Ag on Cu(110)-(2×1)O: Desorption of Oxygen versus Diffusion of Ag†

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The adsorption of silver on the Cu(110)-(2×1)O surface was studied by Auger electron spectroscopy and scanning tunneling microscopy. For deposition at room temperature the CuO layer is overgrown by a highly stressed and therefore rough silver layer. If the sample is annealed, the oxygen will desorb via formation of temporary Ag-O compounds. At the same time silver will diffuse into the copper bulk. The situation is quite different if silver is deposited at 660 K: For the deposition of up to one monolayer of silver no significant desorption of oxygen is observed by Auger electron spectroscopy. It is found that domains of a Ag rich Ag/Cu alloy and the bare CuO phase are spatially separated. Only upon further Ag deposition, oxygen desorption takes place.

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I. INTRODUCTION

The adsorption of silver on clean Cu(110) surfaces is well studied in the literature: For silver coverages well below one monolayer (ML), Kizilkaya et al. [1] have found by means of scanning tunneling microscopy (STM) that silver and copper form a surface alloy. If the Ag coverage is only slightly increased a de-alloying takes place giving rise to a quasi-hexagonal wetting layer (see Ref. [2]). Upon further deposition, Ag nanowires are formed once the Ag coverage exceeds two monolayer [3].

Even better known are the processes involved in the formation of the Cu(110)-(2×1)O reconstruction: Oxygen adsorbs dissociatively on the Cu(110) surface and the oxygen atoms combine with mobile Cu adatoms. Due to strong attractive interactions these CuO compounds agglomerate to form Cu-O chains oriented along the [001] direction [4, 5]. Upon further oxygen chemisorption these Cu-O chains assemble into CuO islands with a (2×1)O adlayer. At temperatures above 600 K, these islands arrange themselves in regular stripes oriented along the [001] direction and separated by bare Cu areas, forming a one-dimensional periodic grating [6], the Cu-CuO stripe phase. At high oxygen coverage, the CuO islands coalesce and a homogeneous (2×1)O reconstructed surface is formed [7–9].

We used such oxygen pre-covered Cu(110) surfaces to study the adsorption of silver at room temperature and 660 K, respectively. Kürprick et al. have studied the influence of oxygen on the diffusion of silver deposited on the Cu(110) surface. Depending on the sample temperature they observed the desorption of oxygen and a drastically decreased mobility of the silver on the oxygen pre-covered surface [10]. Quite recently, we have shown, that it is possible to prepare various surface patterns by co-adsorbing oxygen and silver at 660 K [11]. These self-organized patterns originate from the spatial separation between a Ag/Cu alloy and the CuO phase. This kind of pre-patterned surface can be used as template to tailor the growth of silver nanowires [12].

II. EXPERIMENTAL

The experiments were carried out in an ultrahigh vacuum (UHV) system with a base pressure of about 5×10⁻¹⁰ mbar. As substrate we used a polished Cu(110) surface (Mateck) with a nominal miscut below 0.1°. The sample surface was prepared by argon ion sputtering (900 eV) and subsequent annealing at 900 K for 5 min. The temperature was measured via a thermocouple attached to the manipulator in the vicinity of the sample transfer plate on which the crystal was mounted. The surface was assumed to be clean if a sharp low energy electron diffraction (LEED) pattern was visible and no impurities could be detected by Auger electron spectroscopy (AES). Additionally, the vacuum chamber is equipped with an STM system (Omicron VTXA) and a photoelectron emission microscope (Focus IS-PEEM). All STM images shown in this paper were acquired at room temperature. They represent raw data to which only a background subtraction was applied by using the WSxM software [13].

For the LEED and Auger analysis a four grid LEED optics with a LaB₆ filament (Omicron SPECTALEED) was used. For the quantitative AES analysis the emission current was kept constant within ±1% as monitored by the AES controller. The signal recorded was the second derivative of the electron current, corresponding to dN/dE where N is the number of Auger electrons with a given energy E. The flux of the silver evaporator (Focus EFM 3) was calibrated by a set of Auger experiments shown in Fig. 1. While the Ag flux, measured by the internal ion collector, was kept constant the evaporation time was varied. During silver deposition the sample was at room temperature (RT). The peak to peak amplitude of the Auger signals are plotted in Fig. 1 as a function of the evaporation time. Initially, the Ag Auger peak (359 eV according to Ref. [14]) increases linearly whereas the copper signal

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FIG. 1: Evolution of the Auger signal ($dN/dE$) for copper (922 eV, the peak assignment was chosen according to Ref. [14]) and silver (359 eV) as a function of the Ag evaporation time. The change in the slope of the silver signal (marked by the green circle) was used to calibrate the thickness of the film.

(922 eV) decreases. At about 9 min of Ag evaporation, the slope of both curves changes abruptly to almost zero. This kink was interpreted by Taylor et al. as completion of the first layer [3]. Beyond a coverage of one monolayer silver forms 3D nano-wires on the Cu(110) surface [12, 15, 16]. As the height of the wires increases much faster than their total contact area to the substrate surface, the additional Auger signal arising from these wires is very small compared to the completed monolayer. Yet, the slope of the second part of the curve in Fig. 1 is much smaller than the one for room temperature reported by Taylor et al. [3]. Due to the electron impact during the AES measurement, the temperature of our sample is locally increased by about 50 K (according to the reading of the thermocouple – the actual temperature increase at the surface will be even higher) as we do not have a cooling option on the manipulator. Therefore, during AES observation the mobility is increased leading to a higher diffusion of the silver into the copper bulk (see Ref. [17]) or the formation of larger, mainly higher nanowires (see Ref. [16]). Both effects will lower the additional Ag signal stemming from the wires.

III. RESULTS AND DISCUSSION

A. Oxygen on clean Cu(110)

By exposing the Cu(110) surface at 660 K to 40 L of molecular oxygen, a full, nearly defect free (2×1)O reconstruction is obtained. In this case the nominal oxygen coverage is $\theta = 0.5$. The actual oxygen coverage might be less due to defects like steps on the surface. As a side-effect of the oxygen chemisorption, the terraces are extended to lateral dimensions of a few hundred nm and are separated by step bunches [18, 19]. We studied the thermal stability of such a reconstructed surface by AES. Fig. 2 shows a corresponding set of AES spectra. The signature of the oxygen signal is clearly seen around 507 eV in agreement with the literature [14]. The very same surface was heated to 660 K for 35 min. This time was chosen to be equal to the deposition time for 3.4 monolayer of silver. Due to the annealing, the signal amplitude, defined as the difference between the central minimum and the maximum of the shoulder on the low energy side of the dip, decreases by a factor of roughly 2. Further heating for another 140 min (total of 175 min) leads to an additional attenuation by a factor of 2.

Although Fu et al. [20] do not report any oxygen desorption from the Cu(110) surface for temperatures below 1000 K, our results do not contradict these former thermal desorption data: A thermal desorption experiment usually runs with a temperature ramp of 1 K/s, in the particular case even 10 K/s. In this case, the time the sample was at temperatures above 660 K was only 34 s. Our shortest annealing time (35 min) is more than 60 times longer. So even if the desorption rate at 660 K might be very low, a sizeable fraction of the oxygen monolayer will desorb upon the prolonged annealing. Moreover residual hydrogen in the gas phase or very small amounts of residual silver at the copper surface originating from former experiments might increase the desorption rate of oxygen at 660 K as will be discussed later in the paper. Yet, a survey Auger electron spectrum of the surface did not reveal any other species besides copper and oxygen in the surface near region.

B. Silver deposition at room temperature

On such a fully (2×1)O reconstructed Cu(110) surface, several monolayer of silver were deposited at room temperature. The adsorption of additional silver leads to a rough morphology as depicted in the STM image in Fig. 3. From a Fourier analysis (see inset) the characteristic periodicity in the [001]-direction – parallel to the troughs
FIG. 3: STM image (500×500 nm²) of a 3.4 ML thick Ag film on top of a fully reconstructed Cu(110)-(2×1)O surface. The two arrows mark a step bunch of the Cu substrate. The image was recorded with a setpoint of 1 nA at a bias voltage of -0.6 V applied to the sample. The inset shows a Fourier transformation of the STM image.

TABLE I: Parameters used in Eq. (1) to calculate the inelastic mean free path of the Auger electrons. The data are taken from Ref. [21].

<table>
<thead>
<tr>
<th>k₁</th>
<th>P₁</th>
<th>k₂</th>
<th>P₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>706.2</td>
<td>-1.294</td>
<td>0.06816</td>
<td>0.7803</td>
</tr>
</tbody>
</table>

formed by the oxygen reconstruction – is 6 nm to 7 nm. In the orthogonal [110] direction, the Fourier signal is less intense and indicates a chain dimension of about 15 nm. Since on the clean Cu(110) surface, silver grows in a highly stressed manner [2], it is not surprising that the same happens on the commensurate superstructure given by the (2×1)O reconstruction. Therefore, we attribute the ripple structure in Fig. 3 to be a result of the large stress within the silver layer on top of the CuO-surface. If the surface is only partly (2×1)O reconstructed, i.e., in the presence of CuO stripes on the bare copper surface, the stripe pattern is partly dissolved into smaller Cu-O compounds upon silver deposition as discussed in Ref. [11]. Nevertheless, the data suggest that the Cu-O compounds are stable against silver deposition.

The STM measurements suggest, that the silver resides on top of the CuO-surface. This assumption is corroborated by the AES data shown in Fig. 4. After the deposition of 3.4 ML of Ag, the amplitude of the oxygen peak is clearly reduced compared to the one obtained from the pristine Cu(110)-(2×1)O surface. The ratio of the respective oxygen signals is 0.5. The attenuation factor agrees well with the one predicted on the basis of the inelastic mean free path of the Auger electrons with a given energy \( E = 510 \text{ eV} \):

\[
\lambda = k_1 E^{P_1} + k_2 E^{P_2} = 0.906 \text{ nm},
\]

where \( \phi = 102^\circ \) is the acceptance angle of our LEED optics. The attenuation \( a \) of the oxygen Auger signal for electrons passing through \( n = 3.4 \) layers of thickness \( d = 0.144 \text{ nm} \) (equal to the spacing of (110) planes in fcc Ag) is given by

\[
a = 1 - \exp \left( -\frac{n \cdot d}{\Delta} \right) = 0.50,
\]

which is excellent agreement with the experimental value.

Following the theory of Jablonski [22], the mean escape depth \( \Delta \) is given by

\[
\Delta = \lambda \cdot \sin \phi = 0.886 \text{ nm},
\]

where \( \phi = 102^\circ \) is the acceptance angle of our LEED optics. The attenuation \( a \) of the oxygen Auger signal for electrons passing through \( n = 3.4 \) layers of thickness \( d = 0.144 \text{ nm} \) (equal to the spacing of (110) planes in fcc Ag) is given by

\[
a = 1 - \exp \left( -\frac{n \cdot d}{\Delta} \right) = 0.50,
\]

which is excellent agreement with the experimental value.
above 500 K [17]. This suggests that there might be a diffusion of the Ag atoms through the CuO layer into the Cu bulk which should eventually slow down the oxygen desorption.

Fig. 5 (a)–(c) summarizes the findings so far. Our model also holds if the coverage of oxygen is less than \( \theta = 0.5 \) and a Cu-CuO-stripe phase is formed. Indeed, if more than one monolayer of silver is deposited on such a surface at room temperature and the sample is subsequently heated, no oxygen is detected by AES, suggesting that, again, the desorption of the oxygen is promoted by the presence of silver. After the annealing also the amplitude of the AES peak of the silver is reduced, which is consistent with the diffusion of Ag into the Cu bulk. The finite desorption of the oxygen from the bare Cu(110) surface as observed in Fig. 2, could therefore be explained by small amounts of silver accumulated in the copper crystal during earlier experiments.

C. Silver deposition at 660 K

A completely different situation is encountered if silver is deposited at 660 K rather than at room temperature. As an example, Fig. 6 shows an STM image after deposition of 0.4 ML of silver at 660 K on the Cu-CuO stripe phase, prepared by exposing the Cu(110) surface to 0.3 L of molecular oxygen at 660 K. As before, upon oxygen adsorption and the formation of the Cu-CuO stripe phase, the terraces are extended to more than 500 nm along the [001] direction and are separated by high step bunches[18, 19]. However, after Ag deposition at 660 K, large darker areas (ponds) can be seen in the STM image. The total area of these ponds scales with the oxygen pre-adsorbed on the copper surface. STM images with atomic resolution acquired on the ponds reveal a (2\times1) structure, confirming that these are CuO islands. The CuO ponds are enclosed by brighter areas which we attribute to Ag rich areas, most likely a Ag/Cu alloy[1]. The (2\times1)O reconstructed areas appear flat and homogeneous, indicating that essentially no silver is incorporated within or right below the CuO islands.

We thus suggest that a phase separation between CuO and a Ag/Cu alloy takes place if silver is deposited at 660 K: The former CuO stripes of the stripe phase coalesce into large CuO islands which are surrounded by a Ag/Cu alloy. The STM image in Fig. 6 further reveals the formation of fringes at the step bunches upon silver deposition at 660 K, indicating that some amount of silver is also bound to the step bunches.

The Auger electron spectra shown in Fig. 7 confirm
that some oxygen always remains on the surface even after deposition of several monolayer of silver at 660 K. Surprisingly, the oxygen signal of a fully oxygen covered Cu(110)-(2\times1)O surface is almost not affected by the deposition of a complete monolayer of silver. Only if more than one monolayer of silver is deposited onto this surface at 660 K, a decrease of the oxygen signal can be detected.

As long as the total coverage of oxygen and silver on the surface is less than 1 ML, both can agglomerate in separate regions, yielding large, Ag free CuO domains surrounded by a Ag/Cu alloy (Fig. 6). As a result, Ag atoms and CuO compounds can only react at the sparse domain boundaries and the probability for Ag promoted desorption of oxygen as described above is only very small. This would also imply that Ag atoms landing on top of a CuO island can easily diffuse (at 660 K) to its border onto the oxygen free Ag/Cu areas or to a nearby step bunch, instead of reacting away the oxygen. Even if the surface is nominally completely oxygen covered, as in the case of Fig. 7, the step bunches remain free of oxygen [19]. Therefore, the step bunches always provide space for silver to aggregate away from the CuO areas. Moreover, the diffusion of silver into the Cu bulk at the step bunches will further deplete the effective surface coverage of silver, such that quite a large amount of silver (\( \geq 1 \) ML according to Fig. 7) can be accommodated before the silver actually starts to react away the oxygen at the boundaries of the CuO islands.

IV. SUMMARY AND CONCLUSION

For the deposition of silver on the Cu(110) surface pre-exposed to oxygen two processes have to be taken into account: (i) the desorption of oxygen promoted by the presence of silver and (ii) the diffusion of silver into the copper bulk. Upon adsorption of several monolayer of silver on the oxygen pre-covered surface at room temperature, oxygen remains at the Cu-Ag interface. Annealing this sample to 660 K leads to an enhanced reaction between Ag and Cu-O compounds. As a result, the desorption of oxygen is promoted via the formation of temporary Ag-O compounds whereas the silver also diffuses into the copper bulk.

In contrast, the deposition of silver at elevated temperatures (660 K), is not accompanied with any significant desorption of oxygen if the surface is not saturated by oxygen and silver, i.e., as long as the CuO and the Ag/Cu alloy phase have enough space to form spatially separated domains. In the later case, the aggregation of silver at step bunches and the diffusion of the Ag into the copper bulk further prevent the formation of temporary Ag-O compounds.

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