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Change of the surface structure by F doping in BiS_2-based superconductor $CeO_{1-x}F_xBiS_2$

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Abstract

The observation of the surface structure on single crystalline $CeO_{1-x}F_xBiS_2$ (x = 0.5, and 0.7) was performed successfully using a scanning tunneling microscopy. In the sample with x = 0.5, the square lattice composed of Bi atoms was observed. In addition, defects of the surface atoms and streaks were detected on the surface as in the case of $NdO_{0.7}F_{0.3}BiS_2$ single crystal. With further F doping, the surface structure of sample with x = 0.7 showed a novel structure, termed by the "bone" structure. This result suggests that the F concentration affects the surface structure.

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1. Introduction

It is well known that the superconductors with the layered structure such as cuprates and iron-based superconductors show the high temperature superconductivity and the novel electronic structure. Thus, the layered superconductors are paid much attention in the condensed matter physics. Newly discovered BiS_2-based superconductors have a layered structure composed of the conductive BiS_2 layers and non-conductive block layers [1-15]. Up to now, 13 materials which have different block layers have been found in the BiS_2-based family. Among them, LnOBiS$_2$ (Ln = La, Pr, Ce, Nd, Sm, Yb, and Bi) show superconductivity by the substitution of F^- ions for O^{2-}

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ions. The substitution of F^- ion induces not only carrier doping but also the structural change. It has been pointed out that the superconducting transition temperatures of these materials are sensitive to the crystal structure [16,17]. Furthermore, these materials have been pointed out that there is instability against the formation of charge density wave [18-20]. Thus, the measurements which clarify the structure are crucial in the study of these materials. In fact, the novel electronic structure, so-called "checkerboard stripe" structure, has been observed on the surface of the single crystalline $NdO_{0.7}F_{0.3}BiS_2$ using scanning microscopy (STM) and spectroscopy (STS) measurement [21].

Here, we report on the F concentration dependence of the surface structure of BiS_2-based superconductor $CeO_{1-x}F_xBiS_2$ (x = 0.5, and 0.7) by STM. Square lattice consisted of Bi atoms was observed successfully on the surface of single crystalline $CeO_{0.5}F_{0.5}BiS_2$. Furthermore, an additional structure was observed on the surface of the $CeO_{0.3}F_{0.7}BiS_2$ single crystal.

2. Experimental

Single crystalline samples of $CeO_{1-x}F_xBiS_2$ (x = 0.5, and 0.7) were synthesized by a CsCl/KCl flux method in evacuated quarts tubes [22,23]. Mixtures of Bi, Bi_2S_3, Bi_2O_3, BiF_3, and Ce_2S_3 were ground with nominal compositions of $CeO_{1-x}F_xBiS_2$ (x = 0.5, and 0.7). Bi_2S_3 was obtained by sintering the mixtures of Bi and S in the evacuated quartz tube at 500 °C for 10 hours. The mixture of 0.8 g was mixed with CsCl/KCl powder of 5 g, and sealed in an evacuated quartz tube. The tube was heated at 800 °C for 10 hours and cooled down to 600 °C. After this thermal process, the sintered materials were washed by distilled water to remove the flux. Scanning tunneling microscopy (STM) measurements were performed at 4 K in the He gas using a laboratory-build scanning tunneling microscope. A surface of single crystals was prepared by cleaving the sample at 4K in situ. A bias voltage was applied to the sample in all measurements.

3. Results

Figure 1 shows the STM image of the surface structure on the single crystalline $CeO_{0.5}F_{0.5}BiS_2$. The square lattice with a period of approximately 4 Å can be seen in the surface structure (see Fig. 1(b)). This period is corresponding to the lattice parameter a of $CeO_{0.5}F_{0.5}BiS_2$ [4,24]. Because the cleavage occurs between two BiS_2 layers which bond weakly through Van der Waals force, the exposed surface is BiS_2 layer. The observed atoms are considered to be Bi ions as was reported in $NdO_{0.7}F_{0.3}BiS_2$ single crystal [21,25]. In addition to the periodic lattice, there are several defects of the Bi ions. The ratio of the defects is approximately 2% in the observed area shown in Fig. 1(a). Near the defects, there exist the streaks along the each diagonal direction of the square lattice, as shown in white arrows in the Fig. 1(b). These defects and streaks are also reported in $NdO_{0.7}F_{0.3}BiS_2$, though the ratio of the defects is slightly larger in $NdO_{0.7}F_{0.3}BiS_2$. Thus, the replacement of the block layer from $NdO_{0.7}F_{0.3}$ to $CeO_{0.5}F_{0.5}$ does not change the surface structure of the BiS_2 layer a lot.

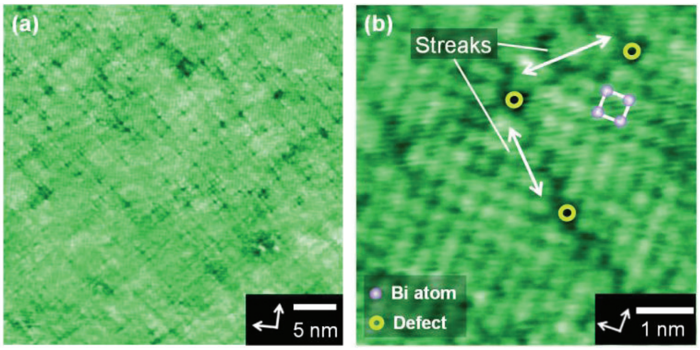

Fig. 1 (Color online)
(a) STM image at the bias voltage of 500 mV on the surface for single crystal of $CeO_{0.5}F_{0.5}BiS_2$. (b) STM image of another area in $CeO_{0.5}F_{0.5}BiS_2$ at the bias voltage of 800 mV. The filled circles formed the square are Bi atoms. The unfilled circles and white arrows show defects, and streaks, respectively.