The decoration of vicinal copper polycrystalline surfaces by Antimony

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Abstract. An Ultra-high Vacuum Variable Temperature Scanning Tunnelling Microscope was used to study the growth mechanism of Antimony on vicinal Cu polycrystalline samples. The STM data after deposition of 0.3 ML Sb at 300°C showed localization of Sb atoms in the vicinity of the step edges illustrative of the Frank van der Merwe type of growth. Kinks provide for the adsorbates a site with a coordination that is higher than for sites at the straight step edge. Thus, kinks act as efficient nucleation sites for the growth of rows during and after growth.

1. Introduction

Polycrystalline films received a rapidly growing interest in the past decades due to their increasing area of application in advanced technologies [1-6]. The properties of polycrystalline materials are controlled by the structure and interfaces they possess – e.g., grain boundaries, atomic steps and kinks. Growth on steps is actively explored as a promising alternative approach for planar nanostructures on surfaces in addition to lithography-based methods [7]. In this respect, STM with its capability to image conducting surfaces with unprecedented resolution provides a unique possibility to study processes for which surface imperfection plays a key role during and after growth processes. Previous studies have shown that introduction of a surfactant -a suitable adsorbate that remains at the free surface during growth- alters the surface free energy and can thus change the growth mode of a film to achieve layer-by-layer growth in both metal and semiconductor systems [8-13]. Copper alloys are important commercial materials which are often used at temperatures where diffusion processes has a huge influence in their properties. An important characteristic of these alloys is that segregation of one component to the alloy surface causes the surface composition to differ significantly from the bulk [13]. The present paper presents a VT-STM study of ~0.3 ML Sb on Cu polycrystalline surfaces studied at various temperatures.

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2. Experimental

All experiments were conducted in a UHV chamber with a base pressure below 5×10^{-10} Torr, equipped with a STM, SPECTA-LEED, EFM3 evaporator system from Omicron Nanotechnology (Germany, GmbH). The Cu pollycrystal polished to 0.25 μm was purchased from MaTeck. The Cu sample was mounted on a Ta baseplate and cleaned by repeated cycles of 2 keV Ar+ ion sputtering at 45° incidence followed by annealing to 530°C until the surface was confirmed clean. Antimony (Sb)was evaporated from an alumina crucible heated resistively in a Knudsen cell. The Sb was evaporated for 3 s at the deposition rates of 0.1 ML s^{-1}. The VT-STM was operated in the constant-current mode utilizing electrochemically etched tungsten (W) tips. The STM data is displayed in a top-view gray-scale representation with darker levels corresponding to lower lying areas. Measurements were acquired at room temperature after two separate annealing temperatures of 500 °C and 700 °C.
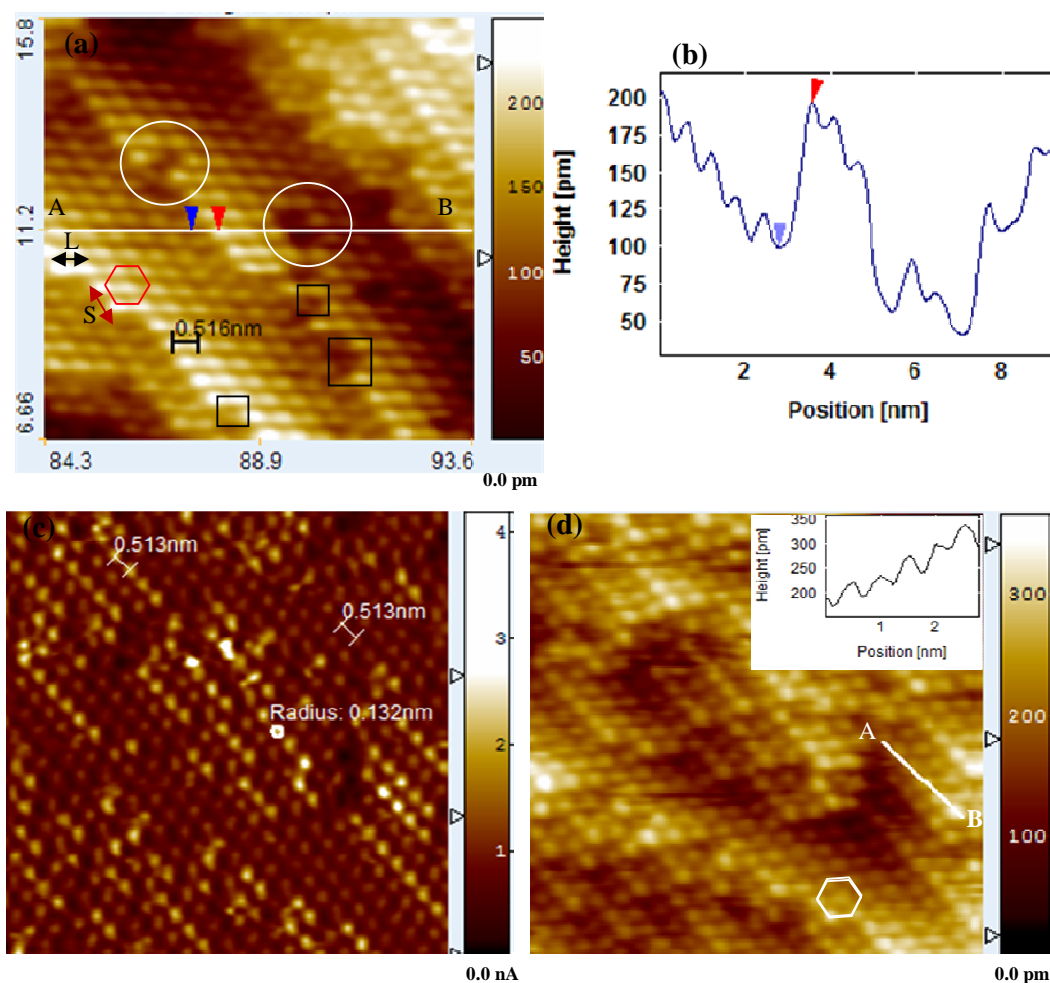
3. Results and discussion

3.1. Sb growth on Cu polycrystalline

After deposition of 0.3 ML Sb onto a cleaned Cu polycrystalline surface, a typical STM image acquired over an area of (9.30 x 9.13 nm) exhibits Sb atoms as bright spots on the atomically resolved stepped Cu polycrystalline surface (figure1(a)). Single embedded Sb atoms decorate the monoatomic step edge. The nearest neighbour distance of Sb atoms along the step edge is 0.515 nm ± 0.003 nm. At the top of the terrace in figure 1(a), Sb atoms occupy substitutional sites, where one Sb atom replaces one Cu atom. Given that the STM images the local density of states, Sb (Z = 51) atoms which appear brighter than Cu (Z = 29) atoms can be easily distinguished. The oval shapes (figure 1(a)) indicate the hollow core of screw dislocations.

A careful examination of the screw dislocation on the far left of figure 1(a) shows that the channel is isotropic. The isotropy is the manifestation of the line tension of the steps with respect to their crystallographic orientation [17]. Since steps with different orientations have different line tensions, this observation leads to the conclusion that the scanned area of the crystal was of the same orientation, possibly (111) plane. Based on the STM data of figure 1 it can be seen that the steps are one atom high and atoms join the crystal at the edges of the steps. Thus the crystal grows by spreading existing layers and generating new ones at the screw dislocations. The measured kink length (L) is 0.515 nm and the kink separation (S) is 1.03 nm (figure 1(a)).

The line scan (figure 1(b)) acquired along line A to B in figure 1(a) illustrates the step spacing *d* which varies from ~0.12 nm for the smallest step spacing to 2.5 nm for the larger step width. At a growth temperature of 300 ˚C, the diffusivity of Sb adatoms on the Cu surface increases. As a result, Sb adatoms are likely to reach a step edge within a given time (*t*). If the time between deposition of Sb is larger than *t*, Sb adatoms will typically reach a step edge before another Sb atom is deposited, and thus no Sb nucleation will occur on the surface. Therefore, increasing the temperature move a system from the nucleation-and-growth regime to the step-flow regime as seen in figure 1.
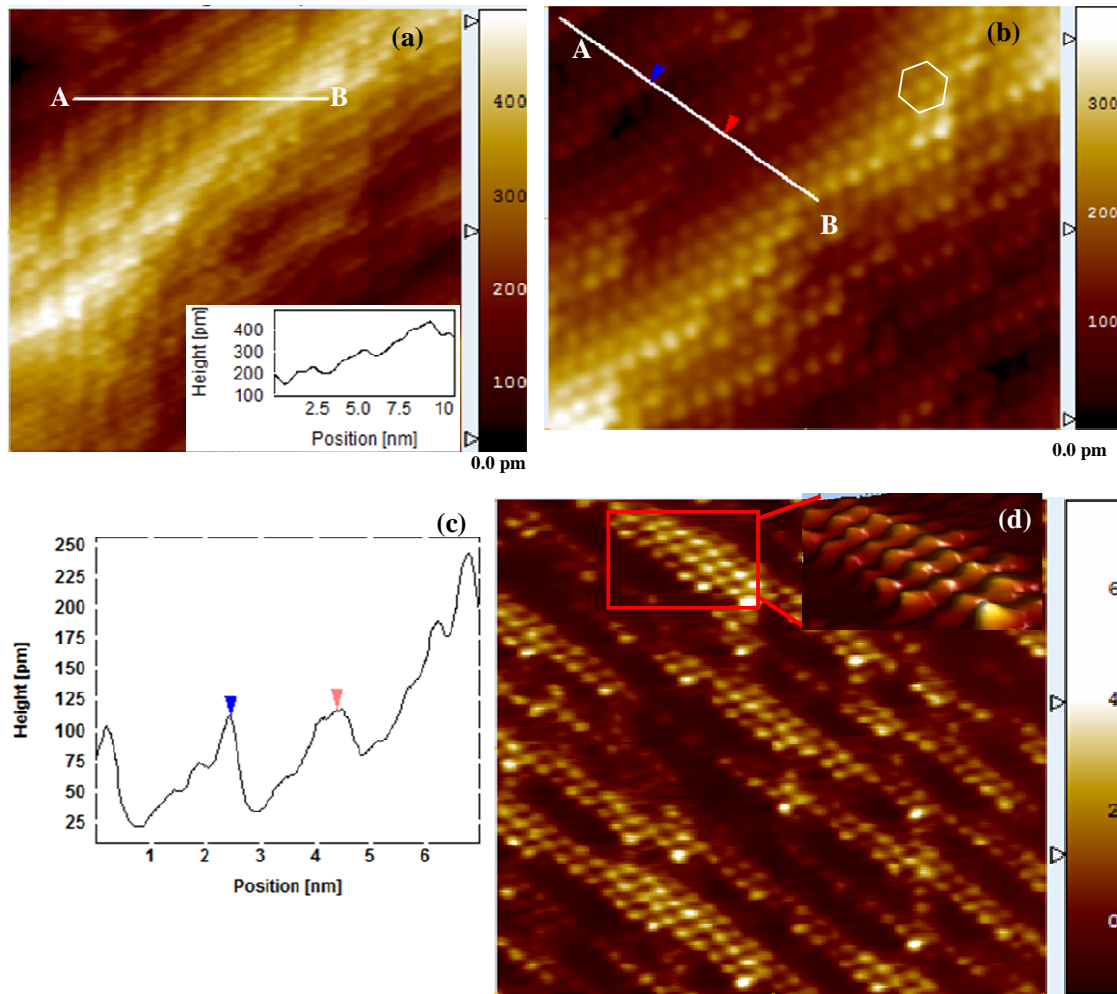
Figure 1. (a) High resolution STM image showing monatomic steps of Cu polycrystalline sample decorated by Sb (-1mV, 2 nA) acquired at an area of 9.30 nm x 9.13 nm after 0.3 ML growth of Sb. (b) Line profile acquired along the line A to B in (a) showing variations of terrace length (step spacing) and step height. (c-d) Constant current STM images (11.3 nm × 11.3 nm) acquired with a positive bias (1mV) The insert in (d) depicts a line scan of the corrugations of a single chain of Sb atoms (from A to B) on a Cu step.

STM images of figure 1(c and d) were acquired simultaneously to illustrate the positions and arrangement of the Sb atoms with respect to the Cu surface (11.3 nm x 11.3 nm). Figure 1(c) represents the variations in tunneling current resulting from both Sb (bright protrusions) and the Cu (darker protrusions) atoms. The Sb atomic radius was measured to be 0.132 nm (compared to the reported 0.133 nm[18]) utilizing the scanning probe image processor software. The measured Sb-Sb distances are comparable to the Cu-Cu atomic distances (0.513 nm). Figure 1(d) is the corresponding height image for figure 1(c). The STM images (figure 1 (c-d)) depict the decoration of atomic steps by a chain of Sb atoms and a large number of kinks are visible. The insert on the top right corner of figure 1(d) shows the corrugation of the about 5 Sb atoms decorating a Cu polycrystalline step.

3.2. Annealing of SbCu poly sample

By increasing the temperature it is well known that the rate of mass transport is substantially increased in regions of low atomic coordination, e.g. at surfaces and in grain boundaries [14-16]. The diffusivity at the surface can be increased by several orders of magnitude as compared with the bulk. The CuSb sample was annealed at 500 ˚C in UHV to study the diffusion characteristics of the Sb atoms on the sample surface. After annealing, successive STM images acquired over an area of (19.3 nm x 19.1 nm) at a positive bias of 0.1 mV show a smooth evolution from very wide terraces with a less smaller number of steps and long step spacing d, to short terrace length and increase in step density (figure 2(a)). A closer look of the terraces in figure 2(a) reveals migration of Sb atoms from the step edge to the terrace.

Figure 2. (a) An STM image (19.3 nm x 19.1 nm) of CuSb surface after annealing at 500 °C showing reduced terrace width and increase in step density (V_{bias}: 0.1 mV, I_{tun}: 2.2 nA). The insert on the lower right corner depicts the step height acquired along the line from A to B. (b) The zoomed-in image of (a). (c) shows the line scan acquired in (b) along line AB. The hexagon is superimposed to show atomic arrangement at the terrace. (d) High resolution STM image of the surface after annealing at 700°C for 12 hours acquired over an area of (15.0 nm x 13.6 nm) at a positive bias of 1 mV and tunnelling current of 3nA. The insert show a 3D view of a small portion of the Sb atoms on the surface.

The formation of step bunches in figure 2(a) is a manifestation of instabilities that occur during step generation or growth of Sb. Step density is seen to vary considerably within the same sample after annealing (figure 2(a)). Thus the evolution of the morphology with the increasing annealing temperature exhibits roughening of the sample surface. It can be deduced from figure 2(b) that even the presence of a neighboring step at the shortest possible distance has no effect on the kink creation energy as shown by the increased number of kinks at the surface. The kinks provide for the adsorbate a site with a coordination that is higher than for sites at the straight step edge. This effect can be seen in figure 2(d) after annealing at 700°C. Sb atoms diffused to the terrace covering ~ 4 atomic rows. Even at this high temperature the Sb atoms retain the arrangement of the underlying Cu surface and there is no change in the Sb – Sb atomic distances. The site with the next highest binding energy is a site close to an atom in a kink position, which may in this case efficiently immobilize the Sb adsorbates. In the initial stages of growth, the kink site belong to the substrate, but it soon become part of a growing one-dimensional adsorbate chain of Sb atoms at the Cu step edge.

4. Conclusion

A VT STM Sb was used to study the growth mechanism of Sb on vicinal Cu polycrystalline surfaces. The morphology of the deposited Sb depends strongly on the defect structure of the Cu substrate before, during and after growth. The sample surface showed roughening with increase in temperature. This temperature dependence of the surface morphology reflects the interplay between diffusion, and step incorporation, which are thermally activated processes. Perfect step decoration can be obtained if the potential energy of Sb adatom at the step edge is significantly lower than on the terrace and the temperature should be high enough such that the essential diffusion processes (terrace diffusion, step diffusion, corner rounding) are active. Step decoration of vicinal surfaces can be tailored and exploited to grow for example quantum wires.

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