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Dynamics of 2D adislands formed by sulfur adsorption on an O/Cu(110) nanotemplate: An STM study

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ABSTRACT

We report on the stability of large sulfur islands, formed by exposing the nanostructured O/Cu(110) surface to H_2S. We have found that these islands, composed of several hundreds of atoms, show a dynamic behavior at room temperature and undergo both Smoluchowski and Ostwald ripening. An additional decay mechanism has been observed at sub-saturation sulfur coverages. The island decay can be described by a classical power law. However, oscillatory deviations from the model have been observed and possible reasons for their occurrence are discussed. At saturation sulfur coverage, the islands are still mobile and undergo ripening, but no decay is observed. In these conditions, a new nanostructured S/Cu(110) surface is formed.

1. Introduction

The investigation of the dynamics of large clusters composed of hundreds of atoms on metal surfaces is important, because their diffusivity impacts the stability of nanostructures and plays a role in various domains, such as crystal and thin film growth, catalysis, sintering, or corrosion. With the invention of FIM and STM, the study of dynamic processes on surfaces at the atomic scale became possible, and hence many experimental studies have been dedicated to the mechanisms of atomic movement on surfaces [1, 2]. Large clusters were believed to be immobile, until the 1980s, when Fink, using the FIM technique, demonstrated the diffusivity of a Pd cluster on W(110) [3]. Since then, various studies investigated the diffusion of large clusters on fcc(100) [4–9] and fcc(111) [10–14] surfaces. Mechanisms such as evaporation–condensation, terrace limited diffusion, and diffusion *via* mass transport along periphery, have been observed and are fairly well understood. On the other hand, the diffusion of large clusters on anisotropic surfaces, such as the channeled fcc(110) surface, is more complex and the studies on this subject are not exhaustive [15].

The self-organized nanostructure, O/Cu(110), discovered by Kern in 1991 [16], is a surface with alternating stripes of oxidized and clean copper. Recently, we have presented a new method for preparation of this surface, consisting in co-adsorption of low amounts of sulfur, which allows, in an easy and controllable way, to enlarge the periodicity of the nanostructure, while keeping the oxygen coverage unchanged [17]. The sulfidation of an oxygen-saturated O/Cu(110) surface initiates at defect sites and step edges [18]. In a separate publication [19], we describe the reaction mechanism of the nanostructured surface, which has been found to depend on the width of the oxidized stripes. The sulfidation of a classically prepared nanostructure with narrow stripes proceeds exclusively *via* Cu–O chain abstraction. The sulfidation mechanism of a nanostructure with CuO stripes wider than ≈10 nm is the combination of the chain abstraction and the formation of sulfur islands on oxidized stripes. In the present paper, we analyze the dynamics of nanostructured surfaces with wide oxidized stripes (>10 nm) exposed to H_2S until all of the oxygen has been removed by reaction and the resulting Cu(1×1) adlayer has been covered by islands of sulfur in the c(2×2) configuration. We report on the stability of the 2D adislands (S-c(2×2) on Cu(1×1) adlayer), observed both for saturation and sub-saturation S coverages. The surface diffusion mechanism has been studied under UHV conditions, by recording consecutive STM images over a long period of time following the exposure of the O/Cu(110) nanostructure to H_2S.

2. Experimental

The experiments were performed in an UHV setup (base pressure of 10^{-10} mbar) equipped with STM and AES facilities, both from Omicron Nanotechnology. The Cu(110) sample from *Surface*

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Preparation Lab [20] has been prepared by cycles of Ar^+ sputtering and annealing at 873 K. The O/Cu(110) nanostructures were prepared following the method described in Ref. [17]. The surface has been exposed for a few minutes to O_2 at a pressure of 10^{-8} mbar and H_2S at 10^{-9} mbar at room temperature and subsequently annealed at 673 K. The amounts of oxygen and sulfur have been controlled by AES. After the surface has cooled down to room temperature, the periodicity of the formed structure was determined locally by STM. In the present study, all periodicities were between 30 and 100 nanometers, with approximately the same width of oxidized and bare copper stripes. The nanostructured surface was subsequently exposed to H_2S, at pressures around 10^{-9} mbar, during STM measurement. The exposure conditions have been chosen to favor the S island formation mechanism over the Cu–O chain detachment, as explained in Ref. [19]. The sulfidation was stopped directly after all of the oxygen has been removed for the study of the island diffusion at sub-saturation sulfur coverages. For the study in the case of saturation, the surface has been exposed to H_2S until the sulfur islands were surrounded by both the c(2×2) and p(5×2) sulfur phases. The presented STM images are raw images with background plane subtraction and drift correction. They have been treated with the WSxM software [21].

3. Results and discussion

Submonolayer coverage of oxygen on Cu(110) annealed at 640 K self-organizes into a periodic pattern of alternating clean copper stripes and “added-row” Cu–O chains elastically relaxed into O-(2×1) stripes. Upon exposure to H_2S, the oxygen is removed from the reconstructed O-(2×1) phase, resulting in unstable low-coordinated Cu rows. The added-rows thus relax into islands of Cu(1×1), onto which sulfur adsorbs in the c(2×2) configuration, known for adsorption of S on Cu(110) [22–25]. These islands are one copper monolayer higher (128 pm) than the surrounding surface and are therefore imaged with a very good contrast in STM. For detailed description of the island formation mechanism consult Ref. [19]. During observation of the subsequent behavior of the S islands in UHV, after all the oxygen has been removed, two different mechanisms of surface diffusion have been identified, depending on the sulfur coverage of the surface. These two types of surface diffusion mechanisms are island ripening and island decay. They are separately discussed hereafter.

3.1. Island ripening

As portrayed in Fig. 1, the sulfidation of a nanostructured O/Cu(110) surface leads to formation of S-c(2×2) islands on the oxidized stripes. Sulfur adsorbs on Cu(1×1) added chains, which are formed after the oxygen is removed from the O-(2×1) phase. Due to the rearrangement of the Cu added chains from (2×1) to (1×1), the sulfur islands cover only half the area, which has previously been covered by the oxidized stripes. This leads to formation of many small separated sulfur islands, as observed in Fig. 1b. This kind of surface is only obtained when the initial surface is pre-nanostructured and the oxidized stripes are wide enough for the island formation mechanism to occur, as discussed in Ref. [19].

As seen in Fig. 1c, the islands eventually coalesce and form elongated structures in the [001] direction. Due to the limited diffusion length, only neighboring islands coalesce during this phase. Although there is probably no preferred diffusion orientation at the surface, because of the pre-nanostructuration, sulfur islands are not evenly distributed and the coalescence thus proceed mainly in the [001] direction of the former CuO stripes, leading to the formation of large elongated islands.

The [001] direction is parallel to the stripes of a nanostructured surface, however it is not the direction with the lowest diffusion barrier for single adatoms. The (110) face of copper has a channeled structure and the barrier for diffusion is known to be the lowest along the $[1\bar{1}0]$ direction, in-channel with the copper close-packed rows [18, 26]. Mechanisms leading to diffusion across the channel are either the cross-channel hopping or the far more favorable exchange mechanism. The energy barrier of the cross-channel hopping mechanism has been found, as expected, to be high, with values around 1.07 eV [27]. During the atomic exchange mechanism, an adatom takes the place of a lattice atom at the side of the channel and it is the displaced lattice atom that continues the diffusion [28]. Its energy barrier is only slightly higher than for the in-channel hopping. An experimental observation of a cross-channel diffusion has been reported for the first time for Pt and Ir adatoms on Pt(110) [29] and has since been observed also for other fcc metals. Evidently, the diffusion of clusters and islands composed of hundreds of adatoms of different chemical species is guided by different processes than simple self-diffusion of a single adatom, for which the diffusion is expected only in one direction on an anisotropic surface. The diffusion of adatom islands on a channeled surface across the channels has already been observed by Linderoth et al. [30]. They studied the diffusion of Pt islands on the missing-row reconstructed Pt(110)-(1×2) surface. At low coverages, the Pt adatoms move only along one direction, however at higher coverages, the motion becomes 2D. The authors propose two kinds of mechanisms for mass transport across the missing-row troughs, which both result from the interaction between neighboring islands. Therefore we infer that the here observed coalescence along the [001] direction is also guided by the attraction between neighboring S islands.

The S-c(2×2) islands, formed during sulfidation of the nanostructured O/Cu(110) surface, are of irregular oval shapes, as shown in Fig. 2. In contrary to the S islands in Fig. 1b, which have been formed on oxidized stripes with a width of ≈20 nm, the islands in this case are not aligned in one row along the [001] direction. The larger width of the initial oxidized stripes (≈30 nm) allowed a formation of islands next to each other and also led to a wider island size distribution.

Compared to the case of narrower CuO stripes, the coalescence of islands may this time proceed in both [001] and $[1\bar{1}0]$ directions, confirming the fact that the diffusion process is mainly guided by the distribution of islands at the surface. The resulting islands after the ripening process are visibly influenced by the width of the original oxidized stripes. The images in Fig. 2 show merging of numerous small islands into fewer larger ones. When all the islands are formed and all the oxygen is removed (first image), the average island size is between 30 and 80 nm^2. After 28 min (last image), areas of up to 1800 nm^2 have been measured. The relaxation of this non-equilibrium system proceeds *via* two different ripening mechanisms.

Examples of the observed ripening mechanisms are shown in Fig. 3. The STM image sequence in Fig. 3a shows two islands merging together and forming a larger one. This process is the dynamic coalescence, also called Smoluchowski ripening [31, 32]. It requires a mobility of the fusing islands. The islands first approach, then connect by a small “neck”, which eventually becomes thicker, as the island rearranges to an energetically more favorable shape. In Fig. 3b, the dissolution of a small island (area of ≈160 nm^2) is shown. Parallel to the dissolution, the larger island in the proximity slightly grows in size (from ≈440 nm^2 to ≈500 nm^2). The observed process is therefore a mass flow from the small island towards the neighboring larger ones, known as the Ostwald ripening mechanism [32–34].

We observed here both ripening mechanisms (Ostwald and Smoluchowski). The type of ripening depends less on the material, but more on the face and type of the island [35]. For example, Smoluchowski ripening has been observed for adatom islands on Ag(100) [7] and vacancy islands on Ag(111) [36]. In contrast, adatom islands on Ag(111) [37], adatom and vacancy islands on Ag(110)

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