thus a good candidate for the elongated grey tails of Fig. 1a and justifies why sombreros are produced in

couples upon vertical manipulation: one unit of the zig-zag row is disrupted and shortens by two lattice spacing along $[1\ 0]$ ejecting two oxygens. Deeper indentations could only be obtained by removing substrate atoms and creating Ag vacancies.

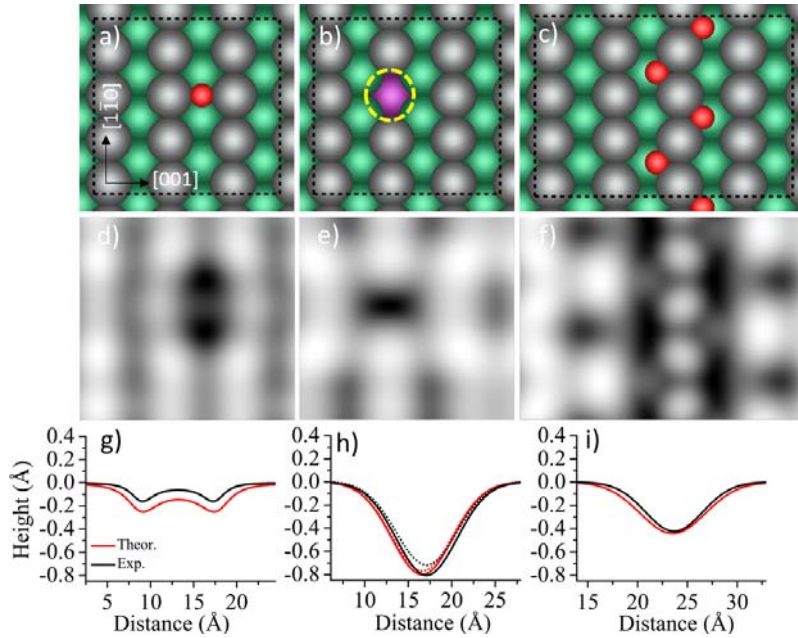


Fig. 2 (a-c) DFT-optimized geometries and (d-f) simulated STM images (at 70 mV) of: a/d) O in LB (S), b/e) Ag vacancy (BD) and c/f) O atoms in three fold hollows, forming a zig-zag chain on Ag(110) (G). (g-i) Comparison of theoretical (red trace) and experimental (black trace) depth profiles for $V=70$ mV. They are obtained from line scans, along $[1\ 0]$ for (d) and (e) and along $[001]$ for (f). To allow comparison with experiment, the calculated profiles were convoluted with a suitable function simulating the tip. A small dependence of the depth profile on the bias voltage is observed in the experimental data, in agreement with Fig. 1 f). Here and in the following, Ag atoms in first, second, and third layers and O atoms are represented by grey, green, purple, and red balls, respectively.

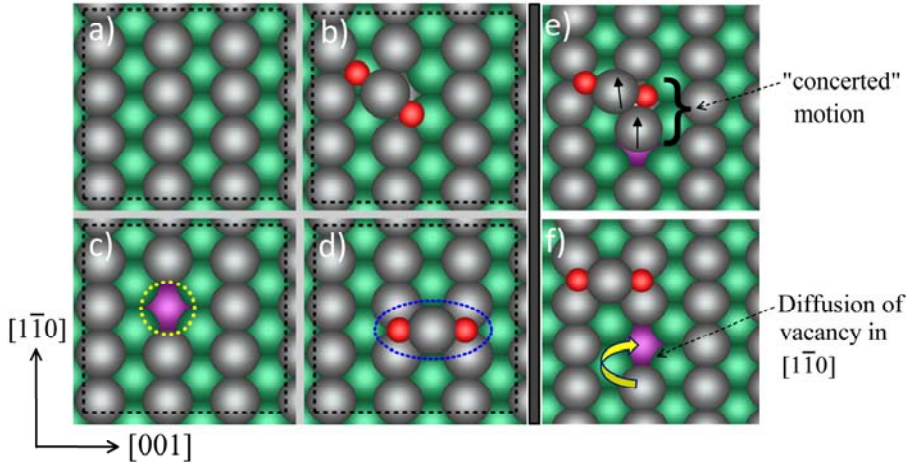


Fig. 3 Schematic representation for the formation of single Ag vacancy and added O-Ag-O unit on Ag(110): a) pristine surface; b) the dissociated O atoms participate to form an O-Ag-O complex, resulting in a weakening of Ag-Ag bonds in the substrate; c) Ag vacancy (yellow dotted); d) O stabilized Ag adatom (blue dotted); e) diffusion of O-Ag-O complex and Ag atom in “concerted” motion; and f) diffusion of vacancy away from the added O-Ag-O complex.

In absence of oxygen, vacancy formation cannot be observed since extracted Ag atoms most likely refill the just created vacancy. Indeed, DFT results show that: i) the formation energy of an Ag vacancy plus Ag adatom on pristine Ag(110) is 0.42 eV. ii) The energy barrier for this process to occur is 0.69 eV, whereas the reverse barrier is 0.27 eV (see Fig. S3a). iii) Such value is much lower than the barrier of 0.47 eV for the diffusion of the Ag vacancy along $[1\bar{1}0]$ (see Fig. S2). Ag vacancy creation and adatom formation on bare Ag(110) occurs thus only for $T > 750$ K [40].

In presence of oxygen atoms vacancy formation on Ag(110) becomes possible (see Fig. 3) since the formation energy $E_v^{ad,O-Ag-O}$ is reduced to 0.055 eV. If E_a to E_d are the total energies for the structures shown in Fig. 3a-d, respectively, we have:

$$E_v^{ad,O-Ag-O} = -\{(E_a + E_b) - (E_c + E_d)\}$$

The formation of an Ag vacancy (Fig. 3c) *plus* an oxygen-decorated Ag adatom (added O-Ag-O unit, Fig. 3d) is thus only slightly endothermic and may take place thanks to the entropic contribution to the free energy. The barrier for the formation of Ag vacancy plus added O-Ag-O unit reduces to 0.52 eV for the “concerted motion” (Fig. 3e) in which the O-Ag-O complex of Fig. 3b diffuses to the nearest

neighbouring hollow (H) site dragging also the Ag atom in the $[1\bar{1}0]$ direction (see also Fig. S3(b)). With increasing O coverage the barrier decreases to 0.46 eV (see Fig. S4). The reverse barrier increases substantially, thus inhibiting the vacancy-destruction process. Once formed the vacancy diffuses therefore away from the O decorated Ag adatom (see Fig. 3f) avoiding recombination (see discussion of Fig. S2), leading to the isolated vacancy (Fig. 3c) and the O-decorated Ag adatom (Fig. 3d). Dissociation of O_2 with production of two O atoms is exothermic with an energy barrier of 0.42 eV [38]. Our Kinetic Monte Carlo (KMC) simulations show that this process is peaked around 157 K (Fig. S5 of SOM), in good agreement with the experimental value of 150 K. Then, the O-Ag-O complex of Fig. 3b forms spontaneously since it is energetically favoured by 70 meV with respect to two oxygen atoms at H sites two lattice spacing apart. In STM such complex is imaged by a grey dot with a whitish side along $[1\bar{1}0]$ which has indeed been sporadically observed in our images (Fig. S6 and S7 of SOM). The complexes formed at 175 K merge together into the grey chains attached to the Ag vacancy. Finally, for vacancy formation, the system needs to overcome the previously discussed barrier of 0.52 eV. KMC simulation (Fig. S5 of SOM) indicates that the latter process is peaked at 185 K-190 K at low O coverage (decreasing with increasing coverage). The relative populations of O-Ag-O complexes and vacancies will thus depend on T and O coverage.

The system then has to cope with the 55 meV endothermicity of the internal energy balance. Such difference can be compensated by the entropic contribution to the free energy (calculated to be ~ 1 meV/K for a square Ag lattice [39]). Vacancy formation is thus possible only above 60 K. Indeed, no vacancy formation was observed by Hahn and Ho [32, 33] in their O_2 disruption experiments performed at 13 K.

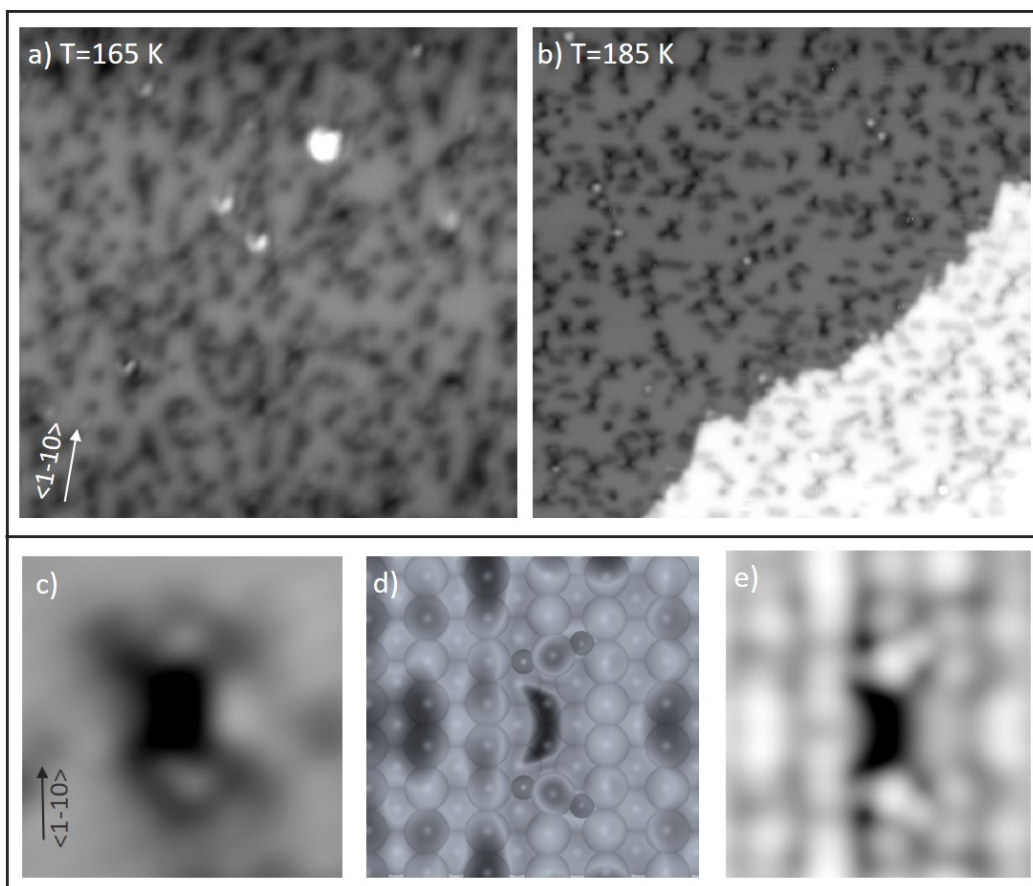


Fig. 4. (a-b) STM images of O/Ag (110) after dosing O₂ at 0.4 eV kinetic energy by SMB, at T=165 K (a) and T=185 K (b). The estimated coverage is 0.06 ML. Image size 450 Å x 450 Å, V=70 mV, I=1.0 nA. c) Enlargement of a “butterfly” structure (Image size 34 Å x 33 Å, V=70 mV). d-e) DFT-optimized geometry and simulated STM image of the “butterfly” unit. See Fig.S10 in the supporting material for the atomic positions.

Fig. 4a-b shows STM images of an O/Ag(110) surface obtained by dosing O₂ with the SMB, corresponding to an estimated O coverage of 0.06 ML. During exposure, T was kept at either 165 K or 185 K (panel a and b, respectively). Overcoming the limit of low coverage, more complex structures form in addition to the previously described ones. In particular, “butterfly” shaped objects (see enlargement in panel c) are now present. They appear as elongated depressions along $[1\bar{1}0]$, ending at both extremities with a round protrusion sided laterally by “wings”. Butterflies are abundant at 175 K and at 185 K but rare when dosing O₂ at 165 K. To unravel this complex structure we performed DFT calculations modelling it with a pair of vacancies and with four

oxygen atoms. As evident from Fig. 4d, in the DFT-optimized geometry the two Ag atoms at the “head” and “tail” of the butterfly are displaced from their original site and each one is sided by two O (see also discussion on Fig. S9a and S10 in the SOM). The simulated STM image (Fig. 4e) of the relaxed structure shows a remarkable agreement with experiment. Notably, the energy of the couple of O is -2.9 eV and the overall structure is asymmetric with respect to $[1\bar{1}0]$.

Multiple Ag vacancies are found to form following the dissociation of additional O₂ molecules. The orientation along $[1\bar{1}0]$ of such chains of vacancies is in accord with the anisotropy of the barrier for vacancy diffusion (see Fig.S2 in SOM). Indeed, at 175 K vacancy migration is active only along the Ag rows. Moreover, attaching an additional vacancy to an already existing one results in energy gain (Fig. S8 in SOM). The process saturates eventually above three Ag vacancies, which compares nicely with the observed lengths of the body of the butterflies of Fig. 4.

The calculated barriers for vacancy formation imply that the relative abundance of black dots and sombreros depends on T and preparation conditions, explaining the different results present in literature.

At low coverage, O-decorated Ag adatoms of Fig. 3d most probably end up at step edges where they are difficult to be identified, while at high coverage they stick at the vacancies forming the wings. Statistically, some vacancies may be filled up by O decorated complexes and O atoms can then be buried into the Ag subsurface region giving a rational for the efficient subsurface migration already at low T.

Finally, the substrate reconstruction of Fig. 3b explains the strong disordering of the Ag(110) substrate upon O₂ dissociation at low T mentioned in the introduction [27]. Indeed, the Ag atoms forming the O-Ag-O complex undergo a vertical displacement of 0.56 Å. The drop in the reflected electron beam intensity is thereby largest at low electron kinetic energies since the electrons are then reflected off the attractive potential barrier which becomes heavily corrugated.

In conclusion, our combined STM investigation and DFT analysis of the O/Ag(110) system provides a detailed insight into the mechanisms involved in the process of vacancy formation. The latter is possible at pristine terraces only in presence of O adatoms and the process gets easier for the higher oxygen coverage, thus leading to “butterfly” formation. Further insight on the disruption mechanism could be gained by STM investigations with deliberate functionalization of the tip and subsequent simulations of the images.

Vacancy formation is remarkable for Ag(110) at 175 K, but it is expected to take place also for the other Ag surfaces, albeit at higher T since more bonds need to be broken to extract Ag adatoms (see Fig. S11 in SOM [43]). A similar scenario may occur also for other metals at high enough T, thus accounting for the still unexplained observations reported for Cu surfaces [10] and for Au(111) [41]. As we learned recently, vacancies form indeed for O/Ag(111) when O₂ is dosed at 433 K [42]. The so-generated adatoms constitute the building blocks for the added row reconstruction on Ag(110), providing the main supply of substrate atoms far from step edges or at low T. This explains thus the observed nucleation of added rows also in the middle of wide terraces. The occurrence of vacancy excavation gives a rationale for the well-known facile access of oxygen to the Ag subsurface region. Finally, the O induced substrate reconstruction explains the drop of the elastic reflectivity of low kinetic energy electron beams observed upon thermal O₂ dissociation [27], since the surface order is disrupted.

Such properties are relevant for the understanding of the catalytic properties of Ag, in particular, and of noble metals in general, since vacancies are under-coordinated and thus inherently reactive. A significant subsurface O content provides, moreover, a precious reservoir of reactants.

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References

- [1] F. Besenbacher, F. B. Nørskov, *Prog. Surf. Sci.* **44**, 5 (1993).
- [2] D.J. Coulman, J. Wintterlin, R.J. Behm, G. Ertl, *Phys. Rev. Lett.* **64**, 1761 (1990).
- [3] F. Jensen, F. Besenbacher, E. Lægsgaard, I. Stensgaard, *Phys. Rev. B* **41**, 10233 (1990).
- [4] Q. Liu, L. Li, N. Cai, W.A. Saidi, G. Zhou, *Surf. Sci.* **627**, 75 (2014).
- [5] L. Li, N. Cai, W. A.Saidi, G. Zhou, *Chem. Phys. Lett.* **613**, 64 (2014).
- [6] T. Zambelli, J.V. Barth and J. Wintterlin, *Phys. Rev. B* **58**, 12663 (1998).
- [7] M. Taniguchi, K. Tanaka, T. Hashizume, and T. Sakurai, *Surf. Sci.* **262**, L123 (1992).
- [8] W. W. Pai, N. C. Bartelt, and J. E. Reutt-Robey, *Phys. Rev. B* **53**, 15991 (1996).
- [9] W. W. Pai, N. C. Bartelt, M. R. Peng, and J. E. Reutt-Robey, *Surf. Sci.* **330**, L679 (1995).
- [10] L. D. Sun, M. Hohage, R. Denk, P. Zeppenfeld, *Phys. Rev. B* **76**, 245412 (2007).
- [11] B. K. Hodnett, *Heterogeneous catalytic oxidation: fundamental and technological aspects of the selective and total oxidation of organic compounds*, John Wiley, 2000.
- [12] *Handbook of Heterogeneous Catalysis*, ed. G. Ertl, H. Knoezinger, F. Schueth and J. Weitkamp, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, (2008).
- [13] W.L. Dai, Q. Liu, Y. Cao, J.F Deng, *App. Catal. A* **175**, 83 (1998)
- [14] J.G. Serafin, A.C. Liu, S.R. Seyedmonir, *J. Mol. Catal. A* **131**, 157 (1998).
- [15] C. T. Campbell, M.T. Paffett, *Surf. Sci.*, **139**, 396 (1984).
- [16] S. Böcklein, S.Günther, and J. Wintterlin, *Angew. Chemie Int. Ed.* **52**, 5518 (2013)
- [17] J. Schnadt, A. Michaelides, J. Knudsen, R. T. Vang, K. Reuter, E. Lægsgaard, M. Scheffler and F. Besenbacher, *Phys. Rev. Lett.* **96**, 146101 (2006).
- [18] M. Schmid, A. Reicho, A. Stierle, I. Costina, J. Klikovits, P. Kostelnik, O. Doubay, G. Kresse, J. Gustafson, E. Lundgren, J. N. Anderson, H. Dosch and P. Varga, *Phys. Rev. Lett.* **96**, 146102 (2006).

- [19] J. Schnadt, J. Knudsen, X. L. Hu, A. Michaelides, R. T. Vang, K. Reuter, Z. Li, E. Lægsgaard, M. Scheffler and F. Besenbacher, *Phys. Rev. B* **80**, 075424 (2009).
- [20] M. Rocca, L. Savio, L. Vattuone, U. Burghaus, V. Palomba, N. Novelli, F. Buatier de Mongeot, U. Valbusa, R. Gunnella, G. Comelli, A. Baraldi, S. Lizzit, G. Paolucci, *Phys. Rev. B* **61**, 213 (2000).
- [21] S. Günther, S. Böcklein, J. Wintterlin, M. A. Niño, T. O. Montes, and A. Locatelli, *Chem. Cat. Chem.* **5**, 3342 (2013).
- [22] T. C. R. Rocha, A. Oestereich, D. V. Demidov, M. H. Vecker, S. Zafeiratos, G. Weinberg, V. I. Bukhtiyarov, A. Knop-Gericke, R. Schlögl, *Phys. Chem. Chem. Phys.* **14**, 4554 (2012).
- [23] L. Vattuone, L. Savio, M. Rocca, *Phys. Rev. Lett.* **90**, 228302 (2003).
- [24] L. Savio, C. Giallombardo, L. Vattuone, A. Kokalj, M. Rocca, *Phys. Rev. Lett.* **101**, 266103 (2008).
- [25] L. Savio, A. Gerbi, L. Vattuone, A. Baraldi, G. Comelli, M. Rocca, *J. Phys. Chem. B* **110**, 942 (2006).
- [26] M. Rocca, L. Savio, L. Vattuone, F. Buatier de Mongeot, U. Valbusa, G. Comelli, A. Baraldi, S. Lizzit, G. Paolucci, J.A. Groenewald, E. J. Baerends, *Phys. Rev. B* **63**, 1404 R (2001).
- [27] L. Vattuone, M. Rocca, P. Restelli, M. Pupo, C. Boragno, U. Valbusa, *Phys. Rev. B* **49**, 5113 (1994).
- [28] U. Burghaus and H. Conrad, *Surf. Sci.* **338**, L869 (1995).
- [29] U. Burghaus and H. Conrad, *Surf. Sci.* **370**, 17 (1997).
- [30] T. Zambelli, J.V. Barth and J. Wintterlin, *J. Phys.: Condens. Matter* **14**, 4241 (2002).
- [31] M. Smerieri, L. Savio, L. Vattuone, M. Rocca, *J. Phys. Cond Matter* **22**, 304015 (2010).
- [32] J. R. Hahn, W. Ho, *J. Chem. Phys.* **122**, 244704 (2005).
- [33] J. R. Hahn, W. Ho, *J. Chem. Phys.* **123**, 214702 (2005).
- [34] S. Schintke, S. Messerli, K. Morgenstern, J. Nieminen, W.-D. Schneider, *J. Chem. Phys.* **114**, 4206 (2001).
- [35] L. Vattuone, M. Rocca, C. Boragno, U. Valbusa, *J. Chem. Phys.* **101**, 726 (1994).
- [36] I. Lončarić, M. Alducin, and J.I. Juaristi, *Phys. Chem. Chem. Phys.* **17**, 9436 (2015).

- [37] M. Smerieri, R. Reichelt, L. Savio, L. Vattuone, and M. Rocca, *Rev. Sci. Instrum.* **83**, 093703 (2012).
- [38] T. B. Rawal, S. Hong, A. Pulkkinen, M. Alatalo, T. S. Rahman, *Phys. Rev. B.* **92**, 035444 (2015).
- [39] A. Savara, *J. Phys. Chem. C* **117**, 15710 (2013).
- [40] T. S. Rahman, Z. Tian, J. E. Black, *Surf. Sci.* **374**, 9 (1997).
- [41] B. K. Min, X. Deng, D. Pinnaduwege, R. Shalek, and C. M. Friend, *Phys. Rev. B* **72**, 121410 R 2005.
- [42] B.V. Andryushechkin, V.M. Shevlyuga, T.V. Pavlova, G.M. Zhidomirov, K.N. Eltsov, *Phys. Rev. Lett.* **117**, 056101 (2016).
- [43] See Supplemental Material [www.aps.org] for experimental and computational details, determination of the position of the observed O related features, diffusion of Ag vacancies, energy barriers for single vacancy formation and their dependence on O coverage, kinetic Monte Carlo simulations, STM image of the O-Ag-O complex, formation of multivacancies and dependence on crystal face, which includes Refs. [44-56].
- [44] M. Smerieri, R. Reichelt, L. Savio, L. Vattuone, and M. Rocca, *Rev. Sci. Instrum.* **83**, 093703 (2012).
- [45] T. B. Rawal, S. Hong, M. Alatalo, T. S. Rahman, J. Pal, M. Smerieri, L. Savio, R. Reichelt, L. Vattuone, M. Rocca, unpublished.
- [46] J.M. Blanco, C. Gonzalez, P. Jelinek, J. Ortega, F. Flores, R. Perez, M. Rose, M. Salmeron, J. Méndez, J. Wintterlin, G. Ertl, *Phys. Rev. B* **71**, 113402 (2005).
- [47] I. Horcas, R. Fernández, J.M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, and A.M. Baro, *Rev. Sci. Instr.* **78**, 013705 (2007).
- [48] a) G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993); b) G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994); c) G. Kresse and J. Furthmüller, *Comput. Mat. Sci.* **6**, 15 (1996); d) G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [49] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [50] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [51] J. D. Pack, and H. J. Monkhorst, *Phys. Rev. B* **16**, 1748 (1977).
- [52] P. Walker and W. H. Tarn, *CRC Handbook of Metal Etchants* (CRC, New York, 1990).
- [53] M. Methfessel, A. T. Paxton, *Phys. Rev. B* **40**, 3616 (1989).

- [54] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes* (Cambridge University Press, New York, 2007); E. Polak, *Computational Methods in Optimization* (Academic, New York, 1971).
- [55] J. Tersoff and D. R. Hamann, *Phys. Rev. Lett.*, **50**, 1998 (1983).
- [56] G. Henkelman, B. P. Uberuaga, and H. Jonsson, *J. Chem. Phys.* **113**, 9901 (2000).
- [57] P. Stoltze, *J. Phys.: Condens. Matter* **6**, 9495 (1994).