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Interaction of Ag and O on W(1 1 0) studied by scanning tunneling microscopy

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Abstract

The structural changes of Ag films on W(1 1 0) upon coadsorption of oxygen have been studied by scanning tunneling microscopy. The exposure of one monolayer Ag to oxygen leads to a phase separation into an Ag bilayer and patches of O-covered W(1 1 0). The effective Ag island thickness increases linearly with oxygen exposure. For Ag submonolayer-islands the onset of the bilayer formation is delayed, the induction period increases with the available free W area. We conclude that the steps of the transport process are (1) dissociation of oxygen on W and on the Ag islands, (2) site exchange of atomic oxygen with Ag atoms predominantly at the island edges – while on W(1 1 0) the oxygen is immobile, (3) diffusion of the displaced Ag atoms to the island edges where they are incorporated into the monolayer and (4) initiation of Ag bilayer formation, once the W(1 1 0) is saturated with O. This indicates an unexpected activity of the Ag monolayer on W(1 1 0) towards oxygen dissociation. In case of a reversed deposition sequence, where submonolayer quantities of Ag are adsorbed on an oxygen-precovered W(1 1 0) surface, growth of Ag clusters is observed. The distribution of cluster size and cluster height depends critically on the spatial order within the predeposited oxygen overlayer – it is obvious that the oxygen overlayer on the W surface acts as a structured template for preferential Ag nucleation.

Keywords: Tunneling microscopy; Silver; W(1 1 0); Oxygen; Ultrathin overlayers; Coadsorption; Atomic structure

1. Introduction

Many studies of coadsorbate systems on metal single crystal surfaces have shown that a more weakly bound monolayer (ML) may be displaced by a more strongly bound adsorbate. For example restructuring of an adsorbed metallic ML may be induced by gas admission after the overlayer was prepared. Moreover, adsorbates can modify the growth of metals deposited subsequent to gas adsorption. However, most studies of the processes mentioned above used laterally averaging spectroscopies. To reveal more structural information we studied the O/Ag/W(1 1 0) and Ag/O/W(1 1 0) systems using scanning tunneling microscopy (STM). Section 3A describes the oxygen-induced rearrangement of Ag sub-ML, ML and double-layer coverage on W(1 1 0). Analysis of restructuring rates gives information about the relative reactivity of the different layers with oxygen. Section 3B outlines growth of Ag on oxygen-precovered W(1 1 0).

2. Experiment

All STM experiments were carried out in a UHV chamber with a base pressure $p < 8 \times 10^{-11}$ mbar. It was equipped with an STM, low-energy electron diffraction (LEED), a mass spectrometer and an indirectly heated alumina crucible for evaporation of Ag. The W(1 1 0) sample was a circular disc of 8 mm diameter, oriented to better than 0.25°, which corresponds to an (experimentally verified) terrace width of several hundred Angstroms. Cleaning

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was accomplished by repeated heating to $T = 1400$–1750 K in 5×10^{-8} mbar of O_2, followed by a rapid flash to T = 2300 K in the absence of oxygen. After cleaning no indications for the well-known C-induced reconstructions on W(1 1 0) could be detected in the atomically resolved STM image and a brilliant substrate LEED pattern with very low background intensity was observed. All images were obtained at RT. The constant current mode was used with 0.04–0.6 eV positive or negative tip bias and tunnel currents of 0.1–0.7 nA. Ag was evaporated at 0.7 ML per minute, with the sample at or slightly above RT. Exposition of the sample to O_2 occured at room temperature with an oxygen pressure of 2×10^{-8} mbar in the vacuum chamber.

3. Results and discussion

3.1. Oxygen-induced rearrangement of Ag on W(1 1 0)

Fig. 1 reproduces STM pictures taken during dosing of 1 ML Ag with O_2. The ML (Fig. 1a) is not completely filled but shows voids with a total area of about 3% of the W(1 1 0) surface. Only very few Ag atoms are deposited in the second layer, nucleating at the steps. Exposure to O_2 leads to large-scale dendritic islands. These remember to the mechanism of diffusion-limited aggregation. However, we must also assume an influence of elastic relaxation of the first monolayer. Ag on W(1 1 0) exhibits a mixed tensile and compressive strain distribution around ML coverage which is locally relieved in an almost periodic superstructure arrangement of light domain walls [1–4]. The latter will influence both atomic diffusion steps and the growth mode within the second layer. With increasing oxygen exposure the area of double layers grows with simultaneous reduction of the ML area. Finally around 100 L (Fig. 1d) the rearrangement from ML to bilayer is almost completed, with negligible ML area remaining. If exposure with oxygen is continued, Ag atoms start to climb up into the third layer (see the three arrows in Fig. 1d). However, the rearrangement rate for the third layer is much smaller than before, indicating that the sample gets increasingly unreactive with molecular oxygen.

The rearrangement process occurs somewhat differently if we expose ML-islands at submonolayer total coverage to oxygen. Typical results at 0.3 ML and 0.2 ML are reproduced in Fig. 2 and Fig. 3. Initially no Ag is moved into second-layer positions. Instead the monolayer islands change their shape and decay into smaller stripes which

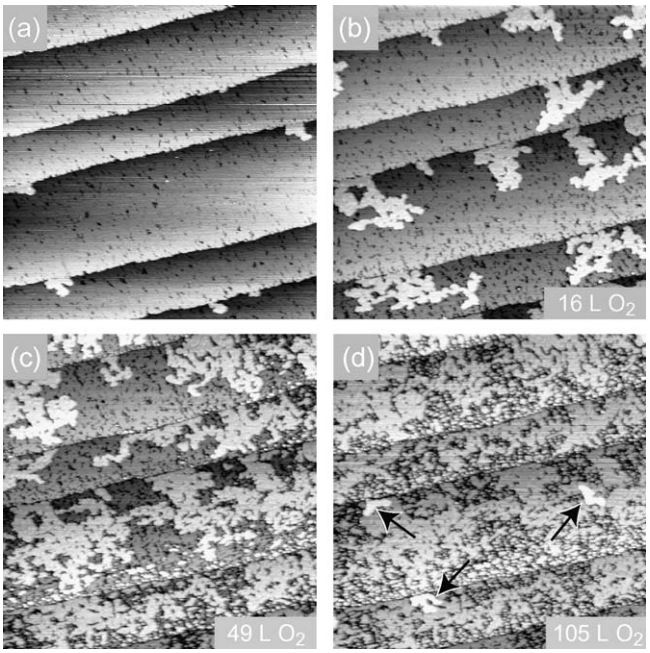

Fig. 1. The STM image of an almost closed monolayer of Ag on W(1 1 0) is shown in (a). Subsequent exposure to O_2 at room temperature results in images (b) to (d). Between 5 L O_2 and 49 L O_2 the rearrangement of Ag in the second layer leads to nucleation of islands with dendritic shape. At exposures above 90 L O_2 growth in a third layer starts; the black arrows in (d) indicate the corresponding sites. Data for sample bias, tunnel current and length scale are 39 mV, 0.30 nA, 3500×3500 Å^2.

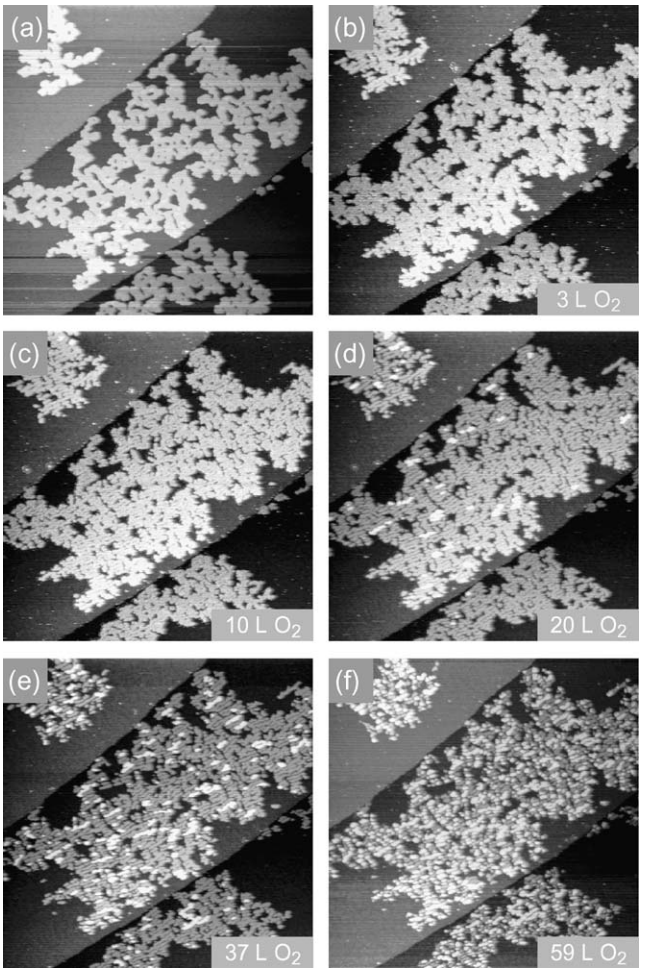

Fig. 2. STM images show the oxygen-induced rearrangement of submonolayer Ag islands on W(1 1 0). The experiment started at a nominal coverage of 0.3 ML, see (a). Subsequent exposure to O_2 at room temperature results in data (b) to (f). Experimental parameters are 29 mV, 0.30 nA, 2800×2800 Å^2.