## A Study of Charge-Density-Waves Associated with the Periodic Lattice Distortion in 1*T*-VSe<sub>2</sub> Using a Low Temperature Scanning Tunneling Microscope

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We have investigated the charge-density-wave (CDW) formation associated with the periodic lattice distortion in 1T-VSe<sub>2</sub> by using a low temperature scanning tunneling microscope (STM) at 4.2 K. To clarify the atomic and the superlattice structures, we used a layer etching technique to fabricate a step of 1T-VSe<sub>2</sub> with a height of  $\approx 6$  Å and investigated the atomic structures at 4.2 K on the newly etched region. The measured images showed a clear isotropic  $4 \times 4$  charge-density-wave structure which was different from the previous results obtained by Coleman *et al.* The high resolution STM images at 4.2 K showed that the center of CDW was surrounded by three surface atoms from those images we were able to identify those atoms as Se. The surface Se atoms determined the STM pattern because of their proximity to the scanning tip.

A reduction of dimensions leads to new and interesting phenomena in physics. No real materials are strictly low dimensional, but there are a few that are highly anisotropic so that they can be considered as quasi oneor two-dimensional. Among these low dimensional materials, the transition metal dichalcogenides (TMDs) show quite interesting physical properties [1]. One of those properties is the formation of CDW due to the periodic lattice distortion [1–2]. Many studies of the TMDs, particularly, related to CDW have been done using electron diffraction, resistivity measurements, and more recently scanning tunneling microscopy [1–4].

The TMDs are layered materials consisting of sandwiches with the formula  $MX_2$  where M is a transition metal and X is a chalcogenide atom. The  $MX_2$  sandwiches can be coordinated either as an octahedral or a trigonal prismatic. These sandwiches can then be stacked in different ways with pure octahedral, pure trigonal, or mixed coordination in the different layers. The bonding within a layer is covalent, while the bonding between sandwiches is of a van der Waals type. The 1T type of TMDs has octahedral coordination between the M atoms and the X atoms. Materials exhibiting 1Tphases are for example TaS<sub>2</sub> (CDW onset temperature is 600 K), TaSe<sub>2</sub> (600 K) and VSe<sub>2</sub> (140 K). TaS<sub>2</sub> and TaSe<sub>2</sub> have relatively strong CDWs, while the CDW in  $VSe_2$  is weaker [1,4].

The CDW pattern of 1T-VSe<sub>2</sub> is known to be quite different from those of the typical 1T types, 1T-TaS<sub>2</sub>, and 1T-TaSe<sub>2</sub> which show the  $\sqrt{13} \times \sqrt{13}$  CDW superlattice, although they have the same crystal structures [1]. This might be due to the fact that 1T-VSe<sub>2</sub> has rather a high value of  $c_o/a_o$  (= 1.82) ratio with the lattice constants  $a_o = 3.35$  Å and  $c_o = 6.10$  Å compared with 1T-TaS<sub>2</sub> ( $c_o/a_o = 1.75$ ) and 1T-TaSe<sub>2</sub> ( $c_o/a_o = 1.80$ ) [1,4]. This ratio influences the strength of the electronion interaction and is critical in determining the CDW pattern. Since preparation of highly stoichiometric single crystals of 1T-VSe<sub>2</sub> is difficult [5] and, in particular, because its CDW transition temperature is relatively low, the study of CDWs in 1T-type TMDs has mainly concentrated on 1T-TaS<sub>2</sub> and 1T-TaSe<sub>2</sub>, which have very large CDW amplitudes even at room temperature [4,6]. Only Coleman et al. studied the CDW formation in this material using low-temperature STM at low temperatures and observed that STM scans show a variability from run to run, which suggests unequal amplitudes for the three components of the triple CDW directions, although they had the dominant  $4 \times 4$  superlattice structure within the layer plane [4,6].

Many different factors make the TMDs suitable for STM imaging. The layered structure makes them easy to



Fig. 1. An STM image (1340 Å  $\times$  1340 Å) of a 1*T*-VSe<sub>2</sub> single crystal showing a newly etched region (darker regions) after a layer etching at 4.2 K. The tunneling current and bias voltage were 1 nA and -200 mV, respectively.

cleave, and the cleavage leaves large flat surface areas [9–10]. The topmost chalcogenide layer is inert and leaves no dangling bonds at the surface, leading to a long-time fresh surface, even under ambient conditions. Since the CDW changes the Fermi surface, it changes the density of states at the Fermi level  $(E_F)$  and modifies the electronic wave functions. STM probes these wave functions and is an excellent tool for investigation of CDWs. Not only does the chalcogenide layer influence the STM imaging, but also the transition metal can give some contributions [9].

In this study, we investigated the CDW formation associated with the periodic lattice distortion in 1T-VSe<sub>2</sub> by using a low-temperature STM at 4.2 K. To clarify the atomic and the superlattice structures of 1T-VSe<sub>2</sub>, we obtained very high-resolution STM images. We fabricated steps of 1T-VSe<sub>2</sub> with height of  $\approx 6$  Å by using a layer etching technique to make a clean surface and investigated the electronic and the atomic structures on the newly etched region at 4.2 K. The measured STM images revealed well-developed isotropic 4×4 CDW structures with surface atomic structures at 4.2 K. The high-resolution STM images at 4.2 K clearly showed that the center of the CDW was surrounded by three surface atoms, and we could identify the three surface atoms as Se.

Single crystals of 1T-VSe<sub>2</sub> were grown by the usual iodine transport method. The samples were cleaved at room temperature in air and set in the STM unit, which was placed in the center of a doubly shielded cryostat in a He exchange gas environment. The STM unit was cooled very slowly to 4.2 K for the low-temperature ex-



Fig. 2. (a) An STM image of 1 *T*-VSe<sub>2</sub> after one molecular layer etching near one of the boundary regions at 4.2 K. The sample bias current and voltage were 1 nA and -200 mV, respectively. (b) The cross-sectional profile along the line denoted by the straight white line in the STM image. The step height was estimated as  $\approx 6 \text{ Å}$ .

periments. Mechanically polished Pt/Ir tips were used. All images were obtained in the constant current mode. Due to the weak van der Waals force between each layer in the TMDs, it was possible to etch away individual layers in a well-defined manner using STM [7,10]. Using this technique, it was possible to make very clean new layers in the TMDs. This also enabled us to study the atomic and the electronic structures on the new clean surfaces precisely under the same tunneling condition.

To check the CDW formation in the samples, we measured the resistivity as a function of temperature. The resistivity measurements showed an abrupt decrease in conductivity around 100 ~ 140 K which depend on the growing conditions and which indicated the CDW transition. We have checked a flesh surface at room temperature before cooling it down and observed the typical triangular atomic structure with a lattice constant  $\approx 3.5$ Å. Figure 1 shows a STM image (1340 Å × 1340 Å) of the 1*T*-VSe<sub>2</sub> single crystal at 4.2 K with a newly etched



Fig. 3. (a) A high-resolution STM image of the surface of the newly etched region in Fig. 1 at 4.2 K. The clear isotropic  $4 \times 4$  CDW modulations can be seen. (b) Profile of the z-deflection along the line indicated in the Fig. 3(a). The z-deflection is dominated by a CDW with a small atomic modulation. The total z-deflection is estimated as  $\approx 1.0$  Å.

region (darker regions). The tunneling current and the bias voltage were 1 nA and -200 mV, respectively. Originally, this area consisted of a very rough surface due to contamination during the cooling process from room temperature to 4.2 K. We did not see any CDW superlattice and atomic structures on this surface at all. By making a continuos scanning process with a relatively small tunneling resistance on the specified area, we could remove a large part of the layer and make a new clean surface as shown in the dark regions of Fig. 1 by using the layer etching method. In this new layer,  $4 \times 4$  CDW superlattice and superposed triangular atomic structures with a lattice constant  $\approx 3.5$  Å were resolved all over the etched surface. Figure 2(a) shows one of the boundary regions of the etched surface at 4.2 K. Figure 2(b) shows a cross-sectional profile along the line indicated by the white line in Fig. 2(a). The step height was estimated to be about 6 Å, which was equivalent to, within experimental error, the lattice constant along the *c*-axis [1,4]. It shows that the step is made up of one Se-V-Se molecular layer dependent on the surface atoms. The STM images near the boundary region show two regions separated by a mono step.

To study the atomic structures in this new layer in



Fig. 4. A high resolution contour plot of 1T-VSe<sub>2</sub> at 4.2 K near the CDW maximum. The center of the CDW is surrounded by three surface Se atoms.

more detail, we also measured the STM image with small scan areas of  $\approx 62$  Å  $\times 62$  Å. Figure 3(a) shows a detailed STM image of the surface of a newly etched region. A clear CDW superlattice with traces of atomic structures is visible in this image.  $4 \times 4$  CDW superlattices with surface atoms extending over three atomic rows with a repeat spacing of  $4a_o$  are clearly resolved in the etched layer. The profile of the STM scan in the Fig. 3(b) shows a pattern of well-defined atoms with a CDW modulation superimposed as a smooth undulation with a wavelength of  $4a_0 = 14$  Å. The amplitude of the CDW is estimated as  $\approx 1.0$  Å, which is relatively small compared with those of 1T-TaS<sub>2</sub> ( $\approx 3-4$  Å) and 1T-TaSe<sub>2</sub> ( $\approx 3-5$  Å) [4,6]. On the other hand, the triangular atomic lattice has an amplitude  $\approx 0.4$  Å, as in Fig. 3(b). We also note that the maximum z-deflection consists of two surface atoms with almost equal amplitudes. The STM images obtained by Coleman *et al.* [4] show a variability from run to run, which suggests unequal amplitudes for the three directional components of the CDW. One diagonal direction shows a strong enhancement, and the other two CDW directions show very weak enhancements at a wavelength of  $4a_{o}$ . However, our STM image shows rather an isotropic CDW pattern superimposed on the atomic modulations. We believe that this discrepancy was caused by differences in sample growing and the STM tip conditions.

Most of the TMDs have a triangular lattice, which has been studied in NbSe<sub>2</sub>, TaS<sub>2</sub>, TaSe<sub>2</sub>, and MoTe<sub>2</sub>. In these materials, it is not possible to distinguish whether the images are due to the surface chalcogenide atoms or due to the underlying metal atoms because they have the same in-plane lattice constants. Kikuchi and Tskuada [11] calculated STM images originating from the chalco-716-

genide atoms, at least for  $NbSe_2$  and  $TaS_2$ . They made band calculations and treated the order parameter as a variable, not explicitly taking the electron-phonon interaction into account.  $WTe_2$  has inequivalent lattice constants and was first believed to show the W atoms rather than the surface Te atoms. However, tip effects and the surface electronic structure make it possible to interpret the images as Te atoms [12]. Although scanning tunneling spectroscopy studies of NbSe<sub>2</sub> revealed that the imaging of Nb or Se atoms depended on polarity, this is still controversial [13]. The possibility of imaging the atomic lattice and the CDW simultaneously gives an opportunity for determining the relative orientations and the degree of commensurability. However, STM images are not only sensitive to the local density of states, but also to a number of other effects which will influence the tunneling matrix elements. According to recent results, it is even possible to observe the effect coming from the second layer far from the tunneling tip in the poly-type TMDs [10,14].

The question of whether the STM images show the top layer Se atoms or the underlying V atoms is also not trivial in the case of 1T-VSe<sub>2</sub>, because the half filled d band at the Fermi level contributed by the V atoms which protrudes vertically to the surface. Based on this argument, we assume that the atomically resolved STM image reflects the positions of the V atoms. Certainly, the  $4 \times 4$ clusterings of 1T-VSe<sub>2</sub> are induced by the *d* electrons of V, and their highest bands are dominated by the V atoms [9]. However, the high resolution contours of constant z-deflection in Figure 4 show that the CDW maxima are located in between two surface atoms. We also note in the profile of the STM scan of Fig. 3(b) that the maximum of the CDW is located approximately midway between the two surface atoms. Taking the CDW maximum as being located at the V position, we can identify the three atoms near the CDW maximum as surface Se atoms, which means the surface Se atoms determine the STM pattern because of their proximity to the scanning tip.

In summary, we have investigated the atomic and the electronic structures on the surface of 1T-VSe<sub>2</sub> prepared by the layer etching technique using a low temperature scanning tunneling microscope at 4.2 K. The high reso-

lution STM images at 4.2 K clearly showed that the center of the CDW was surrounded by three surface atoms, which we could identify as Se atoms. Our STM image at 4.2 K also showed rather an isotropic CDW pattern with no enhanced CDW intensity along one particular direction.

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## REFERENCES

- J. A. Wilson, F. J. DiSalvo and S. Mahasan, Adv. Phys 24, 117 (1975).
- [2] F. J. Di Salvo, B. J. Bagley, J. M. Voorhoeve and J. V. Waszczak, J. Phys. Chem. Solids **34**, 1357 (1973).
- [3] R. H. Friend, D. Jerome, R. F. Frind and A. J. Yoffe, J. Phys. C10, 1013 (1977).
- [4] R. V. Coleman, B. Giambattista, P. K. Hansma, A. Johnson, W. W. McNairy and C. G. Slough, Adv. Phys. 37, 559 (1988).
- [5] K. Tsutsumi, Phys. Rev. B26, 5756 (1982).
- [6] B. Giambattista, C. G. Slough, W. W. McNairy and R. V. Coleman, Phys. Rev. B41, 10 082 (1990).
- [7] B. Parkinson, J. Am. Chem. Soc. **112**, 7498 (1990).
- [8] A. P. Volodin and J. Aarts, Physica C235, 1909 (1994).
- [9] For example and R. Wiesendanger, Scanning Probe Microscopy and Spectroscopy : Methods and Applications 1 (Cambridge University Press, Cambridge, 1994).
- [10] J.-J. Kim and H. Olin, Phys. Rev. B52, R14 388 (1995).
- [11] A. Kikuchi and M. Tsukada, Surface Science **326**, 195 (1995).
- [12] S. L. Tang, R. V. Kasowski and B. A. Parkinson, Phys. Rev. B39, 9987 (1989).
- [13] H. Bando, K. Endo, N. Morita, W. Mizutani, M. Shigeno, K. Kajimura, A. Homma, K. Watanabe, S. Wakiyama and H. Tokumoto, J. Vac. Sci. Technol. A6, 344 (1988).
- [14] W. Han, E. R. Hunt, O. Pankratov and R. F. Frindt, Phys. Rev. B50, 14746 (1994).