Microscopic Study of Domain Structure in Charge Density Wave States in 2H-TaS\textsubscript{1.8}Se\textsubscript{0.2}

S Ohta\textsuperscript{1}, Y Fujisawa\textsuperscript{2}, S Demura\textsuperscript{3} and H Sakata\textsuperscript{4}

\textsuperscript{1}Department of Physics, Tokyo University of Science\textsuperscript{1}, Shinjyuku-ku, Tokyo 162-8601, Japan
\textsuperscript{2}Okinawa Institution of Science and Technology\textsuperscript{2}, Onna-son Kunigami-gun Okinawa 904-0495, Japan
\textsuperscript{3}College of Science and Technology, Nihon University\textsuperscript{3}, Chiyoda-ku Tokyo 101-0062, Japan

E-mail: 1217606@ed.tus.ac.jp

Abstract. Transition metal dichalcogenides 2H-TaS\textsubscript{2} and 2H-TaSe\textsubscript{2} show charge density wave (CDW) state and superconductivity. It has been reported that elemental substitution of chalcogenide suppresses the CDW and enhances superconductivity. However, how the CDW order is suppressed by the substitution has not been clarified yet. To clarify this, we performed real space observation of the CDW state in the commensurate phase of 2H-TaS\textsubscript{1.8}Se\textsubscript{0.2} by scanning tunneling microscopy. The existence of domains separated by walls at which the phase of the CDW shifts was observed. The change in the electronic state on the domain boundaries in 2H-TaS\textsubscript{1.8}Se\textsubscript{0.2} was not as drastic as that in 1T-Fe\textsubscript{1-x}Ta\textsubscript{x}S\textsubscript{2}.

1. Introduction

Transition metal dichalcogenides (TMDCs) show various quantum phenomena such as charge density wave (CDW) or superconductivity. In some TMDCs, it has been reported that the CDW order is suppressed and superconductivity is enhanced by an elemental substitution. For example, superconductivity emerges by substitution of Ta for small amount of Fe about a few percent in 1T-TaS\textsubscript{2} [1]. In 2H-TaS\textsubscript{2}, which is another polytype of 1T-TaS\textsubscript{2}, when Se is substituted by S, i.e. 2H-TaS\textsubscript{2}.\textsubscript{.8}Se\textsubscript{.2}, CDW transition disappears between 0.35 < x < 1.48, and superconducting transition temperature (T\textsubscript{c}) about 4 K appears between 0.1 < x < 1.9, whereas T\textsubscript{c} of pristine 2H-TaS\textsubscript{2} and 2H-TaSe\textsubscript{2} is 0.8 K and 0.14 K, respectively [3].

When the superconductivity emerges, how the commensurate CDW order is suppressed is an interesting problem. In 1T-TaS\textsubscript{2}, the appearance of the peculiar domain structure of the CDW and the drastic change of the electronic state on the CDW domain boundaries were observed when the superconductivity emerges [2].

In this study, we examined the CDW states in 2H-TaS\textsubscript{2} and 2H-TaS\textsubscript{1.8}Se\textsubscript{0.2} microscopically by scanning tunnelling microscopy (STM) to clarify how the CDW order is suppressed by Se doping.
2. Experimental
The polycrystal samples of $2H$-$TaS_2$-$xSe_x$ ($x=0$ and 0.2) were prepared by heating the mixtures of Ta (Kojyundo Chemicals Co. Ltd., 99.999%), S (Kojyundo Chemicals Co. Ltd., 99.99%), and Se (Kojyundo Chemicals Co. Ltd., 99.99%), with nominal compositions in vacuumed quartz tubes at 900°C for 3 days. The single crystals were grown from the polycrystals by chemical vapor transport method using iodine (Wako Chemicals Co. Ltd., 99.5%) as transport agent [4]. The thermal process was the followings. First, the tube was heated up to 900°C in the source zone and 800°C in the growth zone for 8 hours, then, kept for a week, finally, cooled down to room temperature for 16 hours.

Figure 1 shows the temperature dependence of electrical resistivity for $x = 0$ and 0.2 samples. The CDW transition temperature ($T_{CDW}$) can be defined as the temperature where the slope changes abruptly, and $T_c$ is defined as the temperature at which the resistivity becomes zero. From the results, $T_{CDW}$ and $T_c$ were determined as 55 K and 2.6 K for $x = 0.2$ sample, respectively. In $x=0$ sample, $T_{CDW}$ was 78K and $T_c$ was below 2.2 K. The observed suppression of the CDW and the enhancement of the superconductivity in $x = 0.2$ sample are consistent with the results reported in a previous paper [3].

![Figure 1](image_url)

Figure 1 (a) The temperature dependence of the normalized electrical resistivity in $2H$-$TaS_2$ (blue line) and $2H$-$TaS_{1.8}Se_{0.2}$ (red line). (b) Resistivity below 100 K. (c) Resistivity below 5 K.

STM measurements were performed with a laboratory-built STM at 4.2 K. The electrochemically polished Au wire was used as a STM tip. The clean surface of the single crystal was prepared by cleavage at 4.2 K in situ. A bias voltage was applied to the sample in all measurements.

3. Result
Figure 2 (a - d) show the typical STM images and the FFT images of the samples ($x = 0$ and 0.2). The STM image of $x = 0$ sample (Fig. 2 (a)) indicates the triangular lattice of the chalcogenide atoms and 3 x 3 CDW. Corresponding spots can be seen in the FFT image shown in Fig. 2 (b). The STM image of $x = 0.2$ (Fig. 2 (c)) also shows the triangular lattice of the atoms and the superstructure of the CDW with rather large background roughness. The period of the superstructure is same as that of $x = 0$ and corresponding spots can be seen in FFT image shown in Fig. 2 (d). In addition, there are several phase shifts in $x = 0.2$ sample, at which the phase of the modulation wave slips off for $2\pi/3$ or $4\pi/3$, i.e. slips of one or two atoms. Figure 2 (e) shows the inverse FFT image obtained from FFT spots corresponding to atoms and one of the three CDW vectors marked in Fig. 2 (d). As indicated by white arrows, the crest of CDW shifts by one atom near the center of the figure. As can be seen from the figure, a row of such phase shifts, indicated by white broken line, composes a wall which divides the commensurate region into domains.
4. Discussion

From the STM measurements for $2H$-TaS$_2$, we obtained the following two results. The first is the emergence of the phase shifts of the CDW with Se doping. The existence of phase shifts suppresses the coherence of the CDW. Because the contrast of the CDW in the STM images does not change with Se doping, the amplitude of the CDW does not seem to be reduced. Thus, the reduction of $T_{CDW}$ observed in electric resistivity measurements in the sample of $x = 0.2$ is thought to be caused by the suppression of the coherence in the CDW.

The second is the lack of the contrast on the domain walls in STM images. In the STM image shown in Fig. 2 (c), almost no contrast at the domain wall can be seen. This indicates that the electronic state on the domain wall does not change from that in the domains. The same result was obtained in the STM images obtained with negative bias voltage. These results are quite contrasted to that observed in $1T$-Fe$_x$Ta$_{1-x}$S$_2$, where the contrast of the domain wall is quite different from that in the domain in both bias voltages [2]. In $1T$-Fe$_x$Ta$_{1-x}$S$_2$, the possibility that the metallic domain wall is responsible to the superconductivity has been pointed out. In $2H$-TaS$_2$, however, because the electronic state on the wall is close to that on the domains, the wall is not responsible to the superconductivity. Thus the enhancement of the superconductivity observed in $2H$ compound is responsible to the change in the electronic state in the domains by Se substitution unlike $1T$ compounds.

Figure 2 (a - b) STM image of $2H$-TaS$_2$ taken at +300 mV and 300 pA on 20 nm × 20 nm field of view and the FFT image. (c - d) STM image of the $2H$-Ta$_{1-x}$Se$_{0.2}$ taken at +500 mV and 200 pA on 15 nm × 15 nm field of view and the FFT image. (e) Inverse FFT image obtained from FFT spots corresponding to atoms and one of three CDW vectors marked with a white circle in Fig. 2 (d). White broken line indicates a domain wall, which consists of a row of phase shifts.
5. Summary
We performed STM observations in $2H$-TaS$_2$,Se$_x$ ($x = 0.2$), which shows reduced $T_{\text{CDW}}$ and enhanced $T_c$. We found the emergence of the several phase shifts of the CDW, which reduce the coherence of the CDW. We also found the change in the electronic states on the domain boundaries in $2H$-TaS$_{1.8}$Se$_{0.2}$ was not as drastic as that in $1T$-Fe$_x$Ta$_{1-x}$S$_2$.

References
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