Synthesis and Physical Property Measurements in Misfit Transition Metal Dichalcogenide (SbS)$_{1.16}$TaS$_2$

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Abstract. We report the single crystal growth and superconducting transition of a misfit layered compound (SbS)$_{1.16}$TaS$_2$. We succeed in the single crystal growth with flux method. The electrical resistivity measurements revealed the superconducting transition temperature of this material as 2.9 K, which was consistent with the previous research. Scanning tunneling microscopy measurements show two kinds of surfaces corresponding to TaS$_2$ and SbS layers, indicating successful growth of the single crystal consist of stacking of these layers.

1. Introduction
Misfit layer compounds form a class of materials in which hexagonal transition-metal dichalcogenides TX$_2$ layer and cubic monochalcogenides MX layer are alternately stacked one by one. They can be described by the general formula “(MX)$_{1+\delta}$TX$_2$”; where M is a metal atom such as Sn, Pb, Bi, Sb, or a rare-earth element; X represents a chalcogen atom (S or Se), and T is a transition-metal atom (Ti, V, Cr, Nb, or Ta). Perpendicular to this commensurate direction, the lattice constant is in an irrational ratio described by the misfit parameter $\delta$ (0.08<$\delta$<0.28). Several combinations of M, T and X have been examined, and their properties, especially superconducting or charge density wave characteristics, have been investigated.

Single crystals of misfit layered compounds are usually grown by chemical vapor transport (CVT) method [1-3]. However, in some of misfit layered compounds, such as (SbS)$_{1.16}$TaS$_2$, the single crystal growth with CVT method cannot be applicable. Thus, these single crystals have not been synthesized and not been examined. Therefore, alternate crystal growth technique is required.

In this study, we tried the single crystal growth of (SbS)$_{1.16}$TaS$_2$ by flux method. Single crystals were successfully obtained for the first time and CDW transition and superconducting transition were examined. Furthermore, scanning tunneling microscopy (STM) observation was performed to examine the structure microscopically.

2. Experimental
Single crystals of (SbS)$_{1.16}$TaS$_2$ was prepared as follows. First, starting materials (powder of Sb (3N), Ta (3N) and S (4N)) were mixed together in a atomic ratio of Sb : Ta : S = 1 : 1 : 3 and sealed in a quartz tube under vacuum (~10$^{-3}$ torr) to synthesis polycrystalline sample. The ample was heated at 800 °C for 2 days. Single crystals of (SbS)$_{1.16}$TaS$_2$ was grown by flux method with KCl / NaCl flux. KCl / NaCl flux was weighed so that the molar ratio of KCl and NaCl is 1 : 1. The polycrystalline sample and the flux were sealed in a evacuated quartz tube (~10$^{-2}$ torr) at a ratio of 1g of sample to 5g of Flux. The
ample was heated at 850 °C for 12 h and cooled down to 630 °C at a rate of 1.0 °C/h. After this thermal process, the sintered materials were washed by ion exchange water to remove the flux. The size of the obtained crystal was 2 × 2 mm² or more. The obtained single crystals were characterized by X-ray diffraction measurements with Cu-Kα radiation using the θ–2θ method. Temperature dependence of in-plane electric resistivity was measured by using the four-point probe method in the range of room temperature to 2K. The surface structure of single crystals was observed by a laboratory-build scanning tunneling microscope (STM). An electrochemically polished Au wire was used as an STM tip. STM measurements were performed at 4.2K. A sample surface was prepared by cleavage at 4.2 K in situ. STM images were obtained with constant current mode.

3. Result and discussion
All the single crystals obtained in the present work were black-grayish. Figure 1(a) shows a X-ray diffraction profile for the single crystal sample of (SbS)₁₁.₁₆TaS₂. The strong peaks are attribute to a set of parallel planes (0 0 l). The observed θ–2θ profile consists with that in the previous study in polycrystalline sample [4]. The calculated lattice constant in the layer stacking direction was 11.56Å.

![Figure 1. X-ray diffraction patterns of (0 0 l) planes for single crystals of (SbS)₁₁.₁₆TaS₂.](image)

The temperature dependence of in-plane resistivity on a single crystal (Fig. 2) shows metallic-type conduction. CDW transition, which is observed at 75 K in 2H-TaS₂, was not observed. A previous study on polycrystalline sample exhibits metallic electrical resistivity [4]. Thus, the behaviour of the electrical resistivity observed in this experiment is consistent with the result on the polycrystalline sample. The superconducting transition temperature was identified as 2.9K. This result is consistent with the prior research [5]. This temperature is higher than that in 2H-TaS₂ of 0.8K [6]. These results indicate successful single crystal growth of (SbS)₁₁.₁₆TaS₂ by the flux method.
Figure 2. Temperature dependence of the electrical resistivity for single crystal of \((SbS)_{1.16}TaS_2\) in the range from room temperature to 2 K. The inset shows the electrical resistivity from 2 K to 4 K, which shows clear superconducting transition at 2.9 K.

Next, we observed the sample surface by using STM technique to examine the structure microscopically. Because of the layered structure of \(TaS_2\) and \(SbS\) layers alternately stacked one by one, two types of the surfaces are expected by cleavage. We observed two kinds of surface, as expected. One is shown in Fig. 3 (a), where a square lattice was observed locally. Because the observed lattice is a square lattice, this surface corresponds to \(SbS\) layer. FFT image shows two kinds of four-fold spots. Invers FFT images corresponding to each four-fold spot are shown in Fig. 3 (c) and (d). Locally rotated domains of the square lattice were seen. This means that the square lattice which came out of the outermost surface is unstable and reconstructed. The angle formed by two lattices is about 30°. This implies that the lattice beneath the square lattice is triangular lattice.

The other surface is shown in Fig. 4 (a), where a triangular lattice is seen. This surface corresponds to \(TaS_2\) layer. The lattice constant is 3.5Å. This value is close to the distance of 3.3Å between sulfur atoms of 2\(H\)-\(TaS_2\) [6]. FFT image shown in Fig. 4 (b) shows not only Bragg spots of triangular topmost sulphur lattice (surrounded by white hexagonal) but also Bragg spots corresponding to the square \(SbS\) lattice (surrounded by green square). This is recognized as the topmost sulphur lattice is affected by the square \(SbS\) lattice beneath the \(TaS_2\) layer, indicating alternate stacking of two types of the layers. There are many other spots which cannot be simply attributed to the triangular and the square lattice. The spots surrounded by orange circles shown in Fig. 4 (c) can be expressed by superposition of reciprocal lattice vectors of the square and triangular lattice. This imply that these spots are caused by the modulation of the topmost \(TaS_2\) layer caused by the \(SbS\) layer just below. However, the rest of the spots cannot be identified at present. These spots do not necessarily appear in every experiment. This needs further considerations.
Figure 3. (a) STM image of the square lattice of the SbS layer on a $10 \times 10$ nm$^2$. $V_{\text{sample}} = 500$ mV, $I_{\text{setpoint}} = 100$ pA. (b) FFT image of (a). The spots surrounded by red squares and pink squares reflect the two kinds of square lattices. (c) (d) The invers FFT images of the spots surrounded by the red square and the pink square in (b), respectively. The invers FFT images (c) and (d) indicate that there are two kinds of square lattices locally, whose relative angle is about 30 degree, in the STM image (a).

Figure 4. (a) STM image of the triangular lattice of the TaS$_2$ layer on a $20 \times 20$ nm$^2$. $V_{\text{sample}} = -150$ mV, $I_{\text{setpoint}} = 100$ pA. (b) FFT image of (a). In (b), the spots surrounded by a white hexagon and the spots
surrounded by a green square are corresponding to the lattice of topmost sulphur atoms and the SbS layer beneath the TaS$_2$ layer, respectively. (c) The same FFT image as (b). The spots surrounded by an orange circle can be expressed by combination of the reciprocal lattice vectors of the square lattice $a_{\text{square}}$ and the triangular lattice $a_{\text{triangular}}$.

4. Summery
We succeed in the single crystal growth of (SbS)$_{1.16}$TaS$_2$ with flux method. This is the first report of the single crystal growth of misfit compound with flux method. The electrical resistivity measurements revealed the superconducting transition temperature of this material as 2.9 K. The scanning tunneling microscopy measurements showed two kinds of surfaces corresponding to TaS$_2$ and SbS layers, indicating successful growth of the single crystal consist of stacking of these layers.

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