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Modification of local electronic state of MoS_2 under applied electric field studied by in-situ near edge X-ray absorption fine structure

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1 Introduction

Two-dimensional transition metal dichalcogenides have attracted considerable attention as one of the most promising materials for realizing nanoelectronics and spintronics devices in recent years, due to the novel electronic and electric properties [1-5]. MoS_2 shows high electron transport properties with an indirect band gap of 1.2 eV (single-layer MoS_2 has a direct band gap of 1.8 eV), high carrier mobility over 500 cm^2/Vs and high on/off-current ratios of high as 10^8 [2]. In order to obtain further high electron transport properties, the elucidation of the basic physical properties, such as an electronic structure is indispensable. Here studies were conducted for the electronic state of MoS_2 under the applied electric field by employing in-situ near edge X-ray absorption fine structure (NEXAFS). We have successfully demonstrated that the local electronic state was modified by the electric field-effect.

2 Experiment

Figure 1 (a) shows a schematic drawing of the experimental setup of the in-situ NEXAFS measurement. We fabricated a metal-insulator-semiconductor (MIS) capacitor using MoS_2 as a semiconductor layer. Using this device structure, the modification of the electronic state under the applied electric field was investigated in-situ by fluorescence NEXAFS. P-type Si(100) with 300 nm oxide layer was used as a substrate. A MoS_2 film was synthesized on the SiO_2 substrate by the solution-processed method using *N*-methylpyrrolidone as dispersing agent [6]. The layer number of MoS_2 was approximately 20 layers. The specimen was then introduced into a vacuum chamber and a Ru electrode was deposited by RF magnetron sputtering through a shadowing mask. The deposition rate was 0.5 nm/min and the film thickness was 30 nm. By employing Ru as an electrode, the synchrotron X-ray beam can be irradiated selectively on the MoS_2 device region by tracing the Ru $L\alpha$ fluorescence X-ray emission from the Ru electrode (Fig.1 (b)). This enables us to improve signal-to-background ratio. NEXAFS measurements were conducted at BL-27A of the soft X-ray synchrotron radiation beamline of Photon Factory, KEK [7,8]. NEXAFS spectra of the device were measured by fluorescence yield and a region of interest (ROI) at a respective fluorescence peak was used for the detection of the characteristic X-ray from the element of interest.

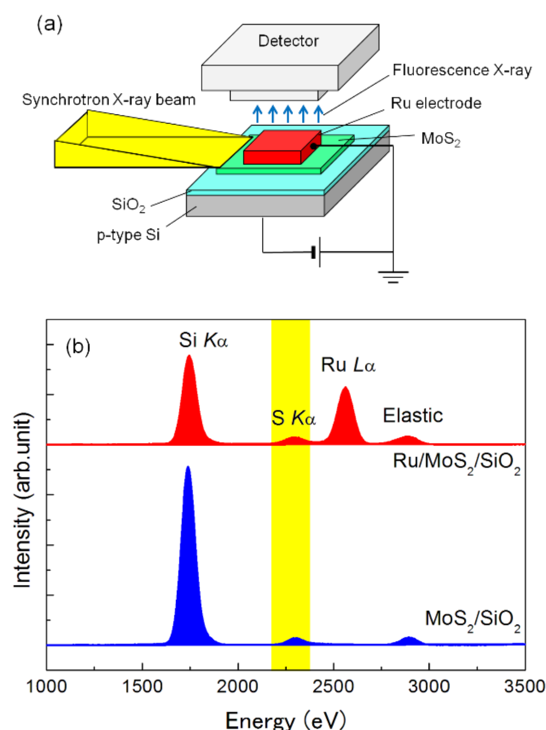

Fig. 1: (a) A schematic drawing of the experimental setup of the in-situ NEXAFS measurement. (b) Multi-channel analyzer (MCA) spectra taken from the $Ru/MoS_2/SiO_2$ region (upper) and the MoS_2/SiO_2 region (lower) in the MoS_2 device.

3 Results and Discussion

Figure 2 shows S *K*-edge and Mo L_3-edge fluorescence NEXAFS spectra taken under applied electric field. The conduction band (CB) minimum in MoS_2 consists of 3*p*- and 3*s*-like states in addition to Mo 4*d*-like states. An intense peak in the Mo L_3-edge NEXAFS (around 2524 eV) is assigned to Mo $2p_{3/2}$ to unoccupied Mo 4*d* band at the CB minimum. On the other hand, an intense peak in the S *K*-edge NEXAFS (around 2471 eV) is attributed to S 1*s* to S 3*p*-like states mixed into the Mo 4*d* band. Another peak in the S *K*-edge spectrum (around 2481 eV) corresponds to transition of S 1*s* electrons to anti-bonding S 3*p*-like state, and a similar peak in the Mo L_3-edge spectrum (around 2533 eV) corresponds to transition of Mo $2p_{3/2}$ electron to unoccupied Mo 5*s*-like states [9]. When electric fields are applied to the MoS_2 device, the spectral changes are clearly seen in the S *K*-edge spectra (Fig.2 (a)). These significant changes arise only at around

2471 eV. This indicates that the modification of the electronic state by the applied electric field arises only in the CB minimum. It is also found that the intensity of the peak increases and decreases according to the polarity of the electric field; the S *K*-edge spectra taken at +10 V and -10 V applied electric field cause the decrease and increase of the peak intensity. This is presumably related to accumulation and depletion of electrons by the electric field-effect. In the Mo L_3-edge NEXAFS spectra, on the other hand, neither the intensity change nor the peak shift is observed under the applied electric field. This suggests that the modification of the electronic state by the field effect might be only around S site. Although the mechanism of the modification of the electronic states caused by the field effect has not been elucidated completely, the present study provides the clue for the essential understanding of the electric transport properties of two-dimensional transition metal chalcogenides.

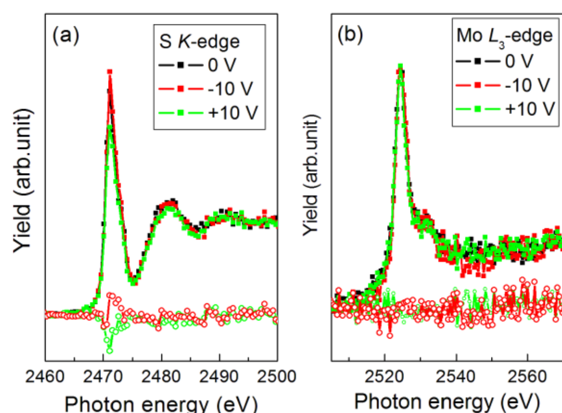

Fig. 2: (a) S *K*-edge and (b) Mo L_3-edge fluorescence NEXAFS spectra of the Ru/MoS_2/SiO_2 device under the applied electric field of 0 V (black square), -10 V (red square) and +10 V (green square). (lower) Difference spectra between the spectrum taken at -10 V and at 0 V (red open circle) and between the spectrum taken at +10 V and at 0 V (green open circle).

References
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