The First Observation of an Atomic Scale Noncontact AFM Image of $MoO_3(010)$

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We have observed $MoO_3(010)$ surface on an atomic level by NC-AFM(Noncontact atomic force microscopy) for the first time. White arrays with 0.40 and 0.37 nm dimensions along [100] and [001], respectively, were observed, which corresponded to the topmost oxygen atoms of $MoO_3(010)$.

Mo oxides are very important as oxidation and hydrotreating catalysts.[1] The active structures of the Mo oxides have been investigated by many techniques such as XAFS, Raman, UV–vis, ESR, and NMR, but the active structures are still controversial and the reaction mechanism is not fully understood. It is necessary to carry out the investigation on a well-defined single crystal surface using modern surface science techniques such as scanning tunneling microscopy (STM). However, a MoO_3 single crystal, one of the most basic Mo oxides, is an insulator which refuses the STM studies because STM requires the electric conductivity of samples. Atomic force microscopy (AFM) is another scanning probe microscopy, which can be applied to insulator surfaces. Although several studies using a contact-mode AFM have been conducted on the $MoO_3(010)$ surface,[2–4] no atomic scale image has ever been obtained. Since the tip made a direct contact with the surface, it is quite difficult to have a real atomic scale image without perturbations of the AFM tip. Recent progress in a noncontact mode AFM (NC-AFM), which has small interaction between the AFM tip and a sample surface, has enabled us to obtain the real atomic scale imaging for some insulator and semiconductor oxide surfaces.[5–8] NC-AFM is an appropriate method to visualize an atomic scale image of the MoO_3 single crystal surface. However, the methodology of NC-AFM on oxide surfaces is still immature[9] and it is not so easy to find conditions to obtain atomic scale images by NC-AFM. In this paper, we will present the first NC-AFM picture of $MoO_3(010)$ with an atomic resolution.

The experiments were performed with OMICRON STM/AFM operated in a noncontact mode under ultrahigh vacuum conditions (below 2×10^{-8} Pa). We prepared a flat MoO_3 single crystal by a flux method.[10] The obtained crystals were washed with nitric acid and deionized water in order to remove a Na_2MoO_4 by-product. A typical sample size was ca. $3 \times 10 \times 1\,mm^3$. The sample was cleaned by repeated cycles of Ar^+ sputtering and resistive heating at 823 K to give clear LEED patterns of $MoO_3(010)$ surface, as shown in Figure 1, with reciprocal vectors of $\bar{\boldsymbol{a}}$ and $\bar{\boldsymbol{c}}$. The structure of MoO_3 is a layer structure stacked on each other parallel to the (010) plane in which each layer is composed of bilayers of Mo oxide octahedrons as shown in Figure 2. In the MoO_6 octahedron, several types of oxygen atoms surround a molybdenum atom. Both sides of the (010) surface of the bilayers are fully covered with an O atom that is strongly bound to a Mo atom (Mo–O distance is 0.167 nm and corresponds to double bond), and such an O atom has little ability to form a new covalent bond outward. Hence each bi-layers is bound with each other through weak interaction such as van der Waals interaction.

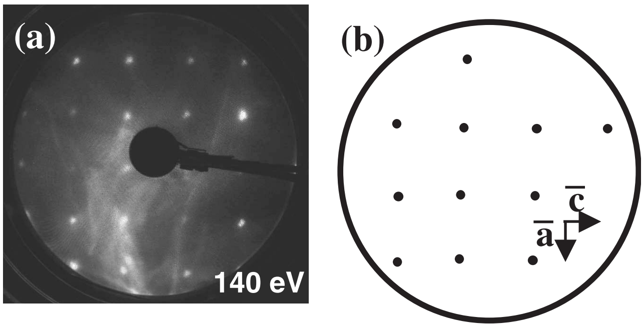

Figure 1. (a) A LEED pattern of $MoO_3(010)$. (b) Schematic drawing of LEED pattern derived from Fig. 1(a). The LEED pattern could be observed with electron acceleration energies between 70 eV and 140 eV.

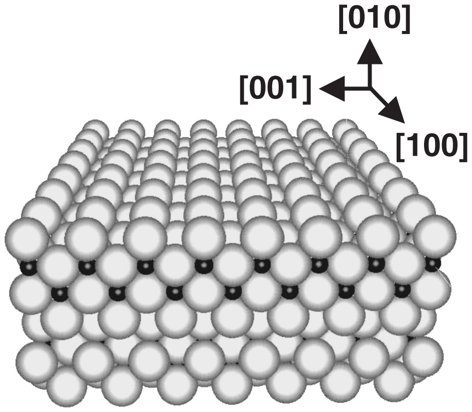

Figure 2. Surface structure model of $MoO_3(010)$. Small circles: Mo atoms; Large circles: O atoms.

We have carried out NC-AFM measurements on this $MoO_3(010)$ sample at room temperature. To remove oxide, hydroxide, and other possible adsorbates on the tip apex, all the cantilevers were sputtered by Ar^+ ions before use. Measurement was carried out in a constant frequency shift mode with constant vibration amplitude of the cantilever.

Figure 3 shows a typical wide-range topographic NC-AFM image of a $MoO_3(010)$ surface with a scan size of $200 \times 200\,nm^2$. The Si cantilever of NCHR(NANOSENSORS, 42 N/m) was used to obtain the image with a frequency shift Δf of -20 Hz. The bias voltage is applied between the tip and the metallic backing plate of the sample to minimize the effect of the electrostatic force between the tip and the sample. Typical sample bias voltage during the observations was about $+0.4$ V. The sample surface consisted of apparently flat terraces typically with ca. 20 nm width separated by steps mostly running

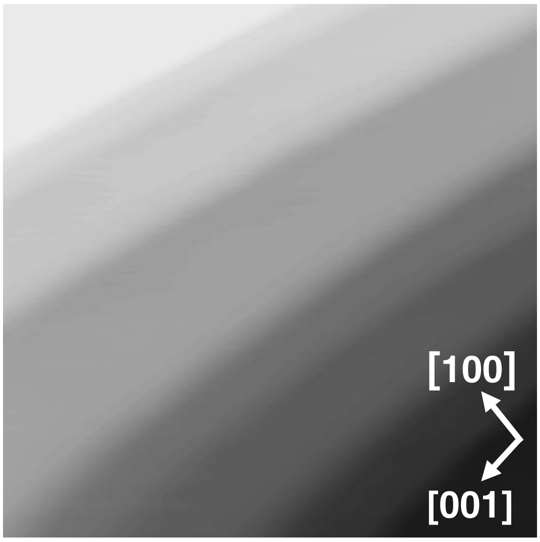

Figure 3. A topographic NC-AFM image of the sputtered and annealed sample surface. $200 \times 200\,\mathrm{nm}^2$, $V_s = +0.4\,\mathrm{V}$, $\Delta f = -20\,\mathrm{Hz}$, $A_0 = 10\,\mathrm{nm}$.

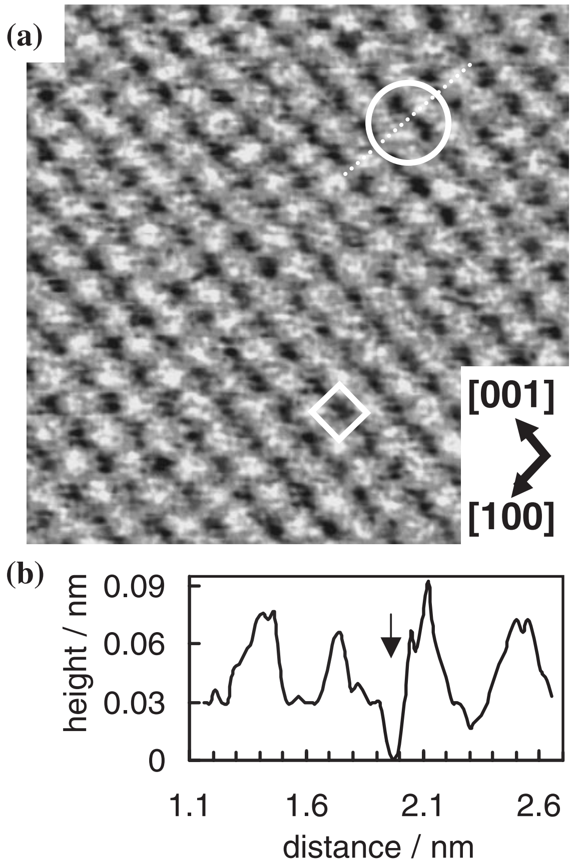

Figure 4. (a)A typical atomic resolution NC-AFM image of the $MoO_3(010)$-(1×1) surface. $5 \times 5\,\mathrm{nm}^2$, $V_s = +0.3\,\mathrm{V}$, $\Delta f = -138.7\,\mathrm{Hz}$, $A_0 = 5\,\mathrm{nm}$. (b) A cross sectional profile along the white dotted line in the [100] direction on the break of the belt (see the text.)

parallel to the [001] direction as show in Figure 3. The height differences between each terrace were corresponding to integral multiple of a half unit cell along the *b* axis (ca. 0.7 nm) ranging from 0.7 to 5.6 nm. This is probably due to the layer-by-layer removal of the $MoO_3(010)$ bilayers during the annealing process. The height difference with integer multiple of 0.7 nm is also observed on a cleaved sample surface in the contact mode AFM work.[3,4]

After many trials, we obtained atomic resolution images of the $MoO_3(010)$ surface by NC-AFM as shown in Figure 4a. A V-shaped cantilever of NSC11(NT-MDT, 48 N/m) was used and the applied Δf of the cantilever was -138.7 Hz. Applied sample bias voltage V_s between the tip and the metallic backing plate of the sample was $+0.3$ V. The rectangular unit cell in Figure 4a showed 0.40 and 0.37 nm along [100] and [001] directions, respectively, which were in good agreement with the values of 0.395 and 0.369 nm expected from the ideal (010) surface of MoO_3. Therefore, we attributed the array of white dots to the terminal oxygen atoms on the $MoO_3(010)$ surface.

Previous NC-AFM visualized cation defects on oxide surfaces in the literatures.[5–8] However, in this NC-AFM image, we have found no defects in the array of white dots. This is because the terminal oxygen is strongly bound to Mo with double bond and the defects are expected to be located at bridging oxygen sites considering the reported structures of nonstoichiometric molybdenum oxide compounds.[11] The white array dots are connected through bright belts running only along [001] and [100] directions. If these belts are corresponding to the underneath bridging oxygen atoms, a break of the belt can be a defect of bridging oxygen. Actually there is a break as shown in a circle of Figure 4a. Figure 4b shows the cross sectional profile on the break of bright belts along the dotted line. The profile indicates that a topographic height of the break, the position of which is arrowed in the figure, is lower than that of the bright belt. In the present work, we can not conclude the break is a defect or not. Further studies must be necessary to obtain clearer image of the second layer oxygen atoms.

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