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Atomic-scale structures and electronic states of defects on Ar^+-ion irradiated MoS_2

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ABSTRACT

We observed MoS_2 surfaces bearing defects generated by Ar^+-ion bombardment at the density of 2.75×10^{-3} ions/nm^2 by scanning tunneling microscopy (STM) and measured local electronic state by scanning tunneling spectroscopy (STS). Two types of concave surface defects, one with a bright feature and one without, were observed in STM images. STS revealed that the two features have different spectra. We elucidated the origins of these defects by comparison of the experimental results with electronic states obtained from density functional theory (DFT) calculation. The dI/dV curve measured at the center of the bright feature has a mid-gap state, which can be assigned to Mo beneath the feature. The bright feature was composed of several S vacancies, leaving a surface with metallic character. The concave defect without the bright feature is interpreted as being formed by layer-by-layer removal of MoS_2. The dI/dV curve measured at the center of this type of concave defect showed a semiconducting property similar to that of a clean MoS_2 surface, and the edge of the concave region shows a peak at −0.5 V from the Fermi level.

1. Introduction

MoS_2 is a new material of great interest, following the report by Radisavljevic et al. [1] of a single-layer MoS_2-based transistor. MoS_2 has anomalous electronic states due to its two-dimensional layer structure, consisting of a molybdenum plane sandwiched by two sulfur layers, and is characterized electronically as a semiconducting material having a band gap of about 1 eV [2,3]. Bulk MoS_2 is known to have an indirect band gap of 1.29 eV [4], but single-layer MoS_2 has recently been reported to exhibit a direct band gap of 1.8 eV [1,5]. The change of band gap of MoS_2 with thickness has been theoretically predicted [6,7]. The room-temperature electron mobility and on/off ratio are strongly affected by defects, because the semiconductor behavior is determined by the levels of inhomogenious components such as impurity and defects. In addition to the semiconducting properties, the nature of defects on a MoS_2 surface has been studied both experimentally and theoretically. A clean MoS_2 surface has natural defects that are observed as point or ring-shaped protrusions in scanning tunneling microscopy (STM) images [8,9]. However, the local electronic states at these defects have not been established.

Although ion-sputtered MoS_2 surfaces have been studied, that work was focused on catalytic activity [10,11] and fabrication of nanostructures [12]. Ar^+-ion sputtered MoS_2 shows a large increase in catalytic activity compared with a clean MoS_2 surface [10]. This may indicate that the electronic states of the defects are important for the semiconductor behavior. Park et al. studied the initial stages of sputtering on MoS_2 surfaces subjected to Ar^+ and He^+ bombardment [13], and they found that Ar^+-ion bombardment with an energy of ∼100 eV produced fort-shape features with loss of sulfur atoms from the surface, while bombardment between 100 eV and 1 keV produced apparent craters and protrusions on the surface. At energies more than 1 keV, deep penetration into the lattice leaves only small structures at the surface. Therefore, surface defects can be generated without destroying the layer structure if the irradiation energy is of the order of 500 eV.

We investigated isolated defects consisting of concave structures with and without a bright feature by means of STM and STS in ultra-high vacuum. These observed features are theoretically interpreted based on density functional theory (DFT) calculations. We discuss the relationship of the partial densities of states (PDOS) at the defect sites to the observed dI/dV spectra.

2. Experimental methods

STM and STS measurements were performed in an ultra-high vacuum (UHV) chamber with a base pressure below 2.0×10^{-8} Pa, equipped with an STM (JSTM 4500XT; JEOL Ltd.). A tungsten wire etched in KOH solution was used as a tip after electron bombardment heating.

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A clean MoS_2 surface was prepared by cleaving the surface layers of a MoS_2 crystal (10 mm × 10 mm × 5 mm) in air with scotch tape. The cleaved clean MoS_2 was pasted on a silicon substrate (2 mm × 7 mm × 0.3 mm) with silver paste. After transfer to a UHV chamber, the sample was degassed by electrical heating at 538 K for half an hour to provide a clean and contamination-free substrate. The sample was irradiated with Ar^+ ions at the energy of 500 eV in the UHV chamber. The irradiation density was 2.75×10^{-3} ions/nm^2, as estimated from the ion current and irradiation times. The incident angle of Ar^+ ion was ±2–3° from the normal of the surface. To remove residual ions on the sample surface after irradiation, the irradiated sample was heated at 583 K for an hour by direct current heating through the substrate.

The observed surface had defects of so low density that individual defects could be separately resolved with the STM. Surface observation with the STM was operated in the constant-current mode at room temperature. *I–V* curves were taken with a sample-tip distance conditioned for the combination of tunneling bias voltage and tunneling current in STM observation. A spectrum was recorded by averaging of 32 *I–V* relations, and the presented spectra are typical of several to ten reproducible curves at the same point. The tip should have little influence in our STS experiments, because a tungsten tip hardly affects local electronic states of substances with semiconductor properties [14].

3. Theoretical methods

All calculations were carried out using the first-principles program package STATE-Senri (Simulation Tool for Atom TEchnology) [15–17], which is based on DFT [18,19] with a generalized gradient approximation (GGA) [20]. Ultrasoft [21] and norm-conserving [22] pseudopotentials are used to represent the interaction between electrons and ion cores. A plane wave basis set was used, and the cut-off energy was set to 16 Ry for wave functions and 64 Ry for charge density. Surfaces were modeled using slab models with periodic boundary conditions. The crystal structures of MoS_2 were made of several MoS_2 sandwich layers. The distance of the vacuum layer is set to 1.2 nm and the Brillouin zone integration was sampled at *k*-points on a 4 × 4 × 1 uniform mesh. We performed defect calculations with the following models:

1) A point S defect (S_1): this model is produced by removal of a single sulfur atom from the topmost layer of the MoS_2 surface, and uses two sandwich layers. The lateral width is 3 × 3 surface unit cells.
2) A point Mo defect (Mo_1): this model is produced by removal of a single atom of Mo in the second layer from the MoS_2 surface, and uses two sandwich layers. The lateral width is 3 × 3 surface unit cells.
3) Three S defects (S_3): this model consists of a triangular defect generated by removal of the topmost three S atoms from the MoS_2 surface, and uses two sandwich layers. The lateral width is 5 × 5 surface unit cells.
4) Seven S defects (S_7): this model consists of a large hexagonal defect generated by removal of seven S atoms from the topmost MoS_2 surface, and uses two sandwich layers. S atoms The lateral width is 5 × 5 surface unit cells.
5) A hexagonal crater (HC): this model consists of a crater-shaped defect in the topmost sandwich layer generated by removal of six MoS_2 unit (six Mo atoms, six upper S atoms and six lower S atoms). The lateral width is 5 × 5 surface unit cells.

Large peaks of the calculated spectra in the lower energy of the valence band were set to be at the same energy, and the Fermi level was defined to fit the experimental STS.

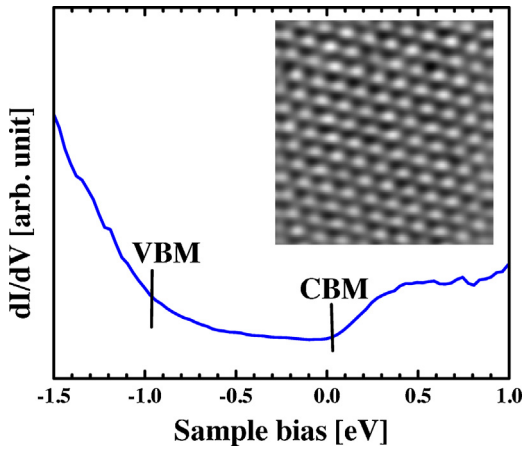

Fig. 1. STS spectrum of a clean MoS_2 surface. The inset is an STM image of the clean MoS_2 surface (voltage: −0.3 V, current: 0.4 nA, image size: 3.2 nm × 3.2 nm).

4. Results

4.1. STM and STS measurements

Fig. 1 shows a d*I*/d*V* curve measured on a clean MoS_2 surface. The sulfur atoms in the topmost MoS_2 layer are clearly resolved, as shown in the inset STM image, where bright points represent the sulfur atoms. The d*I*/d*V* curve has a region of undetectable current between approximately −1.0 (valence band maximum (VBM)) and 0.0 eV (conduction band minimum (CBM)) from the Fermi level. The

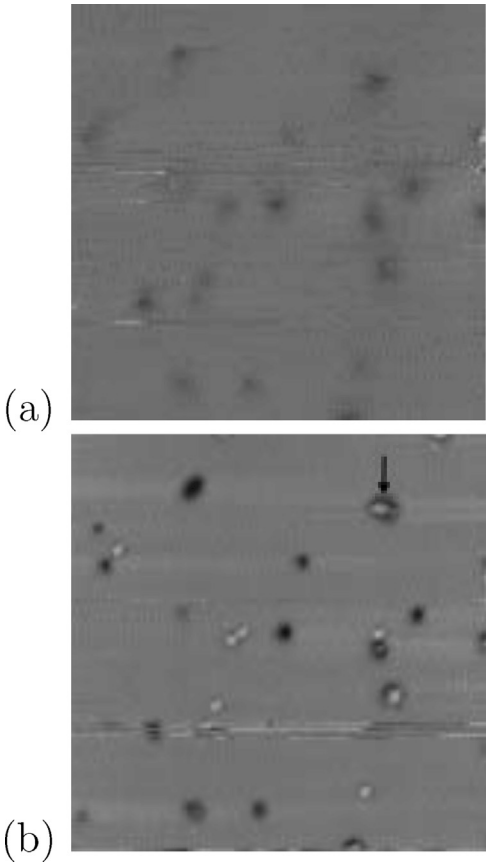

Fig. 2. Dependence of STM image of Ar^+-ion irradiated MoS_2 surface on bias voltage (image size: 100 nm × 100 nm). (a) Sample bias: 1.5 V, current: 0.4 nA. (b) Sample bias: −0.3 V, current: 0.4 nA.