Identification of O atoms on a Cu(110) surface by scanning tunneling microscope light emission spectra

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We have identified the adsorption site of O atoms on the Cu(110)-O surface by studying the light emission spectra from individual atomic sites induced by scanning tunneling microscope (STM). Although the STM image contrast reverses depending on the tip condition, the emission spectrum from the *oxygen* site shows the same characteristic peaks, regardless of the image contrast. These characteristic peaks are identified with the electronic density of states associated with the O 2p orbitals.

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I. INTRODUCTION

Identification of the adsorption sites of atoms on a surface is crucial in many areas of surface science. The scanning tunneling microscope (STM) has proven to be a very powerful tool for the purpose. However, the STM image cannot always visualize the true atomic site nor can one identify the atomic species in the image. The Si(111)- $\sqrt{3} \times \sqrt{3}$ Ag surface¹ is a famous example of this case. The light spots in the STM image correspond neither to the Si nor Ag atoms.^{2,3}

Oxygen molecules chemisorb dissociatively on clean Cu(110) surface with the 1×1 structure at room temperature.⁴ The surface reconstructs to the 2×1 structure with a few Langmuir of oxygen exposure. The Cu(110)-O surface has been investigated extensively by many different techniques, and its structure has been determined as shown in Fig. 1.⁵ Every second row of the topmost layer Cu atoms in the [001] direction is missing, and the oxygen atoms chemisorb at the long bridge sites (i.e., added row reconstruction model). Light spots corresponding to the 2×1 structure are also visualized in the STM image of the Cu(110)-(2×1)-O surface.^{6–8} However, there is disagreement on the interpretation of the atomically resolved STM image, concerning the atomic species that corresponds to the light spots. Chua, Kuk, and Silverman⁶ reported that the light spots correspond to buckled Cu atoms. On the other hand, Ruan et al.⁷ found that the light spots correspond to the adsorbed O sites when the tip is clean tungsten (clean tip) and to the Cu atoms when the tip has adsorbed O atoms (O tip). Buisset et al. also reported a result consistent with that by Ruan et al.⁸

The purpose of the present work is to show that the oxygen atom sites can be identified by the STM light emission spectroscopy. We have measured the STM light emission spectra of the Cu(110)-O surface with an atomic spatial resolution. We found that the oxygen adsorption site can be unambiguously identified from the STM light emission spectra.

II. EXPERIMENT

The sample was the (110) surface of a single crystal of Cu. Its surface was cleaned in ultra-high vacuum by repeated cycles of argon ion sputtering (500 eV) and annealing $(300 \,^{\circ}\text{C})$.⁹ After being exposed to 1 or 20 L of oxygen at

room temperature, the sample was transferred to a low temperature STM operated at 80 K.

The tip was made of polycrystalline tungsten wire by an electrochemical method. The front end of the as-fabricated tip was cleaned by scanning a clean Au surface for a long time. Then isolated light spots were observed in the STM image of the Cu(110) surface exposed to 1 L of oxygen. We call this type of tip "tip A." When a type-A tip was gently crushed into the area that has a 2×1 surface structure (i.e., oxidized area) on the Cu(110) O surface, isolated dark spots appeared in the STM image of the 1-L oxygen-exposed surface. We call this type of tip "type B." Type-A and -B tips correspond to "clean" and "O tips," respectively, of Ref. 7. The present STM light emission measurements were performed with both types of tips.

The STM system and the optical spectroscopy system were described previously.¹⁰ The STM light emission spectra



FIG. 1. Atomic arrangement of Cu(110)- (2×1) O surface (added row reconstruction model). Cu atoms in the first and second layers are represented by circles. Every second Cu atom row along the [001] axis in the first Cu layer is missing. O atoms indicated by the filled black circles adsorb at the long-bridge sites in the first Cu layer. The filled gray circles indicate the third Cu layer.



FIG. 2. (a) STM image of clean a Cu(110)- (1×1) surface. (b) and (c) are isolated and chained light spots, respectively, observed in the STM image of the Cu(110) surface exposed to 1 L of oxygen. (d) STM image of a Cu(110)- (2×1) O surface. These images are measured with the type-A tip. White or black circles indicates the tip locations where the STM light emissions were measured.

were measured with a sample bias voltage of +2.3 V with respect to the tip and a tunneling current of 2 nA. The exposure time was 100 sec. The average tip drift during the exposure time (100 sec) was less than 0.1 nm. The dark counts that arise from optical detector noise have been subtracted from all the spectra shown in this paper.

III. RESULTS AND DISCUSSION

Let us first show the experimental results with a Type-A tip. Figure 2(a) is a constant current image of the clean Cu(110)-(1×1) surface. Individual copper atoms are resolved in this image. Figure 3 shows the STM light emission spectrum of the clean Cu(110)-(1×1) surface. The high-energy cutoff frequency of the spectrum satisfies the quantum cutoff condition $eV_o = h\nu_{max}$. Here *e* is the elementary charge, V_o is the bias voltage applied to the STM gap (2.3 V in this case); *h* is the Planck constant; and ν_{max} is the maximum photon frequency. This result indicates that the emission is caused by inelastic electron tunneling.¹¹



FIG. 3. STM light emission spectrum of a clean Cu(110)- (1×1) surface. Solid and dotted curves correspond to experiment and theory, respectively.



FIG. 4. (a) and (b) are STM light emission spectra with tip located over dark area and the light spot indicated by white circle, respectively, in Fig. 1(b). Solid and dotted curves correspond to experiment and theory, respectively.

Let us first compare the observed spectrum with the dielectric theory that describes the STM light emission due to inelastic electron tunneling.^{12,13} The input parameters for the numerical calculation are the radius of curvature of the tip, the tip-sample distance, and the dielectric functions and the work functions of the tip and the sample. The radius of curvature of the tip was found to be about 50 nm by a scanning electron microscope. The gap distance was taken to be 1 nm. (Small variations in this parameter do not affect the calculated spectrum in any significant manner.) The work functions and the dielectric functions of Cu and W were taken from the literature.^{14–17} The calculated result is shown by the dotted curve in Fig. 3. It agrees well with the observed. The good agreement indicates that the emission from the Cu(110)- (1×1) surface is produced through the localized surface plasmons (LSP's) excited by inelastic tunneling of electrons.

Figures 2(b) and 2(c) show different parts of the STM image of the Cu(110) surface exposed to 1 L of oxygen. We see two isolated light spots in Fig. 2(b) and a chain of light spots in Fig. 1(c) against a featureless background. Presumably the dark featureless area is the bare Cu surface, because 1 L of exposure is far below the saturation coverage level and most of the surface area is not covered by oxygen atoms.

Figure 2(d) is a STM image of the sample surface exposed to 20 L of oxygen. Here the light spots form a 2×1 structure with the rows along the [001] and [110] directions. The entire area seen in the image is covered by oxygen.

Now we wish to identify the atomic species of the light spots in the STM images. First we compare the spectra from the dark area (bare Cu surface) and one of the light spots (indicated by a circle) in Fig. 2(b). These spectra are shown in Figs. 4(a) and 4(b). The dotted curve in Fig. 4(a) is the spectrum calculated by the dielectric theory. We see that the



FIG. 5. (a), (b) and (c) are STM light emission spectra of light spot in Figs. 1(b), 1(c), and 1(d), respectively. (d) is STM light emission spectrum of DS in (d).

theory and the experiment agree well, indicating that the emission is due to LSP's.

To see the difference between the spectra of Figs. 4(a) and 4(b), we calculated the difference spectrum obtained by subtracting the spectrum of the dark area [Fig. 4(a)] from that of the light spot [Fig. 4(b)]. The difference spectrum is shown in Fig. 5(a). In this difference spectrum there are three peaks at 1.80, 1.94, and 2.14 eV. Thus we see that the spectrum from the light spot has three additional components *superimposed* on the broad background of the emission by LSP. These peaks correspond to the emission from localized sitespecific electronic transitions. To focus on the localized emission features in the following discussion, we will hereafter show the difference spectra obtained after subtracting the spectrum of the bare Cu(110) surface.

The vertical dotted lines in Fig. 5 are drawn at the three peak positions found in Fig. 5(a). Figure 5(b) is the (difference) spectrum of the light spot denoted by the white circle on the one-dimensional chain of light spots in Fig. 2(c). This spectrum also has three peaks at energies indicated by the dotted lines. Thus we identify the dots in the chain and the isolated dots in Figs. 2(b) and 2(c) with the same atomic species, namely oxygen.

Figure 5(c) shows the spectrum of the light spot denoted



FIG. 6. STM image of the Cu(110) surface exposed to 1 L of oxygen measured with the type-B tip.

by the white circle in Fig. 2(d). We again find three peaks at the energies denoted by the three dotted lines. Thus the light spots that form the 2×1 structure are identified with the oxygen atoms. Up to this point we have presented the spectra obtained with type-A tips. We have seen that light spots in Figs. 2(b), 2(c) and 2(d) produce very similar spectra to each other. Thus we know that the light spot in different arrangements (isolated, chained, or 2×1) has approximately the same local electronic configuration.

Next let us show the results for the type-B tip. Figure 6 shows the STM image observed with a type-B tip. We see two islands with a 2×1 structure whose atomic rows lie along the [001] direction in the upper left corner and near the center of the STM image. The STM light emission with the tip located over the area between the islands (bare Cu surface) was very weak.

When the type-B tip was located over a light spot in the island area, the STM emission was also very weak. However, when the tip was moved to a dark spot denoted by the white circle in Fig. 6, the spectrum shown in Fig. 5(d) was observed (The emission due to LSP's was not subtracted in this spectrum.) This spectrum again has three peaks at the energies indicated by the three dotted vertical lines.

From the observations described above, we conclude that the spectrum of the light spots imaged with the type-A tip is identical to that of the dark spot imaged with the type-B tip. Thus we see that the electronic levels contributing to the light emission from the light spot with the type-A tip are the same as those from the dark spot with the type-B tip. That is to say, the light spot for the type-A tip and the dark spot for the type-B tip are identical atomic sites. As we have already pointed out in Sec. II, when the clean Cu(110) surface was exposed to 1 L of oxygen, isolated light and dark spots were seen in the STM image with type-A and -B tips, respectively. Thus we conclude that the spectra shown in Fig. 5 are emitted from a single adsorbed oxygen atom. They have three peaks at 1.80, 1.94, and 2.14 eV for the bias voltage of 2.3 V. This means that the final electronic levels of the emission lie



FIG. 7. (a) Theoretical total density of states (DOS) of a cluster consisting of one oxygen atom and 14 Cu atoms. (b) UPS spectrum of the Cu(110)-(2×1) O surface. (c) Partial DOS of the oxygen 2p orbitals. Dotted lines of the left and the right denote the energy of the *d*-band peak in USP spectrum and the Fermi level, respectively.

a few hundred meV above the Fermi level. There are several reports on the electronic states of the Cu(110)-(2×1)-O surface.^{18–20} One can find density of states (DOS) peaks in the relevant energy range. In order to know the origin of the electronic levels, we calculated the partial DOS of the Cu(110)-O surface. From Fig. 5(a) we see that the electronic levels are generated by the adsorption of a single oxygen atom on a clean Cu(110) surface. Hence, we have calculated the DOS of a cluster consisting of one O atom and 14 Cu atoms by the *DV-Xa*. This is an *ab initio* method suitable for calculating the electronic levels of molecules and clusters.²¹ The optimized positions of the O and Cu atoms determined by Schimizu and Tsukada for the added row reconstruction model of the Cu(110)-(2×1)-O surface²² were used in the numerical calculation.

Figures 7(a) and 7(b) show the calculated DOS and the experimental ultraviolet photoemission spectrum (UPS) of the Cu(110)-(2×1)-O surface measured along the surface normal for comparison. The origin of the energy for the UPS spectrum is taken at the Fermi level of the sample. The origin for the DOS was adjusted so that the peak energy of the Cu 3d orbitals in the DOS is aligned with the corresponding peak of the UPS spectrum. The small wiggles in the DOS are



FIG. 8. Energy diagram of the tunneling process and the emission spectrum, showing the relation between the DOS and the spectrum. The spectrum shown on the extreme right is an expanded version of the true scale plot in the middle.

caused by the finiteness of the cluster size. The DOS in the vicinity of the Fermi level is mainly contributed by the 4s-4p hybridized orbitals of Cu. Figure 7(c) shows the partial DOS arising from the oxygen 2p orbitals. We see that it has several structures just above the Fermi level of the sample.

Figure 8 is the electronic energy diagram of the tip, the tunneling gap, and the localized states about the adsorbed O atom. When the bias voltage across the vacuum gap is 2.3 V, the Fermi level of the tip is located 2.3 eV above that of the sample. The partial DOS of the O 2*p* orbitals of Fig. 7(c) is drawn on the right-hand side of the tunneling gap, and the measured spectrum of Fig. 5(c) is also shown aligned with the energy scale on the left. Since the maximum photon energy is $eV_0 = hv_{max} = 2.3 \text{ eV}$, this energy on the energy axis of the spectrum is aligned with the Fermi level of the sample. The experimental spectrum is shown magnified on the extreme right of Fig. 8. Note that the Fermi level corresponds to 2.3 eV on the experimental spectrum.

There are two possible tunneling and light emission processes as indicated in Fig. 8 by the straight arrows. The electron can tunnel from the tip to the sample elastically, becoming a hot electron in the sample, and then decay to one of the unoccupied levels. Alternatively, it can tunnel inelastically and emit a photon during the tunneling process. In either case the emission spectrum is shaped by the final DOS above the Fermi level of the sample, because the initial DOS of the W tip at the Fermi surface is smooth and featureless. From the above argument we conclude that the structures that appear in the light emission spectra of Fig. 5 arise from the localized DOS at the adsorbed O atom.

IV. CONCLUSION

We have measured the STM light emission spectra of various atomic sites on the Cu(110) surface exposed to 1 and 20 L of oxygen, using two types of tips, type A and type B. With the type-A tip, isolated light spots were seen in the constant current image of the surface exposed to 1 L of oxygen. With the type-B tip the isolated spots appeared dark. The emission spectra of the light spot imaged with the

type-A tip and the dark spot with the type-B tip were similar to each other, but distinctly different from the spectrum from the bare Cu surface. This result shows that the adsorption sites of oxygen appear as light spots with the type-A tip, while they become dark spots with the type-B tip. Thus the oxygen adsorption site was identified by the emission spectra independent of the tip conditions. Based on a $DV-X\alpha$ calculation, we conclude that the light emitted from the oxygen adsorption site arises from the electronic

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