Sb (111) abnormal behavior under ion etching

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Abstract

Due to a strong spin-orbit interaction (SOI), the surface states of Sb (111) are similar to those for topological insulators (TI) Sugawara et al. (2006). The surface states are protected by time-reversal symmetry and energy dispersion is a linear function of momentum. Defects in crystal structure lead to a local break of the surface translational symmetry and can modify surface states. It is the primary reason to study defects of Sb crystal structure and their effect on the surface states dispersion. Etching of the Sb (111) surface using Ar⁺ ions is a common way to create defects both in a bulk and on the surface of the crystal. Sb (111) ion etching at room temperature reveals anomalous behavior of surface crystal structure. It results in formation of flat terraces of 2nm in size. Investigation of electronic structure of the etched Sb (111) surface has demonstrated increase of density of states (DOS) at the Fermi level. The results are discussed in terms of local break of conditions of Peierls transition.

Keywords: STM; UPS; LEED; DFT modeling; topological insulator; Pierls transition; ion etching; Sb (111)

1. Introduction

Sb has a rhombohedral crystal structure. Sb crystal structure can be described in terms of a small deformation of simple cubic lattice. The planes (111) through one are shifted along C₃ followed by small uniform deformation...
Molotkov and Tatarskij (1988). The deformations are due to Peierls transition. Planes relocation leads to alternation of chemical bonds: covalent one and one of Van der Waals. Since the Sb lattice parameter is \( a = 4.3 \pm 0.05 \, \text{Å} \), interplanar distances are \( d_1 = 1.5 \pm 0.1 \, \text{Å} \), \( d_2 = 2.3 \pm 0.1 \, \text{Å} \), Zhang et al. (2012).

Experimentally it was established that Sb single crystals cleaves along (111), a long Van der Waals bond between the surfaces being breaking. Surface (111) is not reconstructed; there is a small (about 1-2%) relaxation of the first interlayer distance.

The dispersion of Sb (111) surface states a massless Dirac cone. It is a consequence of the symmetry of the surface, Molotkov and Potapova (2013), while SOI plays a significant role in the formation of electronic spectrum. SOI is comparable with energy parameters of Peierls instability Molotkov and Tatarskij (1988). Surface states are localized in a vicinity of \( \bar{\Gamma} \) point in Brillouin zone (BZ) and are non-degenerated the spin. Due to a small energy gap between the valence and conductive bands in \( \bar{\Gamma} \) point, the surface states are localized near the surface in a layer of 12 nm thick Molotkov and Tatarskij (1988). Defects in crystal structure lead to a local break of surface translational symmetry and can modify the surface states. It is the primary reason to study defects of Sb crystal structure and their effect on surface states dispersion. Studies of ion etching effect on Sb (111) atomic and electronic surface structure are presented in this work.

### 2. Experiments and results

Atomically clean Sb (111) surface was prepared by cleaving in vacuum chamber \( (P \approx 10^{-6} \, \text{Torr}) \) at room temperature \( (T = 300 \, \text{K}) \). Micrograph of cleaved Sb (111) surface is shown in Fig. 1a. The cleaved surface consists of large flat areas up to 3 mm in size. Fig.1b demonstrates typical STM image of the surface. The surface consists of large atomically flat terraces separated by step edges. The surface cross-section along the red line (Fig. 1c) reveals a step with a height corresponding to a single bilayer thickness (3.9 Å).

Fig.1: (a) Sb (111) surface optical image; 4mm x 4mm. (b) Sb (111) STM image. 710 nm x 710 nm. \( (T = 300 \, \text{K}, V_b = 100 \, \text{mV}, I_t = 100 \, \text{pA}) \). (c) The cross section of the STM image along the red line.

Sb (111) surface ion etching was performed at room temperature by \( \text{Ar}^+ \). Beam energy of argon ions was \( E_p = 4 \, \text{kV} \). The STM image of etched Sb (111) surface is shown in Fig. 2a. The image demonstrates significant changes in surface topography. The etched surface consists of a number of flat terraces that is confirmed by a height distribution histogram presented in Fig. 2b.

Indeed, height distribution curve can be fitted by three peaks localized at 0, 2.2 Å and 3.8 Å which is in a good agreement with Sb layered crystal structure. Base layer (corresponds to a peak localized at 0) covers about 40% of the surface. The bilayer (peak at 3.8 Å in the histogram) being placed on a top of base layer, covers about 30% of the surface. It is unexpected that structures one monolayer thick (peak at 2.2 Å in the histogram) appear on the surface. These anomalous layers cover about 30% of the surface.
Fig. 2: (a) STM-image of the etched surface 50 nm x 50 nm. ($T = 300$ K, $V_s = 600$ mV, $I_t = 100$ pA); (b) Heights distribution for large area of STM-image of etched Sb (111) surface.

Surface investigation by the LEED demonstrates that ion etching of the surface resulted in LEED spots broadening (Fig. 3a-b before etching, 3c-d – etched surface). The LEED spot width before ion etching is of $0.05\text{Å}^{-1}$. Ion etching leads to the LEED spots widening to $0.30\text{Å}^{-1}$. Fig. 3 demonstrates surface etching results. Gauss approximation for LEED spot profile (marked in red) corresponds to electron diffraction from terraces 17 Å in width.

Fig. 3: (a) Diffraction pattern of cleaved surface $E_p = 96.6$ eV; (b) Cross-section of cleaved surface LEED-image along the line; (c) Diffraction pattern of the surface etched at $T = 300$K, $E_p = 96.6$ eV; (d) Cross-section of etched surface LEED-image along the line.
The terraces size was investigated as a function of ion etching time. Fig. 4a demonstrates average width of terraces as a function of ion etching time obtained by LEED studies.

Electronic structure of Sb (111) surface states was investigated using ultraviolet photoelectron spectroscopy (UPS). He(I) UPS-spectra were measured with KRATOS AXIS ULTRA DLD. Evolution of the UPS spectrum in a vicinity of Fermi energy Fig. 4b reveals strong dependence of DOS at Fermi level on time of ion etching. Furthermore, increase of ion etching time resulted in more pronounced UPS signal, i.e. in DOS increase at Fermi level (Fig. 4b).

3. Discussion

Peierls transition in Sb leads to the (111) atomic layers displacement along [111] with the bilayer structure formation. As a result, an energy gap appears in electron dispersion. Due to ion etching, the Sb top layers structure is damaged. STM demonstrates that the surface apart of base layer and bilayer islands contains surface areas where complementary atomic layer is absent. Conditions of Pieirls transition at local monolayer structures are broken and the surface metallic properties become more pronounced. In order to confirm this the DOS model calculations of Sb (111) were performed in a frame of density functional theory (DFT) approximation. The model structures slabs were separated by a vacuum gap of 12 Å in the z direction, sampled by a $17 \times 17 \times 1$ mesh in $k$ space, cut-off was 205 eV. Calculations were carried out using plane-wave DFT with the Perdew-Burke-Ernzerhof density functional (Materials Studio, CASTEP Accelrys). Note that DOS calculated for odd-layered structures (marked in red) reveals
a higher value in a vicinity of Fermi level in comparison with one for even-layered structure (Fig. 5).

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References