Investigation of broken symmetry of Sb/Cu(111) surface alloys by VT-STM

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Abstract. This work present an in situ Variable Temperature Scanning Tunneling Microscopy (VT-STM) study of the Sb/Cu(111) system studied at various temperatures. The experimental data support a structural model for the Cu(111) $(\sqrt{3}\ \mathrm{x}\ \sqrt{3})R30^\circ$ - Sb in which Sb atoms displace up to 1/3 of the first layer of Cu atoms and incorporate them into the first Cu layer. In contrast to the clean Cu(111) substrate the surface of the surface alloy is corrugated due to the outward relaxation of the alloy atoms thus breaking the surface structural symmetry. The study report for the first time the observation of the Cu(111)(2 x 2) -Sb superstructure obtained at elevated temperatures.

1. Introduction

Recent developments in nanoscience make it possible to engineer artificial structures at surfaces and to gain control over matter at the atomic scale. The unique ability of scanning tunneling microscopy (STM) to reveal details at the atomic level has been particularly valuable. A great variety of structures are formed after deposition of one metal on the surface of another. In many metal-on-metal systems, it is of interest to consider the possibility of bulk or surface alloy formation [1-4]. Elements which are immiscible in the bulk have been found to form stable two dimensional mixtures at the surfaces [1,3,5,6]. Some surface adsorbate species such as antimony (Sb) are known to act as surfactants in both homo- and hetero-epitaxy; these adsorbates appear to induce layer-by-layer growth in systems which otherwise tend to island growth [7-9]. The adsorption of Sb on the (111) plane of noble metals surfaces such as copper (Cu) and silver (Ag) has long been of practical interest in the fields of surface science and technology. Theoretical calculations and experimental observations have suggested that the energetics of the Sb/Ag(111) system are such that in the ordered 0.33 ML Ag(111) $(\sqrt{3}\ \mathrm{x}\ \sqrt{3})R30^\circ$ - Sb phase, the Sb atoms substitute one-third of the outermost Ag atoms to produce an ordered surface alloy [1,3-5]. The structures of these monolayer surface alloys results from a complex interplay of electronic, stress and geometric effects, all related to each other. This study report on a similar system, Sb/Cu(111) studied by STM, LEED and Auger with a particular emphasis on the structure of the Cu(111) $(\sqrt{3}\ \mathrm{x}\ \sqrt{3})R30^\circ$ - Sb surface phase.

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2. Experimental

The experiments were performed 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(111) crystal were acquired from MaTeck and cut to an accuracy of less than 1°. The Cu single crystal polished to 0.25 μm, 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 and well ordered on the basis of AES, LEED and STM. 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 with the gray-scale representing surface features, the darker levels corresponding to lower lying areas and brighter areas corresponding to higher lying areas. Measurements were taken at room temperature after two different annealing temperatures at 300 ^{o}C and 700^{o}C.

3. Results and discussion

3.1. Sb growth on Cu(111) at room temperature

Figure 1(a) shows a high resolution STM image of atomically resolved hexagonal well ordered Cu (111) surface after sputtering. The distance between the protrusions is measured to ~ 0.257 ± 0.001 nm which is within the experimental uncertainty identical to the Cu spacing of 0.256 nm along the [110] direction [10]. The high resolution image was taken with a negative bias of (-1 mV) at an area of 2.50 nm × 2.50 nm. The “grey” scale next to the image illustrates the depth or height of the features on the image ranging from 0.0 to 39.6 pm. The corresponding line profile (insert) taken along A to B in (a) depicts the corrugation of the Cu atoms. The STM data for all recorded images was acquired at different scanning directions to exclude any tip-induced artifacts. Figure 1(c) depicts the low energy electron diffraction (LEED) pattern of the clean Cu(111) surface in reciprocal space. The (1×1) pattern is represented by bright spots illustrating the periodicity of a well ordered Cu(111) surface.

The STM image in figure 1(b) was acquired after deposition of 0.3 ML Sb on the atomically clean Cu(111) surface, at a temperature of 300°C. The STM image depicts atomically resolved Sb atoms as bright spots on the Cu surface (figure 1(b)). The Sb atoms are more or less randomly distributed and embedded on the Cu surface. The high resolution image was taken with a negative bias of (-1 mV) at an area of 2.50 nm × 2.50 nm. The insert on figure 1(b) illustrates the corrugations of the Sb atoms on the Cu surface along the line C to D. The corresponding LEED pattern (figure 1(d)) is similar to that of a (1×1) clean Cu(111) surface with no extra spots visible on the pattern. The spots remain sharp and with low background after growth. LEED is an averaging technique, thus the Sb atoms are not arranged in a regular pattern within the Cu surface therefore Sb atoms makes no contribute to the electron diffraction process.

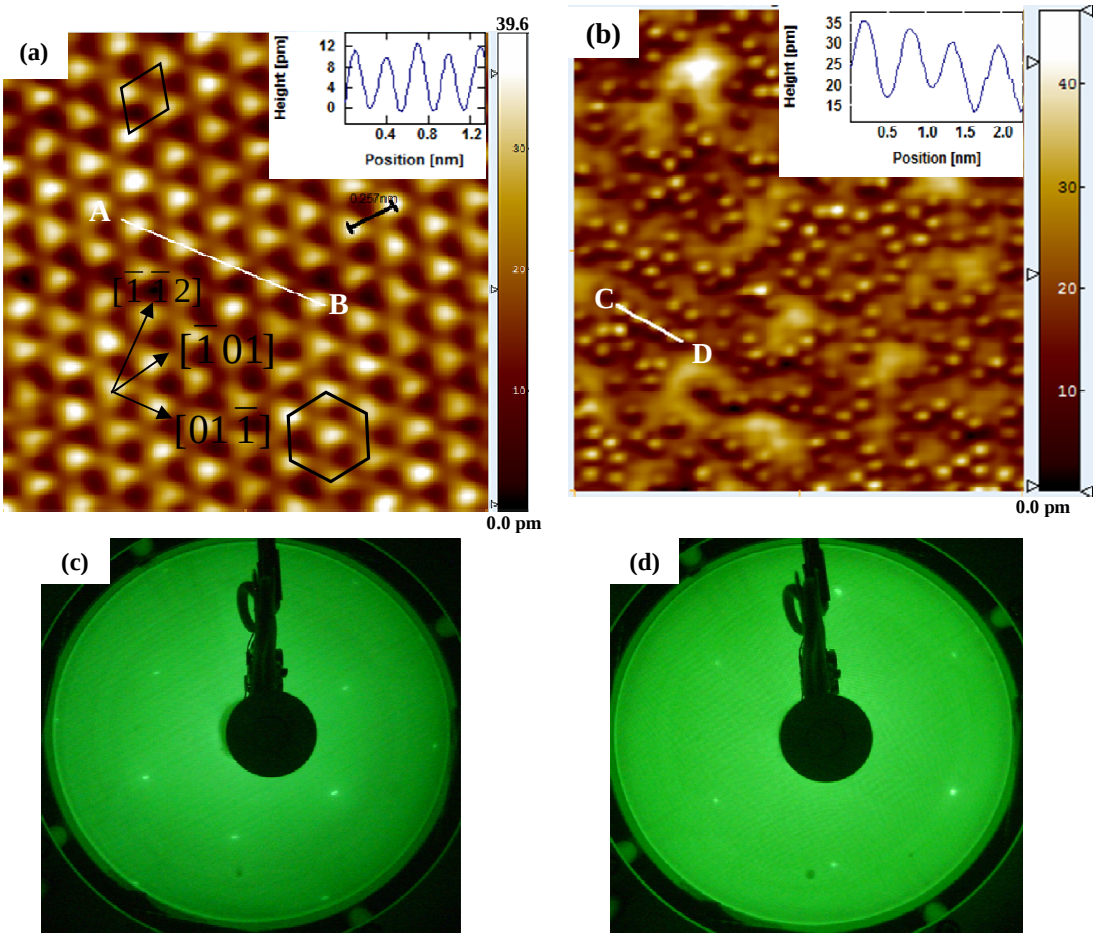

Figure. 1. (a) STM image of atomically clean Cu(111) surface (2.50 nm × 2.50 nm) after cycles of sputtering and annealing at 300°C (V_{bias} = -1 mV, I_{tun} = 2 nA). The black rhombus indicates the primitive unit cell and the hexagon is superimposed to illustrate the arrangement of Cu atoms at the surface. The inserts on the top right of each image show the line scan along A to B and C to D taken along the lines in figure 1(a and b) respectively. (b) Atomic resolution STM image (13.8 nm × 13.8 nm) upon deposition of ~0.3 ML of Sb (V_{bias} = 5 mV, I_{tun} = 2 nA). (c-d) Corresponding LEED patterns (beam energy 114 eV) of the bare Cu(111) surface before and after growth (beam energy 116 eV), respectively.

3.2. Sb dissolution on atomically clean Cu(111) at 400 °C

After the sample was annealed at 400 °C for 12 hours, successive STM images (9 nm × 9 nm, V_{bias} = 1 mV, I_{tun} = 2 nA) captured the Sb dissolution and showed a perfect $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure (figure 2(a)). The corresponding LEED pattern (figure 2(e)) show the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction when taken at the same beam energy (114 eV) as in the clean Cu(111). Extra spots are visible on the diffraction pattern compared to the clean Cu surface of figure 1(c). In both the STM and LEED data, the surface showed long range behaviour as the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and form locally hexagonal arrangement of the Sb atoms. The vertical corrugation of figure 2(a) represent the variation in tunneling current ranging from 0.0 to 800 pA as illustrated by the grey scale. A closer look of figure 2(b) it is possible to discern that Sb atoms occupy substitutional sites surrounded by six Cu atoms, three of them being displaced from the lattice site positions of the (111) plane.

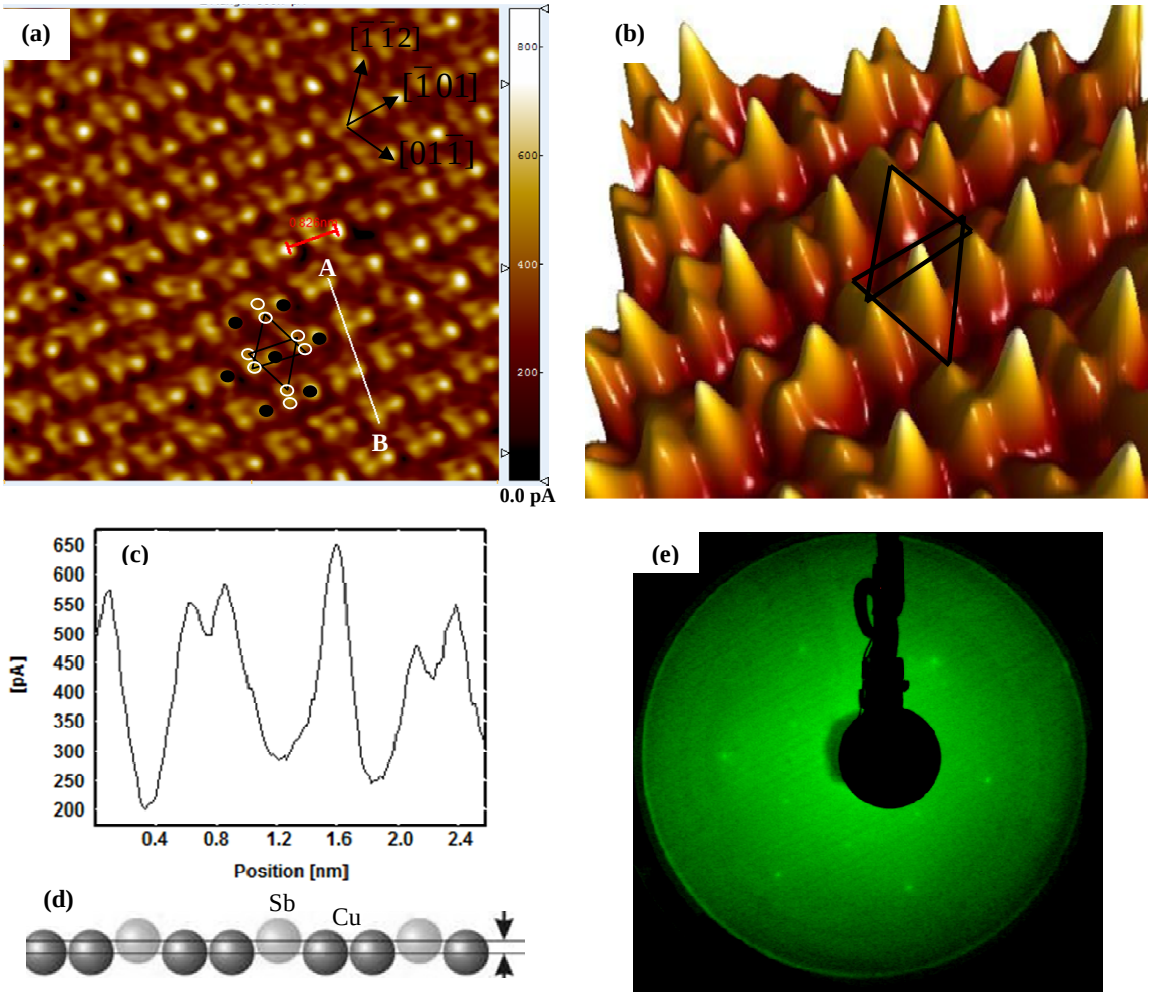

Figure 2.(a) An STM image (8.01 nm × 7.65 nm) clearly showing the six Cu atoms that surrounds each Sb atom in a Sb/Cu(111) $(\sqrt{3} \times \sqrt{3})R30^{\circ}$-Sb reconstruction ($V_{bias}$ = 1 mV, I_{tun} = 2 nA). (b) Three-dimensional (3D) view of the high magnification STM image of the image in (a). The white circles and the black dots are superimposed to represent the position of the Cu and Sb atoms respectively. The superimposed triangles are associated to two in-equivalent Cu atoms and a Sb atom at the centre resulting in surface asymmetry. (c) Line trace along the white line along A to B in (a) showing the amplitude of the corrugation in picoamps vs distance in nm. (d) Schematic representation of the CuSb atomic arrangement at the surface showing rippling. (e) Experimental LEED pattern of the sample sample surface at 114 eV.

From the STM data, Sb atoms buckle outwards (figure 2(d)) by ~0.23 nm (rippling) compared to the previous reported theoretical and calculated values of 0.25 nm [4]. The hexagonal surface symmetry is then broken by this displacement as illustrated in the three-dimensional picture in figure 2(b). From the STM images (figure 2(a-b)), the Sb atoms remain centred in the <112> -type directions and followed by two lower Cu atoms evident in the line scan of figure 2(c). The out-of-plane displacement (rippling) of Sb incorporated into the copper surface is consistent with the picture of the larger antimony atoms substituting for copper as illustrated by the schematic in figure 2(d).). The inclusion of the Sb in the Cu matrix induces strain in the Cu matrix which is reduced by the out the outward relaxation.

The outward relaxation to the strongly enhanced spin-splitting in these surface alloys [2,5,12,13]. This is due to the additional planner component of the potential difference provided by this configuration.

3.3. The Cu(111) -Sb superstructure

The sample was further annealed at ~700 °C for 12 hours and an STM study of the sample surface was conducted at sample temperature of ~ 100 °C. Figure 3(a) illustrates an STM image (6.94 nm x 6.76 nm) of the CuSb surface obtained as the sample was cooling down to room temperature showing Cu(111) $(\sqrt{3} \times \sqrt{3})R30^\circ$ - Sb and Cu(111) (2 x 2) – Sb superstructure.

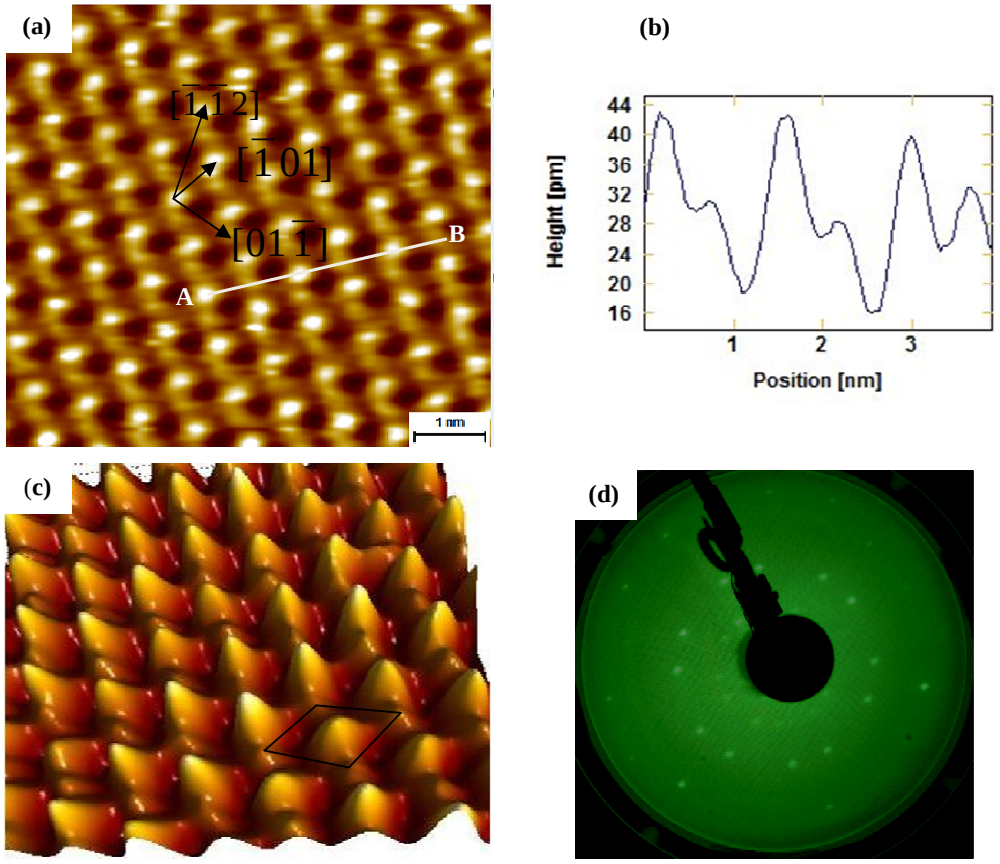

Figure 3. (a) STM image (V_{bias} = 0.7 mV, I_{tun} = 4 nA) CuSb surface after annealing at ~700 °C (6.94 nm × 6.76 nm) forming hexagonal arrangement of a Cu(111)(2 x 2) -Sb. (b) line profile taken along the line in (a), (c) Three-dimensional (3D) view of the STM image and (d) Experimental LEED pattern of the CuSb showing the a Cu(111)(2 x 2) -Sb surface at700 °C, beam energy 66 eV.

From a careful examination of the STM image in figure 3(a) and the corresponding line profile in figure 3(b), it possible to distinguish between the Sb and Cu atoms illustrated by the LEED pattern figure 3(d). The interatomic spacing between the Sb atoms is 0.787 ± 0.02 nm. The images reveal only four Cu atoms instead of the six surrounding each Sb atom. The Cu atoms appears to be centered in the <110> - type directions. The line scan in figure 3(c) taken along the line AB in figure 3(a) depicts the relative corrugations between the Sb and Cu atoms.

The $(\sqrt{3}\ x\ \sqrt{3})R30^{\circ}$ structure is considered to be the more thermodynamically stable configuration, thus the Cu(111) (2 x 2) Sb structure in figure 3(a) observed after annealing at high temperatures might be due to kinetic limitations at the surface. It is highly probable that at this annealing temperature, the Cu atoms desorbed from the surface and desegregate to the bulk to leave a lower copper concentration on the surface. The STM measurements are not enough to distinguish between these possibilities, thus complementary techniques are required for the understanding of the interesting overlayer structure.

4. Conclusion

VT STM has been used to characterize the behaviour of Cu(111) following deposition of 0.3 ML of Sb. Annealing of the CuSb film was found to give rise to two distinct ordered surface structures, Cu(111) $(\sqrt{3}\ x\ \sqrt{3})R30^{\circ}$-Sb and Cu(111) (2 x 2) -Sb. These observations are in agreement with previous studies on CuSb systems. Annealing to ~700°C produces a structure containing less Sb atoms. The Sb that is lost from the near-surface is believed to diffuse into the bulk of the crystal or alrtenatively desorbs from the surface. The data clearly favours a structural model based on Sb atoms occupying substitutional rather than overlayer sites within the top Cu layer.

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