PEEM and Micro-UPS Studies of Cleaved and Exfoliated Molybdenum Disulfide Surfaces

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Thin films of molybdenum disulfide (MoS_2) are generally exfoliated from a mineral crystal. Impurities and contaminants of mineral origin may spoil the expected functions of MoS_2 thin-film devices because they have a strong influence on the properties of the exfoliated films. The effects of surface contaminants on cleaved or exfoliated MoS_2 surfaces were investigated using photoemission electron microscopy and selected-area ultraviolet photoelectron spectroscopy under several exfoliation conditions. The chemical composition and crystallinity of surfaces were also investigated using Auger electron spectroscopy and electron diffraction. The bulk crystal included a limited number of contaminated interfaces, at which the crystal was easily cleaved. Therefore, repeated exfoliations are required to expose a clean surface for exfoliated films. Annealing at ca. 400°C in a vacuum was effective to reduce contamination of the cleaved MoS_2 surface. [DOI: 10.1380/ejsnt.2017.115]

Keywords: Photoemission electron microscopy (PEEM); Photoemission; Work function; Layered materials; Molybdenum-disulfide

I. INTRODUCTION

After Novoselov *et al.* [1] reported a large carrier mobility for monolayer graphene transferred onto a Si wafer by mechanical exfoliation, many two-dimensional (2D) atomic-layered materials have been extensively investigated. Transition-metal dichalcogenides (TMDCs) are one of layered materials with a chemical form of MX_2 , where M represents a transition-metal such as Ti, Zr, Hf, V, Nb, Ta, Mo, and W, and X represents a chalcogen, S, Se and Te. TMDCs have layered structures, where many layers of a chalcogen-metal-chalcogen sandwich are stacked by weak van der Waals forces, so that the crystal can be easily cleaved along the van der Waals gap. MoS_2 is one TMDC that is available as a single crystal from mineral resources. Although there have been many studies on MoS_2 as a solid-state lubricant [2], catalyst [3], and a battery material [4], the semiconductor properties of a few layers of MoS_2 have recently attracted considerable attention, for example, the high electronic mobility of an n-type field-effect transistor (FET) fabricated with monolayer MoS_2 [5]. 2H-MoS_2 , which is the more abundant of its polytypes, is a semiconductor with an indirect bandgap of 1.29 eV for the bulk crystal. However, monolayer MoS_2 instead has a direct bandgap of 1.90 eV [6]. The valence band structures of MoS_2 surfaces were reported from ultraviolet photoemission spectroscopy (UPS) [7–9] and angle-resolved photoemission spectroscopy (ARPES) [10] measurements, where Mo 4d and S 3p derived bands were observed.

Although MoS_2 films can be synthesized nowadays by chemical vapor deposition (CVD) [11, 12] and other techniques [13, 14], there are still many studies that use mechanically exfoliated films from mineral crystals for the measurement of physical properties [5–7, 15–19]. Even though the mineral crystals are more or less considered to be inert, there have been few studies on the impurities of MoS_2 surfaces. Carbon contamination was reported to affect the band-bending of the MoS_2 crystal [15], and the change of the work function suggests contamination of the surface [18, 19]. The desorption of sulfur atoms from MoS_2 by annealing [20] and vacancy formation [21], and changes in polytypism [22] by exposure to an electron

beam could indicate a certain instability of the surface.

Reported work functions for MoS_2 are scattered from 4.5 to 5.4 eV, depending on the study [7, 15–18]; therefore, surface impurities and defects may play an important role. After cleaving under atmospheric conditions, the work function of the MoS_2 surface changed over time [18]. Other studies have shown that the valence band spectra are strongly dependent on annealing procedures [7, 9]. McMenamin and Spicer reported that a clean surface was obtained by exfoliation in a vacuum or annealing at 400°C for 6 h in a vacuum [7]. These studies suggest that MoS_2 the surface is strongly affected by the source of the crystal and the preparation of the surface. Therefore, it is important to evaluate the contamination of MoS_2 surfaces prepared by mechanical exfoliation and to find a process to obtain MoS_2 with a clean surface.

In the present study, we have prepared cleaved and exfoliated MoS_2 surfaces in an air atmosphere or in a vacuum. The surface electronic structures were characterized using photoemission electron microscopy (PEEM) and selected-area UPS (micro-UPS). The chemical composition and surface crystallinity were characterized using Auger electron spectroscopy (AES) and Wissenberg reflection high-energy electron diffraction (W-RHEED). In addition, annealing procedures to reduce contamination of the MoS_2 surface were investigated.

II. EXPERIMENT AND APPARATUS

MoS_2 crystals of natural origin, which had been characterized using X-ray diffraction and Raman spectroscopy measurements, were purchased from EM Japan Co., Ltd. Adhesive tape was used to cleave and exfoliate the crystals, and the exposed surfaces were then characterized using PEEM, micro-UPS, atomic force microscopy (AFM), AES and W-RHEED. Two types of samples were prepared, cleaved bulk crystals and exfoliated thin flakes transferred onto Si wafers. The cleaving of the bulk crystal was conducted under vacuum or under an air atmosphere for comparison. A bulk MoS_2 crystal was mounted on a Mo sample holder, as schematically shown in Fig. 1(a). Adhesive tape was then pressed on the front

FIG. 1. (a) Schematic illustration of the sample holder with adhesive tape for cleavage. (b) Photograph of the cleaved MoS₂ crystal mounted on the holder. (c) Optical microscopy image of MoS₂ TFs transferred onto a Si wafer.

side of the crystal and removed to cleave the crystal. For cleavage under vacuum, the tape was removed in a load-lock chamber (ca. 10^{-5} Pa), and the cleaved crystal was immediately transferred to the PEEM ultrahigh vacuum (UHV) chamber (ca. 10^{-7} Pa) for surface analysis. Only a single cleavage could be performed for each pumping down of the chamber; therefore, it was difficult to obtain a visibly smooth surface, and the surface was rather fuzzy due to the turning up of thin MoS₂ layers. On the other hand, smooth surfaces were selected from several exfoliations attempts under atmospheric conditions because the flatness of the specimen is crucial to obtain a good PEEM image. Figure 1(b) shows a photograph of a crystal surface mounted on the sample holder, which was exfoliated under an air atmosphere. In this case, the exfoliated crystal was installed into the load-lock of the vacuum chamber and then transferred to the PEEM stage under UHV.

Samples of thin flakes (TFs) were prepared in the atmosphere by repeated exfoliation of MoS₂ films. Exfoliated films from the crystal onto the tape were again exfoliated by another tape, and the procedure was repeated approximately ten times prior to transfer onto a naturally oxidized Si wafer. Figure 1(c) shows an optical microscopy image of a TF on a Si substrate. A relatively large TF was selected for optical microscopy and PEEM observations. The thickness of the TF was measured as ca. 800 nm using AFM.

Two separate UHV apparatus were used in the present study. One was used for PEEM and micro-UPS, which has been described elsewhere [23]. The PEEM apparatus (IS-PEEM, FOCUS GmbH) is equipped with a micro-analyzer [24] and three UV sources: a Hg lamp (ca. 4.9 eV), Xe lamp (ca. 6.7 eV) and a He discharged lamp (He-I: 21.2 eV). The sample could be heated up to ca. 900°C by electron bombardment from the backside during PEEM observation. The base pressure of the PEEM apparatus was ca. 10^{-8} Pa. Valence band spectra were measured with the PEEM system using the He-I source. A region of interest on the image can be selected by an iris aperture at the first imaging plane. Electron spectroscopy can then be performed for the selected area down to a few square micrometers. It should be noted that the photoelectron acceptance angle is strongly dependent on the size of the contrast aperture (CA) at the back focal plane of the PEEM apparatus. One of five CAs with different

diameters can be selected with the present PEEM apparatus to optimize the image. A smaller CA generally results in good spatial resolution, but with a loss of intensity. The role of the CA is to limit the acceptance angle of the photoelectrons, and it will thus affect the shape of the valence band spectra.

The W-RHEED and AES system, which uses a “macro” electron beam (ca. 100 μm), which is described elsewhere [25, 26]. The samples are mounted on a Ta ribbon and can be heated by passing a DC current through the Ta ribbon. The crystallinity and chemical composition of the surfaces were measured with this apparatus.

III. RESULTS AND DISCUSSION

A. Cleaved bulk crystal surfaces

Typical PEEM images of the MoS₂ crystal surface and UPS spectra are shown in Fig. 2. The two lower spectra were measured from the surface cleaved under vacuum and the corresponding PEEM images, excited with the Hg lamp, are shown at the right side of the spectra. The lowest spectrum was measured from the “Bright” domain of the structure-rich area shown in the bottom image, and the second spectrum from the “Dark” domain of the rather uniform area shown in the middle image. For the vacuum cleaved samples, the “Bright” domains were relatively dominant over the surface. In Fig. 2, the spectra were measured with CA 500 μm, with which the acceptance angle was ca. 45° around the valence region. The valence spectra for “Bright” and “Dark” domains were similar; the spectra were rather structure-less and showed weak intensities above -4 eV. The secondary cut-off regions of the spectra are shown in Fig. 3, where the horizontal axis of Fig. 3 is the kinetic energy from the Fermi level, so that the work function can be directly read from the cutoff point. As expected from the brighter image, the “Bright” domain had a lower work function of 4.15 eV (± 0.05 eV), while the “Dark” domain showed a gradual cut-off at ca. 4.8 eV.

A valence spectrum for the surface cleaved in air is also shown in Fig. 2 and the corresponding PEEM image is shown at the top of the right side. The surface of the air-cleaved sample is rather smooth and uniform. From a

FIG. 2. Left panel: Valence band spectra for cleaved MoS₂ surfaces. Peaks are assigned in accordance with the previous work [10] for an annealed surface. Right panel: Corresponding PEEM images, excited by a Hg lamp.

comparison of the spectra with those reported in the literature [7–10], the air cleaved and vacuum cleaved spectra, i.e. lower three spectra in Fig. 2, resembled the air cleaved surface observed by McMenamin and Spicer [7]. The cause of the observed shift between the spectra for the vacuum-cleaved and air-cleaved samples is unclear, although the fuzzy morphology of the vacuum-cleaved sample may affect the PEEM and micro-UPS observations. The air-cleaved sample was then annealed at 400°C for 2 h, and a spectrum was measured at the same position. As shown in Fig. 2, the spectrum was changed significantly by annealing. The spectrum measured after annealing reproduced that for a clean surface reported by McMenamin and Spicer [7], where the spectrum was measured using an angle-integrated spectrometer. Furthermore, the peaks can be assigned in accordance with previous ARPES measurements and theoretical study by Böker *et al.* [10]. In both studies [7, 10], clean surfaces were carefully selected from surfaces prepared by cleaving in a vacuum. The states above -4 eV were explained by Mo $4d$ and S $3p$ derived bands, and those from -4 eV to -8 eV were attributed mainly to S $3p$ origin. The peak at -2 eV could be assigned to the d_{z^2} band of Mo $4d$ and the surface state (ss). The peak around -3.6 eV can be interpreted as the overlap of (d_{zx}, d_{yz}) and $(d_{xy}, d_{x^2-y^2})$ bands. The secondary cut-off region of the spectrum is also shown in Fig. 3. The cut-off showed a tail for the air-cleaved sample, which suggests inhomogeneity of the sample, and the work functions are dispersed from 3.7 to 5.0 eV. The cut-off became relatively steep after annealing and the resultant work function was 4.65 eV.

In the present photoemission study, a clean surface

could not be obtained from the bulk crystal, even that cleaved in a vacuum, although it was obtained in the previous studies [7, 10]. However, a clean surface was achieved after annealing in a vacuum. Contamination by the residue of the adhesive tape can be excluded in the present cleaved surfaces, because the observed surfaces did not directly touch the adhesive tape, where the exfoliated counterpart, i.e. MoS₂ film, fully covered the tape. Thus, any contamination originated from the bulk crystal.

To characterize the contaminants, AES and W-RHEED measurements were conducted with separate UHV systems for another air-cleaved surface. AES spectra measured before and after annealing (450°C, 2 h) are compared in Fig. 4(a). There was a significant C KLL peak in the spectrum before annealing, in addition to Mo MNN and S LMM peaks, although no O KLL peak was observed. Thus, the exfoliated surface was heavily contaminated by carbon, which may originate from a natural hydrocarbon species. The C KLL peak was strongly suppressed in the spectrum after annealing, which is consistent with the photoemission results.

A horizontal slice of the three-dimensional (3D) reciprocal map, constructed from a ca. 70° W-RHEED scan [25, 26] for the annealed sample is shown in Fig. 4(b). As shown in the inset, the Ewald sphere was rotated in the azimuthal direction so that the reciprocal map is obtained in the area of a butterfly shape. Clear spots were observed after annealing, although only blurred spots were evident before annealing. Most of the observed spots in Fig. 4(b) are consistent with a 1×1 hexagonal lattice of the MoS₂ surface, so that the surface consisted of domains with a single crystal orientation. The macroscopic AES and W-

FIG. 3. (a) Secondary cut-off region of micro-UPS spectra. The lower four spectra were measured from the cleaved bulk samples, and the upper three spectra were measured from transferred TF samples.

RHEED results indicated that the contaminants were removed from the surface, and a MoS₂ surface with a good crystallinity was available by annealing at 400–450°C in UHV.

B. Transferred TF Surfaces

PEEM images of MoS₂ TFs transferred onto a Si substrate are shown in Figs. 5(a) and (b), where a Xe lamp was used to enhance the contrast between the substrate and the TFs. TFs were imaged as dark domains on the bright substrate. The TF shown in Fig. 5(b) is the same as that shown in Fig. 1(c). The TF in Fig. 5(a) has a uniform “Dark” contrast on the substrate, while the large TF in Fig. 5(b) consists of several contrast domains. Valence band spectra for the TFs and the substrate region are shown in Fig. 5(c). Spectra were measured for ca. 10×10 μm regions labeled as “A”, “B1”, “B2” and “subst” in Figs. 5(a) and (b). The spectrum labeled “subst” in Fig. 5(c) was measured at the substrate. There is no state near the Fermi level, and the O 2*p* states of SiO₂ around 7–8 eV were dominant in the spectrum. Two spectra from region “A” are shown [27]. One spectrum was measured with a larger CA (500 μm) and the other with a smaller CA (150 μm). The spectrum measured with CA 500 μm is almost identical to that from the annealed surface shown

in Fig. 2. A significant change of the valence spectrum can be observed, depending on the CA size, due to the different acceptance angle of the photoelectrons with PEEM. Acceptance angles were estimated to be ca. 15° and 45° with CA 150 μm and CA 500 μm, respectively. Thus, only the vicinity around the Γ point was detected with a CA of 150 μm, while the whole first surface Brillouin zone (SBZ) was integrated with CA 500 μm. When the spectra measured with CA 150 μm are compared with those of the previous studies, the spectrum features agree well with those reported for a clean MoS₂ surface around the Γ point [9, 10], and those features can be assigned to MoS₂ states reported from ARPES measurement and theoretical study [10]. The strong peak around −4 eV is assigned to (*d_{zx}*, *d_{yz}*) states around the Γ point. The peak at −1.6 eV is explained by a *d_{z2}* state, and that at −2.4 eV should be assigned to (*d_{xy}*, *d_{x2-y2}*) and ss around the Γ point. The *d_{z2}* state is steeply dispersed downward from the Γ point to the zone boundary, so that the peak at −1.6 eV should not be observed with CA 500 μm, in which the *d_{z2}* state around 2 eV near the zone boundary is dominant. Thus, the present spectra indicated that the surface of the TF with a “dark” contrast in Fig. 5(a) could be a clean MoS₂ surface.

There were several domains with different contrast for the TF in Fig. 5(b). The darkest domain near the center was uniform in contrast and had a similar contrast to that in Fig. 5(a). (Please note the scale is enhanced to show the contrast detail in Fig. 5(b).) There are brighter domains at the right upper part and the left part of the TF, and they were not uniform in contrast. Spectra were measured at “B1” for a darker uniform domain and “B2” for a brighter domain. The spectra measured before and after annealing at 300°C for 2 h are also shown to evaluate the change by contamination. The sample was heated by electron bombardment from the back side of the substrate at the PEEM sample stage under vacuum. For “B1” the valence spectrum was not changed by annealing and the spectrum is almost identical to that from “A” while the work function was slightly increased (ca. 0.1 eV) after annealing. These results support that the extent of contamination is very small for “B1”. The intensity of the valence region for “B2” was significantly weak, and its work functions was 0.4 eV lower than that of “B1” as shown in Fig. 3. The valence structures were slightly degraded after annealing. The brighter domains were not uniform in the PEEM image, which suggests the surface may be inhomogeneously contaminated.

Here the contamination from adhesive tape residue should be considered. The counterpart of such small flakes on the tape could not be checked; therefore, it is difficult to know whether the surface was that freshly cleaved or that which touched the tape. There is no clear evidence; however, the adhesive tape residue is one candidate for contamination of the brighter domains on TFs.

C. Discussion

The photoemission results indicated that a large fraction of the surfaces were relatively clean and inert for transferred TFs, even though they were exfoliated and transferred in air. On the other hand, no clean surface

FIG. 4. (a) AES spectra measured before and after annealing for a MoS₂ surface exfoliated in air. (b) Horizontal section of 3D reciprocal map by W-RHEED for the MoS₂ surface after annealing. Inset shows how a section of Ewald sphere scans the reciprocal space during the azimuthal rotation. Reciprocal points for an ideal MoS₂ surface are superimposed as white dots in the lower right quadrant.

FIG. 5. (a,b) PEEM images of MoS₂ TFs transferred onto a Si substrate. The flake in (b) corresponds to that shown in Fig. 1(c). (c) Valence band spectra of selected areas for “subst”, “A”, “B1” and “B2” labeled in (a) and (b). Peak assignments are shown for “B1” in accordance with the previous work [10].

was observed when the bulk crystal was cleaved, even under vacuum. These results could be interpreted as an indication that the contaminated interfaces originated in the mineral crystal. It is probable that a relatively thicker crystal of such layered materials includes many, although a limited number, of contaminated interfaces. Such contaminated interfaces may be weakly binding, so that contaminated surfaces tend to appear by the cleavage of bulk crystals. When a thin film was obtained by repeated exfoliation, such as those for the present TF samples, the contaminated interfaces would be run out by repeated exfoliation. Finally, a clean surface would be available by

cleavage at a clean interface, which is a plausible reason for the clean surfaces observed for the transferred TFs. The contamination and quality of crystals are strongly dependent on the mineral source. Clean surfaces were successfully selected from samples cleaved under vacuum in the previous studies [7, 10]. It is important to pay attention to the contamination of exfoliated MoS₂ crystals for applications. Therefore, annealing at ca. 400°C in a vacuum may be an easy and effective method to reduce contamination from cleaved MoS₂ surfaces. The air-cleaved and annealed surface showed a smaller work function (4.65 eV) than that from the “B1” area of the

TF sample (5.00 eV), although both surfaces were sufficiently clean to show a “clean” valence band spectrum. It has been reported that annealing at 400°C induces sulfur vacancies in TFs [20], and the smaller work function is consistent with those reported for sulfur deficient samples [16, 18]. Thus, the difference in the work function may suggest sulfur deficiency by annealing. Control of the stoichiometry may thus be required for the application of annealed MoS₂ films. In addition, annealing may be incompatible with certain processes required in device fabrication; however, this could be avoided by annealing prior to the such processes.

IV. CONCLUSIONS

Cleaved and exfoliated MoS₂ surfaces were investigated using PEEM, micro-UPS, AES and W-RHEED. The valence band spectrum and work function were sensitive to

contamination of the surface. A clean surface could not be obtained by cleavage, even under vacuum, with the present bulk crystal surfaces. However, the surfaces of TFs that were transferred onto Si wafer substrate after repeated exfoliation were relatively clean and inert. The present results suggest that a typical bulk crystal includes a limited number of contaminated interfaces. To obtain a clean surface, repeated exfoliation is thus crucial. In addition, annealing at ca. 400°C in a vacuum is an effective method to reduce contamination at the MoS₂ surface.

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