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Atomically flat surface preparation for surface-sensitive technologies*

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Surface-sensitive measurements are crucial to many types of researches in condensed matter physics. However, it is difficult to obtain atomically flat surfaces of many single crystals by the commonly used mechanical cleavage. We demonstrate that the grind-polish-sputter-anneal method can be used to obtain atomically flat surfaces on topological materials. Three types of surface-sensitive measurements are performed on CoSi (001) surface with dramatically improved quality of data. This method extends the research area of surface-sensitive measurements to hard-to-cleave alloys, and can be applied to irregular single crystals with selective crystalline planes. It may become a routine process of preparing atomically flat surfaces for surface-sensitive technologies.

Keywords: grind-polish-sputter-anneal, atomically flat, single crystal surface, topological materials

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1. Introduction

Since the invention of advanced surface technologies, like low-energy electron diffraction (LEED), reflection high-energy electron diffraction (RHEED), molecular beam epitaxy (MBE), scanning tunneling microscope (STM), and angle-resolved photoemission spectroscopy (ARPES), they have become the most indispensable methods of studying condensed matter physics.[1–4] Specifically, STM and ARPES are the most direct way to measure the electronic structures of real space and momentum space. And owing to their surface-sensitive property, extremely atomically flat and clean surfaces are necessary for proper measurement. Mechanical cleave is the most widely used method of obtaining flat and clean surfaces.[5] In previous studies, most of the crystals were cleaved by using the so called "post-cleave method". However, it may not provide fair results when the single crystals have strong bonds and lack preferred cleavage plane, which limits the research scope of those surface-sensitive technologies.

The grind-polish-sputter method has been widely used for cleaning samples for TEM, XPS, and UPS measurements.[6–8] And the grind-polish-sputter-anneal method has been applied to pure element single crystals, such as Au and Cu.[9,10] This method is rarely used for multielement crystals because it can easily introduce defects and change the stoichiometry on the surfaces of crystals.[11] Topological surface states in topological materials are protected by symmetries[12,13] and the topological properties are robust against impurities. Therefore, the grind-polish-sputter method can be used for topological materials. In this paper, we obtain atomically flat surfaces of several topological materials by using this method, and apply them to RHEED, ARPES, and STM measurements for the first time. What is more, by adjusting the sputtering and annealing conditions, we find that it can be applied to many kinds of materials, and thus extending the research areas of those surface sensitive technologies.

Recently, it has been proposed that the family of chiral crystals in space group 198, including CoSi, RhSi, RhSn,

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and AlPt, possess multifold degeneration nodes with a large Chern number. These chiral crystals host unconventional chiral fermions and exotic topological nontrivial Fermi arcs surface states, whose exotic electronic structure has some unusual quantum phenomena. However, the family of chiral crystals have cubic structure and strong covalent band, surfaces by mechanical cleavage are not smooth enough.[14,15] Using the grind-polish-sputter-anneal method, we demonstrate that atomically flat surfaces of CoSi can be obtained. From the well-prepared samples, the topological surface states can be clearly observed.

2. Experiment

We illustrate the whole process of sample preparation in Fig. 1(a). First of all, Laue or XRD method was used to verify the desired crystal plane. The unique property in CoSi, where the projection of spin-1 nodes and charge-2 nodes on (001) surface[16–19] were connected by surface Fermi arcs, was investigated. So, we picked the (001) surface, and glued it to the bottom of a mold upside down, where epoxy resin solution was used afterwards to fix the sample into a cylindrical shape.

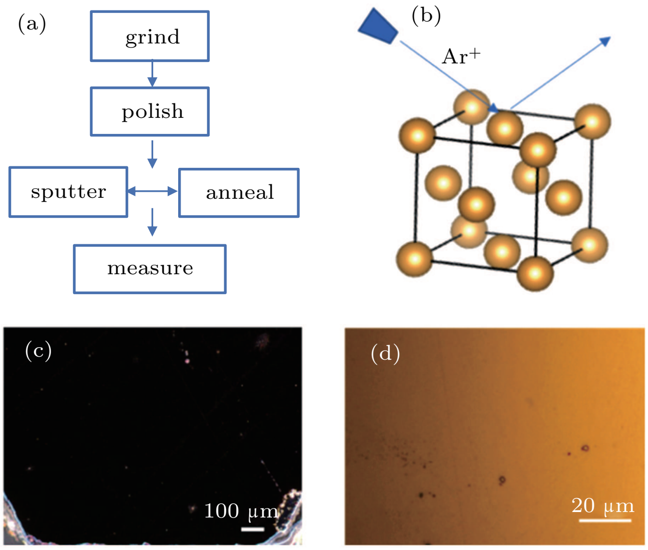

Fig. 1. (a) Grind-polish-sputter-anneal process, (b) sketch map of Ar^+ ion sputtering bombard, (001) surface of CoSi after grinding and polishing, with magnification of 50× (c) and 1000× (d).

The crystal surface was smoothened for 5 min at 50 rpm roughly by using the sandpaper with grit of P800 and P1500 sequentially. Then, polishing pads rotated at 100 rpm for about 20 min by using 3-μm grade diamond abrasives as polishing fluid. The desired crystal surface became shiny and showed no sign of scratches under 50× and 1000× magnifications as shown in Figs. 1(c) and 1(d). Sputtering and annealing procedure were carried out in a UHV chamber with a base pressure better than 1×10^{-9} torr (1 torr = 1.33322×10^2 Pa), which was connected with ARPES chamber. The ion source was IQE10 from SPECS, with Ar^+ ions generated by collision with electrons bombarding single crystal surfaces as illustrated in Fig. 1(b). First, we degassed the sample at 500 °C until the pressure was better than 5×10^{-9} torr. Then opening the leak valve Ar gas came in and the pressure rose to 5×10^{-5} torr. The beam energy of sputtering is 1.5 keV and the sputtering lasted 20 min. After finishing the sputtering procedure, the sample was annealed at 780 °C for 2 h. The sputtering and annealing procedure were repeated several times. The key factor should be the annealing temperature, which depends on type of material in use. The annealing temperature was chosen to be about 50%–70% of the melting point temperature.[11]

3. Results

Eventually, we attained atomically flat surface as manifested by reflection high-energy electron diffraction (RHEED), which is quite direct and can be easily accessed. Figures 2(a) and 2(b) are the RHEED pattern of CoSi (001) surface and CoSi (111) surface, respectively showing that our method has a great advantage in choosing desired crystalline planes. Atomically flat Mn_3Sn and TiRhAs are also obtained as seen in Figs. 2(c) and 2(d), respectively. The high order diffraction spots and Kikuchi lines are signs of high-quality surface.

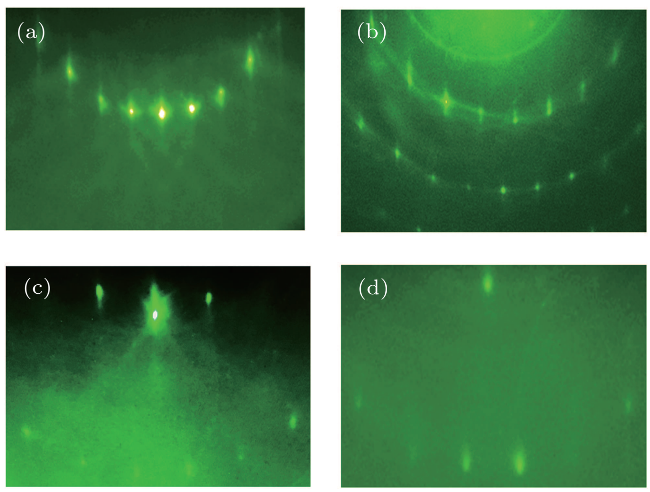

Fig. 2. (a) RHEED pattern of CoSi single crystal (001) surface after grind-polish-sputter-anneal process, (b) RHEED pattern of CoSi (111) surface, RHEED pattern of (c) Mn_3Sn and (d) TiRhAs.

STM has very high requirement for the flatness and cleanness of sample surfaces, we carry on STM measurement on processed CoSi (001), (011), and (111) surfaces to demonstrate that atomically flat surfaces are obtained. As we can see in Figs. 3(a)–3(c), the atomic resolution is realized. The lattice constant is close to 4.445 Å of CoSi, showing that the crystal structure has no big change. This is stronger demonstration that the grind-polish-sputter-anneal method works well on selective crystalline planes.

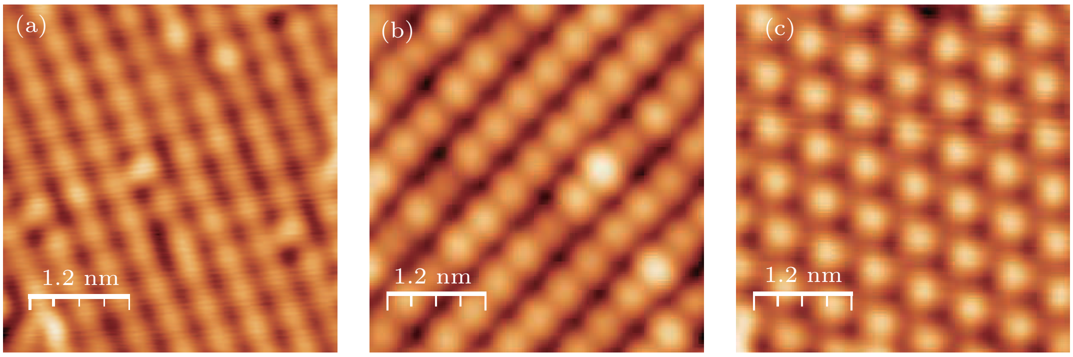

Fig. 3. (a) STM image of CoSi (001) surface at $U = -1$ V and $I_t = 100$ pA, (b) STM image of CoSi (011) surface at $U = +500$ mV and $I_t = 100$ pA, and (c) STM image of CoSi (111) surface at $U = -1$ V and $I_t = 100$ pA. The selected area is 4 nm × 4 nm.

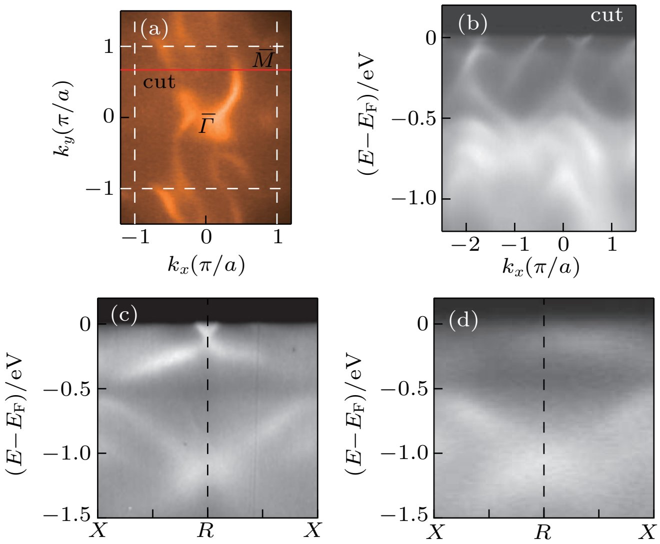

Fig. 4. (a) ARPES map of CoSi (001) surface BZ after grind-polish-sputter-anneal process at 110 eV, (b) cut along $k_y = 0.67\ \pi$ /a as indicated in panel (a) through Fermi arc surface state, (c) bulk band at R point measured at 435 eV, and (d) bulk band of CoSi by mechanical cleave.

Finally, we measure the CoSi single crystals after grind-polish-sputter-anneal by ARPES. In order to obtain the translational symmetry to reveal the electronic structures, sample surfaces must be atomically flat on a macroscopic scale, at least in the size of the beam size. We measure ARPES with a beam size of about 200 μm, the data show that our sample is atomically flat at least in a range of several hundreds of microns. Figure 4(a) clearly shows that two Fermi arcs traverse the (001) surface BZ to connect the projections of nodes ($\bar{\Gamma}$ and $\bar{M}$ points) with opposite Chern number at E_F. In ARPES measurements, different photon energy measurement corresponds to different k_z site in momentum space. The surface states are from several layers of atoms on the surface of the crystal, the band structures of them have no k_z dispersion. When we change the photon energy, none of the surface states change in momentum space. In contrast, for three-dimensional bulk states, their band structures have strong dispersions along the k_z direction. When the photon energy is changed, the band dispersion will be changed. We can distinguish between the surface states and the bulk states by varying photon energy in a three-dimensional system. In order to prove their surface origin, we carry out the ARPES measurements by using different photon energy. That the momentum location of Fermi arcs do not change proves that the Fermi arcs come from surface states, high-resolution cutting-of surface state is shown in Fig. 4(b). Besides, we measure the bulk states at R point by soft-x-ray ARPES at 435 eV as shown in Fig. 4(c). An electron-like band cross with hole-like band at about 0.2 eV below E_F is observed, which is consistent with the calculated bulk band dispersion. It should be noted that comparing with the cut by mechanical cleavage shown in Fig. 4(d) and other ARPES results on CoSi or RhSi,[14,15] the ARPES data collected by the sputter-polish-anneal method have dramatically improved as seen in Figs. 4(a)–4(c).

4. Conclusions

In this work, the grind-polish-sputter-anneal method has proved to be effective in preparing CoSi (001), (011), and (111) surfaces, RHEED, STM, and ARPES have demonstrated that we obtain extremely atomically flat and clean surfaces. And by controlling condition of sputter and anneal process, this method may be applied to other single crystals, and thus expanding its research areas and promising to become a routine process for atomically flat surface preparation.

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