The influence of oxygen on the growth of silver on Cu(110)

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ABSTRACT

The influence of the $(2 \times 1)O$ reconstruction on the growth of Ag on a Cu(110) surface was studied by scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES). On the bare Cu(110) surface, Stranski–Krastanov growth of silver is observed at sample temperatures between 277 K and 500 K: The formation of a Ag wetting layer is followed by the growth of three-dimensional Ag wires. In contrast, on the oxygen-precovered Cu(110) surface, the growth of silver depends heavily on the substrate temperature. Upon Ag deposition at room temperature, a homogeneous, polycrystalline Ag layer is observed, whereas at 500 K, three-dimensional wires separated by $(2 \times 1)O$ reconstructed areas are formed. The behavior of a deposited Ag layer upon annealing is also influenced greatly by the presence of oxygen. On the bare surface, annealing does not change the Ag wetting layer and gives rise to Ostwald ripening of the Ag wires. On the oxygen-precovered surface, however, the initial polycrystalline Ag layer first transforms into Ag wires at around 500 K. Above this temperature, the depletion of the $(2 \times 1)O$ reconstructed areas due to Ag-induced O desorption is balanced by the formation of a Ag wetting layer. On both, the bare and the oxygen-precovered Cu(110) surface, the deposited silver diffuses into the Cu bulk at temperatures above 700 K.

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1. Introduction

Recently, the combination of oxygen chemisorption and silver deposition on a Cu(110) surface has proven its potential for creating well defined nanostructures. In STM and photoelectron emission microscopy (PEEM) studies, we showed how phase separation between CuO and Ag/Cu alloy areas leads to the formation of tunable nanopatterns which in turn can be used as templates for growing three-dimensional Ag nanowires [1–3].

Both oxygen chemisorption and silver deposition on the Cu(110) surface have been studied separately in great detail in the last decades. It is therefore well known that molecular oxygen chemisorbs dissociatively from the gas phase onto the Cu(110) surface. The oxygen atoms combine with mobile Cu adatoms to form Cu–O compounds. Upon further oxygen chemisorption, these compounds agglomerate into $(2 \times 1)O$ reconstructed islands until, finally, a complete (2×1) superstructure is formed [4–9]. If silver is deposited on such a surface at room temperature, the $(2 \times 1)O$ reconstruction is overgrown by a homogeneous, polycrystalline Ag layer [2,3,10].

The growth of silver on the bare Cu(110) surface, on the other hand, is known to be of the Stranski–Krastanov type, i.e., the silver initially forms a complete monatomic wetting layer on which three-dimensional wires grow upon further Ag deposition [11–15].

In this paper, we want to study in more detail the interplay between copper, silver, and oxygen on the surface. Indeed, previous studies have shown that not only processes directly on the surface are important but also diffusion of silver into the Cu bulk and oxygen desorption [2,10].

2. Experimental

The STM and AES measurements presented in this paper were performed in two different ultrahigh vacuum (UHV) systems with base pressures around 5×10^{-10} mbar. Both vacuum chambers are equipped with an argon ion gun for sample preparation and an electron beam evaporator for Ag deposition. The STM chamber is additionally equipped with an Omicron VT STM XA, a Focus IS-PEEM and a four-grid LEED/AES system to check sample cleanliness. The AES chamber contains a cylindrical mirror analyzer AES system (Omicron), which produced the data presented below.

We used as substrate a disk-shaped single-crystal of copper (10 mm diameter, 2 mm thickness) with a polished (110) surface (nominal miscut below 0.1°). The sample temperature was measured with a thermocouple attached to the manipulator close to the sample. As the sample was mounted differently in the STM and AES experiments, the temperature readings may differ slightly.

In the course of our work, the Cu crystal was used repeatedly in Ag deposition experiments, resulting in the accumulation of a certain amount of silver in the bulk of the crystal. Fig. 1 shows the AES signal obtained directly after sputtering the single crystal at room temperature and after subsequent annealing steps. At low temperatures the Ag concentration at the surface remained below the detection limit

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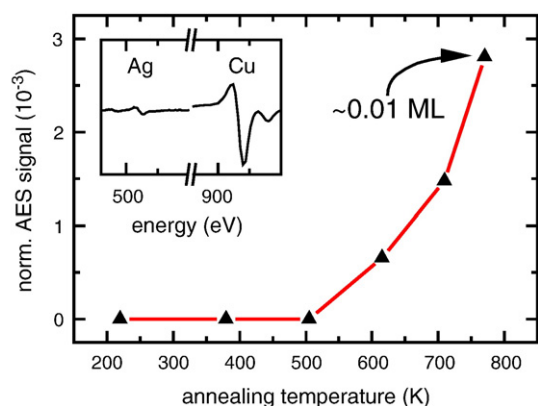E-mail address: peter.zeppenfeld@jku.at (P. Zeppenfeld).

Fig. 1. (color online) AES peak-to-peak amplitude of silver (359 eV) recorded from the (110) surface of a Ag-doped Cu single-crystal after sputtering at room temperature and subsequent annealing steps. The AES intensity was normalized to the signal of a thick Ag film. The value of $\approx 3 \cdot 10^{-3}$ thus corresponds to $\approx 1\%$ of a Ag monolayer. The corresponding AES raw data for this particular data point are shown in the inset.

of the AES system. Above 500 K, however, the silver segregated to the surface. Wang et al. used AES to study the equilibrium concentration of silver on the Cu(110) surface [16]. Although these authors reported an appreciable Ag concentration at temperatures below 500 K, their data do not contradict our findings. Whereas Wang et al. tempered their sample for very long times at a given annealing temperature T_{an} to achieve equilibrium, we heated our sample with a linear temperature ramp of 1 K/s. As soon as the desired temperature T_{an} was reached, the sample was cooled down immediately. In our case, thermal equilibrium was therefore never reached at the temperature T_{an}, and the Ag concentration at the surface was thus much lower than that found by Wang and coauthors. In order to minimize the influence of residual silver on the surface in the experiments described below, the surface was prepared by argon ion sputtering followed by a short period of annealing at 900 K. The silver, which had segregated to the surface during the high temperature annealing step, was then sputtered away. Finally the surface was annealed at a temperature of 500 K, which is low enough to prevent further segregation of silver to the surface.

The evaporators used for Ag deposition were calibrated using AES. To this end, the AES amplitude of Ag was measured as a function of evaporation time. The sharp kink observed in this curve (see Fig. 2) defines the completion of the Ag monolayer [12].
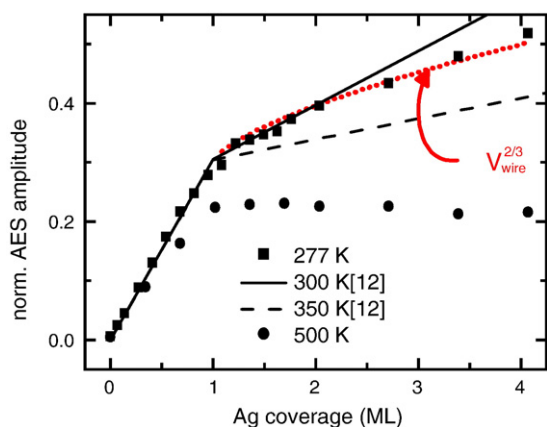
3. Results and discussion

3.1. Ag growth

In Fig. 2, we plotted the peak-to-peak amplitude of the AES signal as a function of the coverage. The steep initial slope of the Ag signal corresponds to the formation of a monatomic Ag wetting layer. After completion of this layer, indicated by the kink in the evolution of the peak-to-peak amplitude, in excess deposited silver forms three-dimensional islands which are elongated in the [1$\bar{1}$0] direction.

Fig. 3(a) and (b) show STM images of such "wires" grown after deposition of 3.7 monolayer (ML) Ag at room temperature and after subsequent annealing at 500 K, respectively. Clearly, annealing leads to fewer but higher wires. The same is true if Ag is deposited directly at higher temperatures. The great height of the wires results in effective self-shadowing and, therefore, in a slower increase in the Ag AES signal [12]. At a deposition temperature of 500 K (circles in Fig. 2), the area covered with wires is so small and their height is so great, that the AES signal is almost entirely due to the wetting layer. The smaller initial slope of the 500 K curve may either be an indication of silver diffusing into the Cu bulk or of an early formation of three-dimensional Ag wires. In Fig. 2, linear fits to the data of similar experiments carried out at 300 K and 350 K by Taylor et al. [12] are indicated by solid and dashed lines, respectively. For high coverage, Taylor et al. also found a discrepancy between the linear fit and the experimental data, because the projected area of the wires scales as $V_{wire}^{2/3}$, where V_{wire} is the volume of silver deposited after completion of the wetting layer. Therefore, we added a fit that is proportional to $V_{wire}^{2/3}$ (red dotted line in Fig. 2). Since the linear fit to the 300 K data [12] almost matches the signal we measured at 277 K (squares in Fig. 2), we assume that the difference in sample temperature between the two laboratories is actually smaller. Besides the exact location of the thermocouple, another possible source of errors in the temperature reading might be a temperature gradient across the sample induced by the electron beam of the Auger electron spectrometer itself.

As mentioned above, Ag deposition at 277 K on the oxygen-precovered Cu(110) surface leads to a completely different type of growth. The smooth increase in the AES amplitude (squares in Fig. 4 (a)) represents the growth of a rough but homogeneous layer of polycrystalline Ag. Kürpick et al. interpreted their photoelectron spectroscopy data in the same way [10]. An STM image of the surface after deposition of 3.7 ML of Ag at 277 K on the Cu(110)–(2×1)O surface is shown in Fig. 4(c). Ag deposition at 500 K, however, leads again to the formation of wires and, therefore, a smaller AES amplitude (circles in Fig. 4(a)). As can be seen in the STM image in Fig. 4(d), these wires are very similar to those grown on bare Cu(110), and we assume that they grow directly on the Cu interface. This assumption is supported by recent studies which showed that – as soon as the surface mobility is sufficiently high – silver and oxygen tend to form laterally separated phases on the Cu(110) surface [1–3]. Therefore, in order to create space for the Ag wires, a small amount
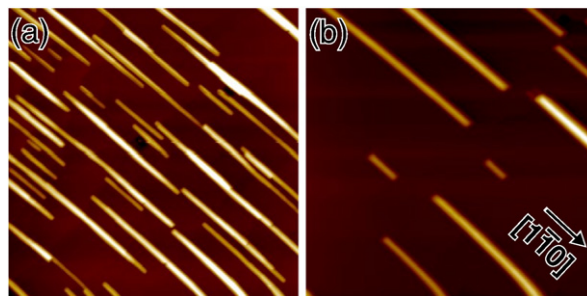

Fig. 2. (color online) AES amplitudes of silver (359 eV) during Ag deposition on the bare Cu(110) surface at 277 K (squares) and 500 K (circles). Similar measurements performed by Taylor et al. [12] at 300 K and 350 K are represented by the dotted and dashed lines, respectively. The red dotted line represents a polynomial fit taking only the projected area of the Ag wires into account. The AES intensities were normalized such that an AES amplitude of 1 corresponds to the signal amplitude expected from a thick Ag film.

Fig. 3. (color online) (a) $1 \times 1\ \mu m^2$ STM image of the Cu(110) surface after deposition of 3.7 ML of silver at room temperature and (b) after subsequent annealing with a linear temperature ramp up to 500 K.