



In situ STM studies of Sb(111) electrodes in aqueous electrolyte solutions

V. Grozovski, S. Kallip, E. Lust*

Institute of Chemistry, University of Tartu, 14A Ravila Street, 50411 Tartu, Estonia

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ABSTRACT

The in situ STM studies of Sb(111), which was cleaved at the temperature of liquid nitrogen inside the glove box, and of Sb(111), which was electrochemically polished in the KI + HCl aqueous solution, have been performed under negative polarizations from -0.8 to -0.15 V (versus Ag|AgCl in sat. KCl aqueous solution) in the 0.5 M Na_2SO_4 + 0.0003 M H_2SO_4 aqueous solution. The atomic resolution has been achieved. The in situ STM data show that there are no quick surface reconstruction processes and the surface structure of cleaved and electrochemically polished Sb(111) is stable within the potential region investigated, similarly for Bi(111) single crystal electrode, previously studied [S. Kallip, E. Lust, *Electrochem. Comm.* 7 (2005) 863].

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1. Introduction

The base boundary structure, adsorption properties and electrochemical kinetics of various interfacial charge transfer reactions at the solid surfaces depend significantly not only on the chemical composition but also on the morphology of the surface studied [1–22]. Thus, the surface morphology and roughness are important properties as most electrochemical parameters are extensive quantities [9,10]. Atomically resolved STM studies require the preparation of a very flat surface with a well-defined structure [8]. Electrochemical or chemical polishing (Bi) [23–25], (Au, Ag, Cu) [1,6] and electrochemical capillary growth techniques for deposition of the single crystals (Ag, Cd) [26,27] have been used as the alternative or additional steps to thermal annealing as in the case of Au(hkl) and Pt(hkl) [1–6,12–16,18–22]. The so-called atomic layer deposition from gas phase, as well as e-beam evaporation and sputtering provide another avenue for producing the flat highly oriented films [26,29–31].

It was found that the different preparation methods led to the different mesoscopic structures like step bunching that depends on specific preparation procedures used [1–6,8,12–16,28–37].

The influence of the electrode potential on the surface structure of Au(hkl), Pt(hkl) and Ag(hkl) and other face centered cubic metals has been discussed in many papers [1–4,6–8,12–16,28–34].

In contrast, the shape of the cyclic voltammograms and impedance data for Sb(hkl) and Bi(hkl) planes do not depend on the electrode potential scan direction as well as on the potential scan rate (v) [10,11] and there is no quick surface reconstruction of Sb(hkl) within the region of ideal polarizability of the electrode [10,11,35–42]. Thus, the surface reconstruction phenomena do not take place for Bi and Sb single crystal planes.

In ultra-high vacuum (UHV) conditions the atomic resolution data for bismuth [43] and antimony [44] single crystal electrodes has already been achieved. The UHV STM studies at the cleaved Sb(111) surface (cut at the temperature of liquid nitrogen) [44,45] demonstrate the nearly ideal structure of the Sb(111) surface which makes further investigation quite interesting under electrochemical conditions using in situ STM techniques.

According to our knowledge, there are no data for Sb(111) plane electrode obtained under the in situ STM electrochemical conditions in the literature. Therefore, the main aim of these investigations was to develop the experimental conditions needed to obtain the atomic resolution STM data within the wide electrode polarization region of the Sb(111) electrode similar to our previous work analyzing Bi(111) single crystal electrode behavior in electrolyte solution [23]. The electronic configuration of Sb is s^2p^3 and it is similar to Bi. Sb crystallizes in a simple trigonal Bravais lattice system with two Sb atoms with co-ordinate $u = 0.233$ nm linked to each lattice point of the unit cell [46–48]. The Sb unit cell has an axial angle of $\alpha = 67^\circ 31'$ and a cell parameter of $a = 0.431$ nm. The melting point of Sb is 903 K. Sb has a stratified structure and two types of bonds in the lattice, i.e., semiconducting intralayer (s^2p^3 valence state) and metallic interlayer bonds (with the participation of hybrid sp^3d^2 orbitals) between the atoms in the lattice, which leads to a sharp anisotropy of the volume and surface properties of the individual crystallographic phases/planes of Sb. The presence of the covalent semiconducting bonds between the atoms in the Sb lattice probably fixes the position of the surface atoms more rigidly (similar to Bi) than in the case of typical sd- and sp-metals (Au, Cu, Pt, Pd, Cd) [1–3,6,8,9]. Sb is also known for its specific properties of increasing the catalytic activity of Pt and for Pt/C catalysts in direct formic acid fuel cells [49]. Similar to Bi decorated Pt single crystal surfaces [50–54] and Pt nanoparticles [55], Sb increases their electrocatalytic activity towards formic acid oxidation [49].

* Corresponding author. Tel.: +372 7 375 165; fax: +372 7 375 160.
E-mail address: enn.lust@ut.ee (E. Lust).

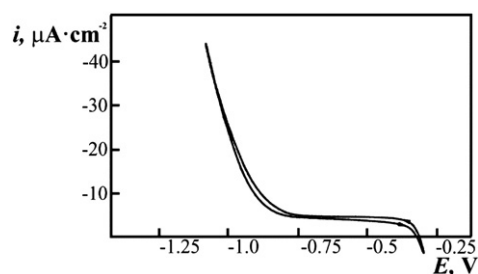


Fig. 1. Cyclic voltammogram for Sb(111) in 0.5 M Na₂SO₄ + 3 × 10⁻⁴ M H₂SO₄ aqueous electrolyte at potential scan rate 5 mV s⁻¹.

2. Experimental

The surface of the basal Sb(111) plane has been prepared by electrochemical polishing in the KI + HCl aqueous solution at current density $j < 1.5 \text{ A cm}^{-2}$ (mentioned as Sb(111)^{EP}) or by cleaving a Sb single crystal at the temperature of liquid nitrogen (mentioned as Sb(111)^C) inside the glove box (Ar (92%) + H₂ (8%) atmosphere) and submerged under cathodic polarization ($E = -0.8 \text{ V}$ vs. Ag/AgCl in saturated KCl aqueous solution) into the 0.5 M Na₂SO₄ + 0.0003 M H₂SO₄ aqueous solution (previously saturated with Ar (92%) + H₂ (8%) mixture). The self-made hermetic three-electrode cell with large Pt counter electrode and Ag/AgCl reference electrode, connected to the in situ STM cell through Luggin capillary, has been used. The region of ideal polarizability ($-0.8 \leq E \leq -0.15 \text{ V}$ vs Ag/AgCl) has been obtained using cyclic voltammetry and a good agreement with the results discussed in [10,11,35–42] has been established. The Molecular Imaging PicoSPM™ measurement systems applying the Apiezon™ coated tungsten STM tips, prepared in our laboratory, were used. The STM-tips and measurement system were tested and calibrated using HOPG basal plane C(0001)^C (SPI™). All STM images were recorded in constant current mode with tunneling currents from 0.5 to 10.0 nA. For image processing and surface roughness analysis the Nanotec Electronica WSxM™ [56] and Gwyddion [57] free software were used.

Water for the preparation of electrolyte solutions was treated with the Milli Q+ purification system. Solutions were prepared volumetrically using H₂SO₄ (double distilled, Aldrich) and Na₂SO₄, purified by triple recrystallization from water, and treated in a vacuum to dryness. Na₂SO₄ was also calcined at 700 °C immediately prior to the measurements. The temperature during the experiment was kept at 298 ± 0.1 K.

3. Results and discussion

Fig. 1 represents cyclic voltammetry data for Sb(111) electrode in 0.5 M Na₂SO₄ + 0.0003 M H₂SO₄ aqueous solution. Current density does not exceed $-10 \mu\text{A} \cdot \text{cm}^{-2}$ within the region of E from -1.0 to -0.45 V . At -0.42 V , the current passes through zero and the dissolution of antimony starts according to the equation [35]



From the impedance data, shown in ref. [35], the potential of zero charge for Sb(111) is $E_{q=0} = -0.46 \text{ V}$, which almost coincides with the potential, where antimony surface starts dissolving according to the voltammetry data given in Fig. 1. It is obvious that slightly acidified electrolyte solution shifts the point where the dissolution of Sb(111) starts, as discussed in ref. [35].

The surface of Sb(111)^C cleaved at the temperature of liquid nitrogen consists of large and atomically smooth terraces and steps of height $3.6 + 0.2 \text{ \AA}$ (Figs. 2 and 3) or of multiple heights. Thus, in a good agreement with the data for Sb crystallographic structure ($d = 3.37 \text{ \AA}$), such structure is always formed by cleavage occurring between two planes separated by somewhat a large distance. Therefore, mainly the van der Waals bonds have been broken and the steps have mainly monoatomic height rather than diatomic, as well as previously observed for Bi(111) single crystal electrode [23]. The boundaries of the most terraces are close to the straight lines of the atomic rows on the Sb surface along the [1 1 0] direction (Fig. 2(a)) [46,47]. However, there are some areas having considerably curved boundaries and rounded islands of the triangular shape. No random hollows of nanometric dimension are present on Sb(111)^C when compared to Bi(111) [23]. At higher magnifications, some terrace boundaries show considerable dispersion and can deviate from the direction of atomic rows (Fig. 3). Of course, the behavior of the boundaries depends on their direction and the length and thermal motion are the reasons for the more extended boundaries being slightly diffused. However, different behaviors of the boundaries can be caused by their various steepnesses on an atomic scale provided by the packing of layers along the [1 1 1] direction [46,47]. In the same places, the dislocation outcrop can be seen and in some surface regions the very small steps with a height lower than the lattice period for Sb have been observed, which may have been probably caused by the screw dislocations generated during the crystal growth by using the vertical Chohralsky method. The data are in a good agreement with the UHV STM studies

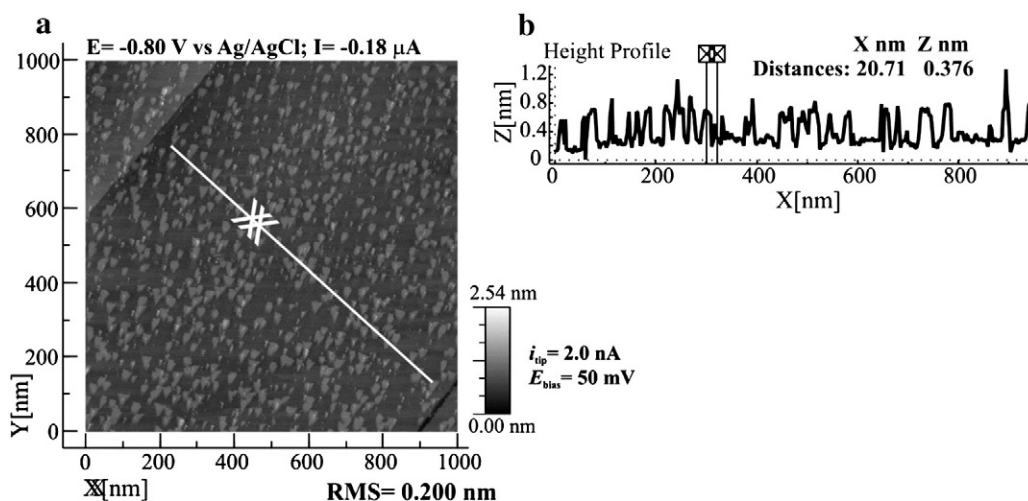


Fig. 2. In situ STM image (a) and selected surface profile (b) for cleaved at the temperature of liquid nitrogen Sb(111)^C plane in 3 × 10⁻⁴ M H₂SO₄ + 0.5 M Na₂SO₄ aqueous electrolyte.

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