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Combined STM, LEED and DFT study of Ag(1 0 0) exposed to oxygen near atmospheric pressures

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Abstract

We have investigated the interaction of molecular oxygen with the Ag(1 0 0) 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 O_2, the individual oxygen atoms are randomly distributed on the surface. When the sample is exposed to 10 mbar O_2 at room temperature, small, $p(2\times2)$ reconstructed patches are formed on the surface. After oxidation at ≈470 K and 10 mbar O_2 pressure the surface undergoes a $c(4\times6)$ reconstruction coexisting with a (6×6) superstructure. By ab initio thermodynamic calculations it is shown that the $c(4\times6)$ reconstruction is an oxygen adsorption induced superstructure which is thermodynamically stable for an intermediate range of oxygen chemical potential.

Keywords: Oxidation; Surface relaxation and reconstruction; Scanning tunneling microscopy; Low energy electron diffraction; Density functional calculations

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 O_2, two other molecular oxygen species were identified [26]. One of them is the superoxo-like molecular species (O_2^-) which was observed during non-thermal O_2^+ adsorption on Ag(1 1 1) [26]. The other molecular oxygen species is peroxo-like (O_2^{2-}). Its appearance was evidenced experimentally on Ag(1 1 0) [27] and was explained by electron transfer from the metal to the O_2 antibonding π^* orbital of the O_2 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(1 1 0) 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 O^{2-} charged state [28].

Recently it has been shown that silver oxide clusters [29] and silver oxide thin films [30] could be potential

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candidates for optical memories. The conversion from n to p-type semiconductor with varying oxygen stoichiometry in thin Ag_2O 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 O_2 at high temperature and atmospheric pressure. Rocca et al. [6] used a supersonic molecular O_2 beam in order to obtain a higher sticking coefficient (S=0.7). Bare et al. have used NO_2 as a source of atomic oxygen [15].

On the Ag(1 0 0) surface the following detailed reaction scheme of O_2 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 O_2 at low temperature ($T \leqslant 120$ K) leads to molecular absorption with O_2 molecules in hollow sites, forming a $c(2\times4)$ structure [6,14]. Further heating leads to the dissociation of oxygen molecules (already at ≈130 K), and at around 190 K a $c(2\times2)$ LEED pattern is reported to appear [6]. Based on XPD a missing-row $p(2\sqrt{2}\times\sqrt{2})R45^\circ$ structure with the oxygen atoms forming a $c(2\times2)$ 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 $p(2\sqrt{2}\times\sqrt{2})R45^\circ$ structure is thermodynamically more stable than the $c(2\times2)$ adatom structure [22]. It is reported that by heating this structure above 320 K the reconstruction is lifted and only a $p(1\times1)$ 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(1 0 0) surfaces. It will be shown that O/Ag(1 0 0) 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(1 0 0) 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 $c(4\times6)$ and $p(6\times6)$ 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 substraction of a background image. The Ag(1 0 0) 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

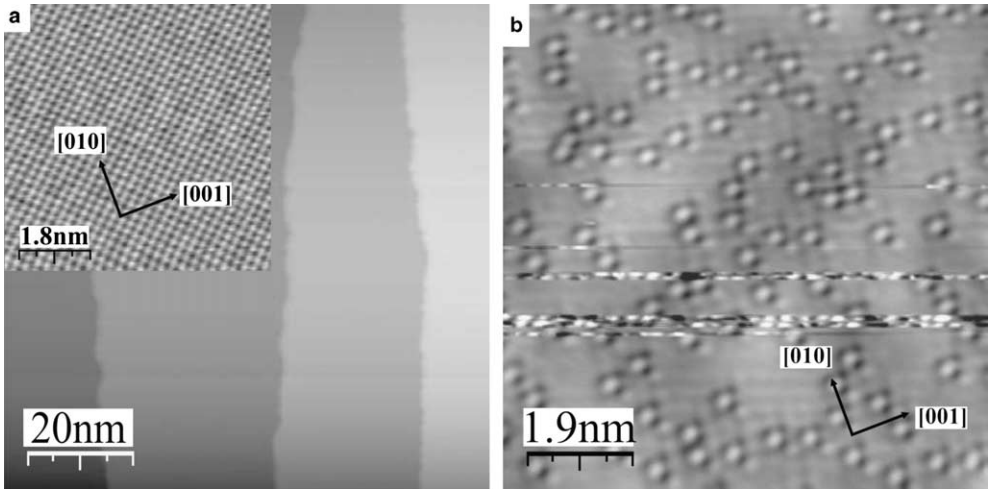

Fig. 1. (a) STM constant current topograph (100×100 nm^2, $V_{sample} = -0.9$ V, $I_t = 1$ nA) of the clean Ag (1 0 0) surface. Inset: atomically resolved image (9×9 nm^2, −0.1 V, 2 nA); (b) STM image (taken in UHV at 80 K) after exposure to 6000 L O_2 at 130 K (−0.2 V, 1 nA).