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Formation mechanism of the O-induced added-row reconstruction on Ag(110): A low-temperature STM study

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The formation of the O-induced added-row reconstruction on Ag(110) was studied by scanning tunneling microscopy at 190 K. At this temperature critical surface processes are slow enough to be followed on the atomic scale. Ag atoms, which are required for the formation of the reconstruction, detach from steps in a row-wise fashion, starting from kink sites. The growth rate of the added rows is constant and controlled by the detachment rate of Ag atoms from the steps. The data provide evidence for a reconstruction mechanism in which the release of the metal atoms from the steps and the formation of lateral oxygen metal bonds are independent processes. [S0163-1829(98)01640-3]

I. INTRODUCTION

Oxygen induces a characteristic type of reconstructions of the (110) surfaces of Cu, Ni, and Ag, consisting of chains of alternatingly oxygen and metal atoms along the [001] crystallographic direction, which lie on the topmost, unreconstructed metal layer.[1,2] These ‘‘added-row’’ structures form from oxygen and metal atoms, both diffusing across the substrate terraces, where they ‘‘condense’’ into rows. This mechanism was deduced from scanning tunneling microscopy (STM) observations of an ‘‘etching’’ of steps during oxygen adsorption[3–10] indicating that steps are the sources of the mobile metal atoms, and of strong fluctuations of the steps of the clean metals at 300 K [for Cu and Ag(110) see Refs. 9 and 11], identified with rapid exchange processes of metal atoms between step sites and the terraces. However, because neither the rapidly diffusing O_{ad} and M_{ad} atoms were resolved, nor individual atomic detachment events from the steps, the transport processes themselves could not be followed on the atomic scale. An alternative mechanism, in which the O_{ad} atoms react with atoms directly at the steps, followed by transport of preformed added-row segments to the terraces, can therefore not really be ruled out (see the discussions in Refs. 9 and 12), considering also the significant mobility of the added rows at 300 K.[3–5,11] An influence of the mobile oxygen atoms on the step fluctuations, which would support such a mechanism, has not been reported, but would also be difficult to detect at 300 K since the large supply of M_{ad} atoms from the steps[9,10] quickly consumes the O_{ad} atoms by reconstruction formation. We therefore studied the reconstruction formation of the Ag(110) surface at a reduced temperature, using a variable temperature STM, to slow down the rapid processes that preclude to follow the reconstruction process on the atomic scale at 300 K.

II. EXPERIMENT

The experiments were performed in an ultrahigh-vacuum chamber (base pressure 5×10^{-11} Torr), equipped with standard facilities for sample preparation and characterization. The STM of the beetle type could be cooled by liquid He to temperatures as low as 55 K; higher temperatures were adjusted by radiative heating from a hot filament. Temperatures were measured with a NiCr-Ni thermocouple attached to the sample. The temperature reading was checked against the desorption temperature of 77 K of CO from the Ag(110) sample.[13] The STM data were obtained in the constant-current mode with tunnel currents typically between 0.3 and 1 nA and voltages of 0.5–1.0 V. The Ag(110) single-crystal surface was prepared by cycles of Ar^+ sputtering (1 μA/cm^2, 700 eV, 10 min at 300 K) and annealing at 750 K until no contaminations could be detected by Auger electron spectroscopy, and STM resolved large, defect-free atomic terraces.

III. RESULTS AND DISCUSSION

An STM image of the the clean Ag(110) surface at 300 K is shown in Fig. 1. Steps appear blurry in the horizontal (fast) scanning direction, confirming earlier observations for this and other surfaces.[11,14,15] For Ag(110) (Refs. 9 and 10) this effect was explained as an exchange of atoms between the steps and the terraces, which is fast relative to the scanning frequency.

By forming the reconstruction at higher temperatures and imaging at low temperatures the temperature dependence of the sticking coefficient was obtained which was needed for the analysis of the following measurements. Figure 2(a) shows the Ag(110) surface at 100 K after dosing of 50 L oxygen at 500 K (note the stable appearance of the steps due

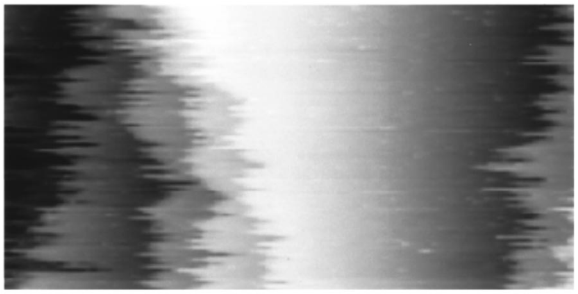

FIG. 1. STM image of the clean Ag(110) surface at 300 K with fluctuating steps (340×180 Å^2, $V=-0.5$ V, $I=0.1$ nA).

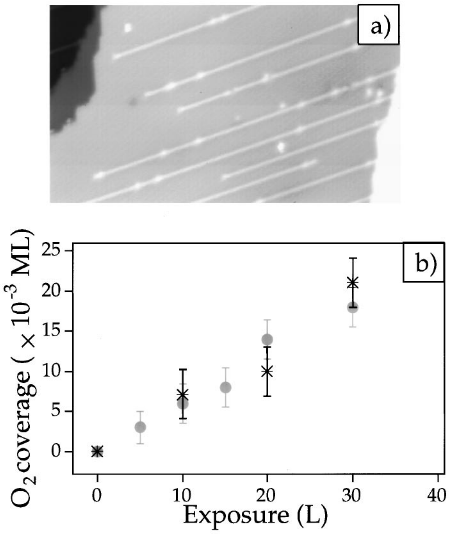

FIG. 2. (a) STM image of the surface at 100 K after dosing 50 L oxygen at 500 K (460×250 Å^2, $V=-0.6$ V, $I=0.3$ nA); (b) oxygen coverage vs O_2 exposure obtained from low-temperature STM data, after dosing at $T=100$ K (circles) and $T=500$ K (asterisks).

to the inhibited mobility of surface Ag atoms at this temperature). The terraces are covered by immobile white lines oriented along the [100] direction, which resemble the added-row reconstructions on the fcc (110) surfaces at 300 K (Ref. 1) and are identified with -Ag-O- added rows. From our studies on the thermal dissociation of oxygen on the Ag(110) surface[16] adsorbed O atoms are immobile at 100 K also if not bound in the reconstruction and hence would be resolved if present. We conclude that all adsorbed O atoms are contained in the reconstruction rows, allowing to determine the initial sticking coefficient of oxygen at the higher adsorption temperature. Figure 2(b) shows the results for nondissociative O_2 adsorption at 100 K (circles) and dissociative O_2 adsorption at 500 K (asterisks). In the case of molecular adsorption at low temperature, the coverages were extracted directly from STM data in which individual oxygen molecules could be resolved.[17] For exposures smaller than 30 L, both series of data show a linear behavior, with equal slopes within experimental errors, corresponding to sticking coefficients of $(1.7\pm0.2)\times10^{-3}$ at 100 K and $(1.9\pm0.4)\times10^{-3}$ at 500 K. This confirms earlier results based on other techniques,[18] but disagrees with a variation of the initial sticking coefficient by a factor of 2 between molecular and dissociative oxygen adsorption, concluded from high-resolution electron energy-loss spectroscopy (HREELS) experiments.[19] This may be explained by the fact that the analysis of the HREELS data involved the saturation coverage of molecular oxygen, which is not well known.[20]

A sequence of STM frames recorded *in situ* during oxygen adsorption (5×10^{-8} Torr) at 190 K is shown in Figs. 3(a)–3(d). The area imaged [Fig. 3(a)] contains flat terraces separated by monoatomic steps, with the resolved atomic rows along the [110] direction of the Ag(110) lattice. In Fig. 3(b), recorded on the same area 400 s after starting the exposure, a bright line (1) along the [001] direction has appeared at kink *B*. This structure is imaged identically as the added rows obtained by adsorption at higher temperatures [Fig. 2(a)] and is identified with a nucleus of the added-row reconstruction. Both kinks *D* and *E*, which in Fig. 3(a) are two atomic rows wide, have shrunk to only one row, indicating that atoms have been removed from the step. Kink *A* has moved towards the lower part of the image and has become three rows wide by the removal of one atomic row from the step above. In addition a second type of structure (''cluster'')

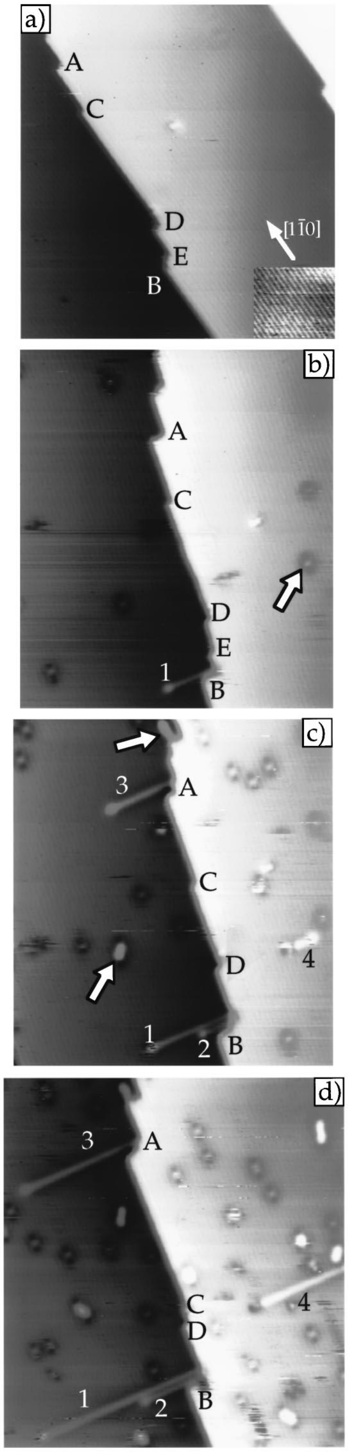

FIG. 3. (a) STM image of Ag(110) at 190 K; in the inset the contrast is enhanced to visualize the atomic Ag rows in [110] direction (240×260 Å^2, $V=-1.0$ V, $I=0.3$ nA); (b)–(d) same area as in (a) during O_2 dosing, after 400, 600, and 1300 s (O_2 pressure 5×10^{-8} Torr).

has formed, which is marked by an arrow.

The motions of the kinks were observed not only in the presence of oxygen on the surface, but also on the clean surface. This indicates that O_{ad} atoms are not directly reacting with atoms at the steps, but that Ag atoms detach from kink sites, as on the clean metal. There are also no effects indicating the motion of Ag-O segments away from the steps, all added-row features are immobile.

In Fig. 3(c), recorded after 600 s, the reconstruction row 1 has grown, and further bright lines along [001] (2 and 3) have formed at kinks *A* and *B*. An additional row (4) is seen in the center of the upper terrace. At the same time that the kinks *A*, *B*, and *C* have shifted towards the bottom of the image, kink *E* has disappeared, indicating an ongoing detachment of Ag atoms. The arrow in the middle of the lower terrace marks a new structure, which is associated with the merging of two ‘‘clusters.’’ After 1300 s [Fig. 3(d)], when the segments have grown further and the number of the ‘‘clusters’’ has increased, also the kinks have moved again. Kink *C* has joined kink *D*, and a small bay has developed at kink *B*.

The changes in position and width of the kinks demonstrate that Ag atoms detach from the step edges at temperatures as low as 190 K. This indicates that even under these conditions the added-row reconstruction of Ag(110) follows the formation scenario from diffusing O atoms and metal atoms evaporating from the steps originally derived for Cu(110) at 300 K.[3–5] The other species, the clusters, could not be identified so far. They do not evolve at slightly higher temperatures so that they must be a metastable product. Contaminations are unlikely, otherwise we would have found similar structures upon dosing oxygen at around 100 K, where oxygen adsorbs molecularly, which was not the case.[17,21] Similar ‘‘clusters’’ were obtained at intermediate temperatures, about 15 K lower than here, where oxygen dissociates but does not induce the reconstruction yet.[16] We interpret them therefore as metastable agglomerates of Ag and O atoms.

With the above sticking coefficient of molecular oxygen, and taking into account that the tip shields the surface under *in situ* conditions (typically, *in* and *ex situ* measurements differed by a factor of 5 in the coverages[16]), the number n_s of oxygen atoms, arriving on the scanned area, can be estimated to be of the order of 1 atom/s in the experiment of Fig. 3. Although the area must therefore have a significant concentration of O_{ad} atoms not yet contained in the reconstruction these are apparently highly mobile and are not detected by the STM. This is consistent with the observation that at $T \approx 100$ K, where the mobility is frozen, they are resolved easily. Analogously, the Ag atoms diffusing on the terraces could not be seen, but their presence is attested, for example, by the reconstruction row 4 [Fig. 3(c)], that nucleates and grows in the middle of a terrace. Calculations for the Ag(110) surface diffusion barriers[22] revealed values of 0.25–0.32 eV and 0.31–0.42 eV along the two principal directions, where the differences are partially compensated by the different preexponential factors. The resulting hopping rates are between 10^4 and 10^6 s^{-1} at $T = 190$ K, which by far exceeds the STM scan frequencies and explains why they are not resolved.

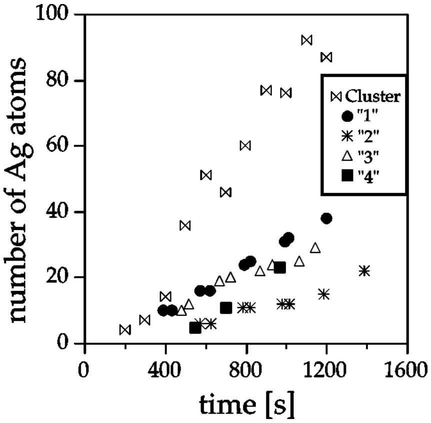

FIG. 4. Time evolution of the number of Ag atoms contained in Ag-O added rows and in clusters during exposure of O_2 on Ag(110) at 190 K (from the data in Fig. 3).

Differently from room temperature, where reconstruction rows were found randomly all over the surface,[7–10] at 190 K the reconstruction nucleates predominantly at steps, nuclei in the middle of terraces were scarcely observed. This is explained by the small concentration of mobile metal atoms under these conditions, making homogeneous nucleation unlikely. Clearly, the clusters formed on the terraces are not preferred reconstruction nuclei. The data show a preference for kink sites over sites at straight parts of the steps, which is associated with more stable configurations with adsorbed O atoms at less highly coordinated Ag atoms. Such an explanation is consistent with calculations of the stability of the added-row reconstruction of Cu(110) (Ref. 23), which was traced back to an altered electronic structure of the low-coordinated metal atoms in the added rows. That reconstruction rows do not develop at every kink signals that the growth of existing nuclei is preferred over nucleation once a sufficient number of nuclei has developed. The attachment of diffusing atoms to the protruding ends of the Ag-O rows is expected to be even more favorable than to a kink site. Altogether, the behavior agrees with standard nucleation and growth schemes.

The development of the four reconstruction rows and the ‘‘clusters’’ in Fig. 3 as a function of time is shown in Fig. 4 (we assume for simplicity that every cluster contains only one Ag atom). All four rows grow linearly with time and almost at the same rate of 0.02 Ag atoms per second, corresponding to a ‘‘consumption’’ rate of Ag atoms of about 0.1 s^{-1} on the area scanned (neglecting the clusters). The number of clusters grows slowly initially, later at a faster, constant rate. These generally linear rates cannot be a consequence of the constant oxygen pressure during the *in situ* experiment. The above estimated rate n_s at which the O atoms arrive at the scanned area is approximately ten times higher than the growth rate of the four rows together so that the oxygen coverage must be increasing. On the other hand, the average rate of ≈ 0.05 s^{-1} by which Ag atoms evaporate from the individual kinks is comparable to the growth rate. Even with the uncertainties of these estimates (the shielding factor of the tip is not well known, and the scanned area is small) it is clear that there must be a surplus of mobile oxygen atoms on the surface and that, therefore, the growth of the added rows must be limited by the supply of Ag atoms from the steps. This conclusion is supported by the observation in other experiments that the added rows kept growing after the exposure of oxygen molecules from the gas phase was stopped. Moreover, the constant growth rate means that the Ag atoms cannot be directly released by the action of the oxygen atoms, because the oxygen coverage increases. The observed detachment rate of Ag atoms from the kinks is also in agreement with expectations from previous work. Assuming 10^{13} s^{-1} for the preexponential factor, a barrier of 0.6 eV is obtained. These observations are in agreement with recent STM measurements, where Ostwald ripening of Ag islands on Ag(110) revealed substantial Ag evaporation from kinks for temperatures exceeding $\approx$160 K, in agreement with energetics obtained from effective medium calculations.[24]

Finally, we have to consider the possibility that Ag atoms do not evaporate from the kinks to the terraces, but move only along the step edges, which appears energetically more favorable and was found in STM experiments on a stepped Cu(100) surface.[15] According to calculations the latter process is, in fact, more likely.[25,26] Since most of the added rows originate at step sites one could then conceive a mechanism by which Ag atoms diffuse along the steps until they arrive at a reconstruction row, along which they would then travel to the growing end, without being released to the terraces. However, row 4 [Fig. 3(c)] nucleates without contact to a step and grows at a rate comparable to the other rows, demonstrating that such a mechanism is not generally applicable. Furthermore, row 2 grows only at about half of the rates of the other rows (Fig. 4), which is most easily rationalized by the fact that the neighboring longer row 1 [Figs. 3(c) and 3(d)] shields the area from which atoms can reach 2 on one side, i.e., roughly by a factor of 2. The STM data can only be understood completely if the growth of the reconstruction rows proceeds by direct capture of diffusing Ag or O atoms on the terraces at their protruding ends. This conclusion is in agreement with recently published STM data of step fluctuations of the Ag(110) surface at 300 K (Ref. 9), which could be interpreted as an attachment-detachment process.

IV. CONCLUSIONS

STM observations of oxygen adsorption on Ag(110) clarified the formation mechanism of the added-row reconstruction at low temperature. The data show that the general mechanism suggested earlier for room-temperature formation of this reconstruction type holds over a wide temperature range. Added rows form from oxygen and metal atoms, both diffusing across the terraces, with metal atoms originating from atomic steps. A row-wise evaporation of metal atoms from kink sites was observed. The evaporation process is independent of the presence of an excess coverage of mobile oxygen atoms, i.e., it is driven by thermal activation. Accordingly it was found that the growth rate of the reconstruction rows can be smaller than the supply rate of oxygen atoms and remains constant while the oxygen atom coverage increases. The immobility of the added-row features at 190 K demonstrates that the reconstruction does not form via transport of preformed Ag-O segments from the steps to the terraces.

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