CONDENSED MATTER: STRUCTURE, MECHANICAL AND THERMAL PROPERTIES

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Imaging of the Al Structure of an Ultrathin Alumina Film Grown on Cu-9 at.%Al(111) by STM *

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An ultrathin alumina film grown on a Cu-9 at.%Al(111) substrate is investigated using low-temperature scanning tunneling microscopy and spectroscopy. The topographic images show a zigzagged corrugation characterized by the heptagonal and pentagonal organization of interfacial aluminum atoms and by a dependence on the bias voltage. Furthermore, the dI/dV maps and the spectrum reveal an unoccupied state locating at about +0.26 eV, which most likely originates from the aluminum-oxygen hybridization and is possibly responsible for the heptagonal and pentagonal arrangements of Al atoms.

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Ordered oxide films supported by metal substrates have attracted great interest because of their remarkable stability and complex physical properties.[1] As a sensitive tool for surface detection, scanning tunneling microscopy (STM) not only provides the information of the structure of oxide films,[2–6] but is also used to address the electronic properties of oxide films.[7–9] In STM measurements, a constant current topography acquired on oxide surfaces is closely related to the bias voltages applied between tips and samples and reflects the local density of states (LDOS) with energies ranging from Fermi level to the applied values. For example, the different morphologies of the line defects formed between domains of alumina film on NiAl(110) at high bias voltages reveal unoccupied gap states induced by domain boundaries.[9] In addition, two types of superstructures are imaged at different positive bias voltages on alumina/Ni_3Al(111), which illuminates a lateral variation of LDOS within the unit cell of the oxide thin film.[10]

As a typical aluminum alloy surface, Cu-9 at.%Al(111) is a suitable substrate for growth of a well ordered alumina film.[11–14] Compared to other alumina/metal systems, only one monolayer alumina can be prepared on the Cu-9 at.%Al(111) surface.[11] The alumina film consists of one oxygen layer and one aluminum layer and their contributions to the tunneling signal are anticipated to be different as the changes of the bias voltages. The images with different bias voltages could provide details of geometric structures and electronic properties of atomic layers, which is very important in aspects of metal deposition because it can influence the growth mode, for example, large triangle-shaped Pd island growth.[12] However, to our best knowledge, few studies have been performed on this aspect, especially about the spatial distribution of electronic states at energies inside the band gap. Owing to the tip-surface interaction, the atomic structure and electronic properties of alumina inside the band gap can be probed by STM.[15] In this work, we determine the geometric and electronic structures of alumina films inside the band gap by STM and differential conductance (dI/dV) mapping.

The experiments were carried out by an ultrahigh vacuum (UHV) low-temperature STM (Unisoku) system with a base pressure of $< 1.0 \times 10^{-10}$ Torr. The Cu-9 at.%Al(111) substrate with 9 at.% randomly-distributed Al impurities in Cu was cleaned by several cycles of Neon sputtering and annealing to about 950 K. The alumina film was grown by exposing Cu-9 at.%Al(111) to about 120 L (1 Langmuir $= 10^{-6}$ Torr $\cdot$ s) of oxygen at the substrate temperature of about 920 K. The STM measurements were performed with electrochemically etched W tips at about 79 K. The dI/dV spectra and mappings were measured by a lock-in technique with a closed feedback loop. Sinusoidal-bias modulation voltage with the value of 6 mV was applied at a frequency of 1.605 kHz. To exclude the tip effect, we checked the formation of the standing waves on pristine Cu(111) (not shown) by dI/dV mapping using the same tips as those performed on alumina film.

The monolayer alumina film can be grown on Cu-9 at.%Al(111).[11] Figure 1(a) shows the constant current topographic images acquired on Cu-9 at.%Al(111). The surface clearly reveals a zigzagged

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corrugation of the alumina layer as marked in Fig. 1(a) and the structure presents a rectangular unit cell with the lattice length of $18.2 \times 10.6\,\text{Å}^2$. A corresponding two-dimensional (2D) Fourier-transform (FT) image further demonstrates that the reciprocal spots are arranged as a rectangular grid (see the inset of Fig. 1(a)). The imaged atoms are stacked in terms of the heptagon and pentagon (marked by black lines in Fig. 1(a)), in good agreement with the case of the interfacial Al layer on NiAl(110), NiAl(110), FeAl(110) and Cu(111).[4,5] This fact implies that the organization of the interfacial Al atoms is independent of the properties of the substrates. According to the model of alumina on NiAl(110),[4] a proposed schematic of the alumina unit cell is displayed in Fig. 1(b). The structure of the alumina film corresponds to a stacking sequence of two atomic layers which consist of 16 Al atoms locating at the interface and 25 O atoms locating on the top.

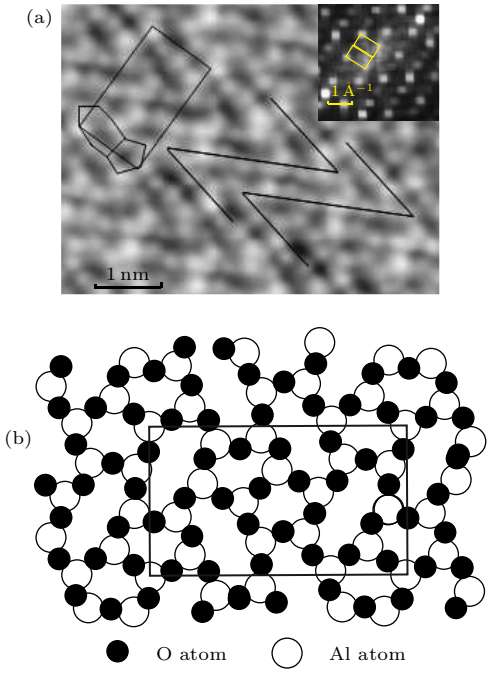

Fig. 1. (a) STM images of the alumina layer grown on Cu-9 at.%Al(111) (image size: $4.4 \times 5.7\,\text{nm}^2$; $V_b = 0.49\,\text{V}$; $I = 0.5\,\text{nA}$). The inset shows the 2D Fourier-transform power spectra of (a). The unit cells of the reciprocal lattice are marked by white rectangles. (b) Structural schematic of the alumina layer. The unit cell is marked by a black rectangle.

Figure 2 shows the atomically-resolved topographic images obtained on the alumina surface at different bias voltages. It is found that the observation of the zigzag structure shows a weak dependence on the bias voltage. The image at the bias voltage of $-0.35\,\text{V}$ clearly reveals a zigzagged corrugation with the rectangular unit cell. However, when the bias voltage approaches to the Fermi level, the zigzagged corrugation becomes faint as shown at the bias of 0.05 V. With further increasing the bias voltage to 0.2, 0.25, 0.3 and 0.4 V, the clear zigzagged corrugation is observed once again but with different contrasts.

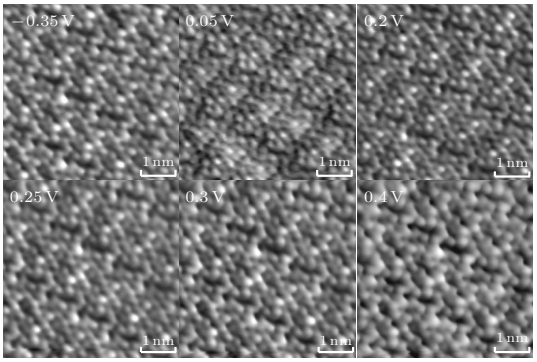

Fig. 2. STM topographic images of alumina on Cu-9 at.% Al(111) taken at the indicated biases (image size: $5 \times 5\,\text{nm}^2$; $I = 0.5\,\text{nA}$).

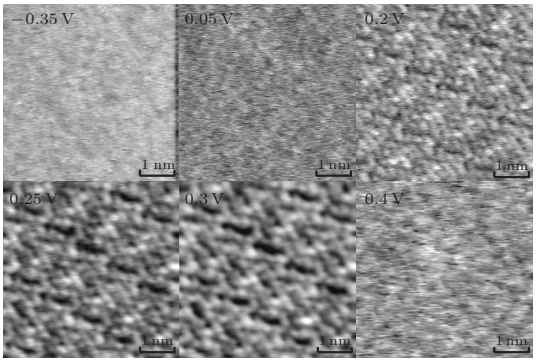

Fig. 3. The dI/dV images of alumina on Cu-9 at.%Al(111) simultaneously recorded with Fig. 2. The images were taken at the indicated biases (image size: $5 \times 5\,\text{nm}^2$; $I = 0.5\,\text{nA}$).

To understand well the bias dependent feature of the structural observation on alumina/Cu-9 at.%Al(111), we performed the measurements of dI/dV mapping which exclusively probe the spatial distribution of the electronic states with an energy close to the applied bias voltage. Figure 3 shows the dI/dV images acquired on the alumina layer with simultaneous measurements of the topographies in Fig. 2. At negative ($-0.35\,\text{V}$) and low positive ($+0.05\,\text{V}$) biases, the images are featureless. This implies that no occupied or unoccupied states are available in these bias voltages. However, at bias of $+0.2\,\text{V}$ the weak zigzagged patterns are observed. With the bias voltage increasing to $+0.25\,\text{V}$ and $+0.3\,\text{V}$, the zigzagged corrugation is prominent and the heptagonal and pentagonal organizations can be clearly resolved. The structure is consistent with the topographic image of Fig. 2 acquired at the same bias voltage. Further increasing the bias voltage to $+0.4\,\text{V}$ results in the invisibility of the zigzagged feature. This experimental result indicates that an unoccupied gap state may locate at around $+0.3\,\text{eV}$.

In order to confirm this unoccupied gap state, we record dI/dV spectra which provide a much better evaluation of LDOS of the sample surface. The dI/dV spectrum in Fig. 4 was obtained by averaging about 50 spectra recorded at different fixed points of the alumina surface using different tungsten tips. It is found that this spectrum exhibits a distinct peak locating at about +0.26 V, indicative of a localized electronic-state inside the band gap. The existence of this state is consistent with the observation of the zigzagged structure at the bias voltages +0.25 V and +0.3 V in Fig. 3. It illustrates that the unoccupied electronic state with the energy of about +0.26 eV possibly relates to the heptagonal and pentagonal construction of Al atoms.

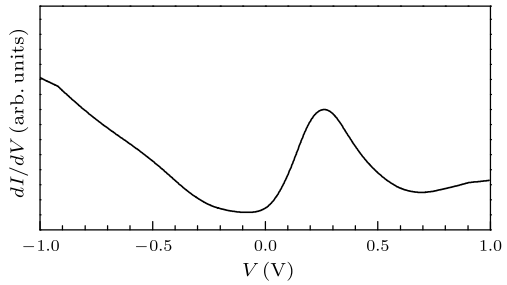

Fig. 4. The dI/dV spectrum measured on alumina/Cu-9 at.%Al(111). The feedback loop was cut at a tunneling current of 0.5 nA.

As discussed above, the zigzag structure of the alumina films is independent of the properties of the substrates since similar heptagonal-pentagonal patterns are observed on the alumina films grown on Ni(111), NiAl(110), FeAl(110) and Cu(111).[4,5] This indicates that the zigzag corrugation, a structural defect, is the result of the stacking equilibrium of Al and O in the 2D thin films. On the other hand, the LDOS of alumina on NiAl(110) calculated by Kresse *et al.* shows weak gap states just above the Fermi level for both interfacial Al and O atoms (Fig. S1 in the supporting online materials of Ref. [4] http://www.sciencemag.org/content/308/5727/1440/-suppl/DC1), which implies the hybridization between the interfacial Al and O atoms. Therefore the observed unoccupied state locating at about +0.26 eV in Fig. 4 most likely originates from the Al-O hybridization. We believe that the hybridization between Al and O atoms should be responsible for the heptagonal and pentagonal arrangements of Al atoms.

In summary, we have investigated the structural and electronic properties of a well-ordered alumina monolayer grown on Cu-9 at.%Al(111) by low temperature STM. An alumina layer shows a zigzagged corrugation which depends on the bias voltages. Furthermore, by analysis of the dI/dV maps and spectra, we find that an electronic state locating at about +0.26 V is responsible for the heptagonal and pentagonal structures. This state most likely originates from the Al-O hybridization.

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