Scanning Tunneling Microscope Light Emission Spectra of Au(110)-(2 × 1) with Atomic Spatial Resolution

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We have measured the STM (scanning tunneling microscope) light emission spectra of Au(110)-(2 × 1) at 80 K with atomic spatial resolution. The individual Au atoms along the (2 × 1) rows could be resolved in the STM image. Distinctly different emission spectra are observed depending on whether the tip is located over the atomic row or over the valley between the rows. The spectrum obtained over the row atoms can be ascribed to the emission by localized surface plasmons. The spectrum found over the valley contains emission from excitations atomically localized in the valley.

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Since the discovery of visible light emission from the scanning tunneling microscope (STM) [1] many interesting and novel results have been reported on STM light emission from extremely small structures on solid surfaces. Berndt *et al.* [2] have found that the integrated emission intensity varies out of phase to the atomic corrugation on the reconstructed Au(110)-(2 × 1) surface. On a semiconductor sample Alvarado *et al.* [3] obtained a light emission intensity map of a GaAlAs/GaAs superlattice, demonstrating the spatial resolution on the order of 1 nm. The light emission spectra of *individual* nanostructures on the surface of porous Si were measured by Ito *et al.* [4]. Very recently Downes and Welland [5] succeeded in obtaining a photon intensity map of the Si(111)-(7 × 7) surface with an atomic resolution. However, it has not been possible to achieve an atomic spatial resolution in STM images and simultaneously measure the optical emission *spectra*; that is, to obtain the emission spectra from well-defined regions separated by atomic distances and observe *the dependence of the spectra on position.*

We have obtained the atomic image of the Au(110)-(2 × 1) reconstructed surface, and at the same time obtained the emission spectra that depend on the location of the tip over the valley between the rows or over the top of the atomic row. In this Letter we demonstrate by this example that optical spectroscopy in combination with an atomic spatial resolution has now become attainable.

The sample was a single crystal surface of Au(110). It was cleaned by a well-known procedure [6] that consists of repeated Ar ion sputtering and annealing in ultrahigh vacuum (UHV). This procedure is known to produce the (2 × 1) reconstructed structure of the Au(110) surface. The sample surface was confirmed to have the reconstructed (2 × 1) structure by low energy electron diffraction (LEED). The cleanliness of the surface was checked by Auger electron spectroscopy and x-ray photoemission spectroscopy.

The STM light emission spectra were measured, using a low temperature STM housed in an UHV chamber with a base pressure less than 5×10^{-11} mb. The sample temperature was 80 K. The STM tip was made of polycrystalline tungsten, and the tip radius was about 50 nm as measured by a scanning electron microscope (SEM). The light emitted from the tip-sample gap region was analyzed by a grating spectrometer in combination with a multichannel photon counting detector. The exposure time for all the reported spectra was 200 s. The thermal drift distance during this exposure time is estimated to be 0.038 nm.

Figure 1(a) shows a topographic image of the Au(110) surface with the image of atoms on the (2 × 1) reconstructed rows. A clear atomic image is obtained only when the tip condition is optimal, and often the images do not show individual atoms on the row [2,7,8]. The corrugation between the atoms on the row is approximately 0.05 Å. The observed structure corresponds to the missing row model of the Au(110) surface [9]. Figure 1(b) shows the change of the topographic image when a surface damage is caused during a photon counting measurement. We will discuss this case later in detail.

The emission spectra were measured at a constant current of 2 nA for bias voltages V_0 of 2.3 and 2.5 V. The current direction was from the sample to the tip; i.e., electron injection into the sample. Figure 2 shows the STM light emission spectra obtained when the tip is located over the top of the row, 2(a) and 2(c), and over the valley between the rows, 2(b) and 2(d), for bias voltages of 2.3 and 2.5 V, respectively. The integrated photon counts for these spectra were ~3.5 counts/s on average, and the dark counts were 1.1 counts/s. The photon energy resolution was set at ~55 meV. The solid curves are the measured spectra obtained after subtracting the dark counts.

When the bias voltage was 2.3 V, there was no change in the topographic image before and after the special measurement; i.e., no surface modification was caused during the optical measurement. Both spectra in Figs. 2(a) and 2(b) are averaged over four separate exposures of 200 s each. The cutoff photon energy is at $h\nu_{\max} = 2.3$ eV as expected from the relation $h\nu_{\max} = eV_0$ [1], where $\nu_{\max}$ is the maximum photon frequency and h is the Planck

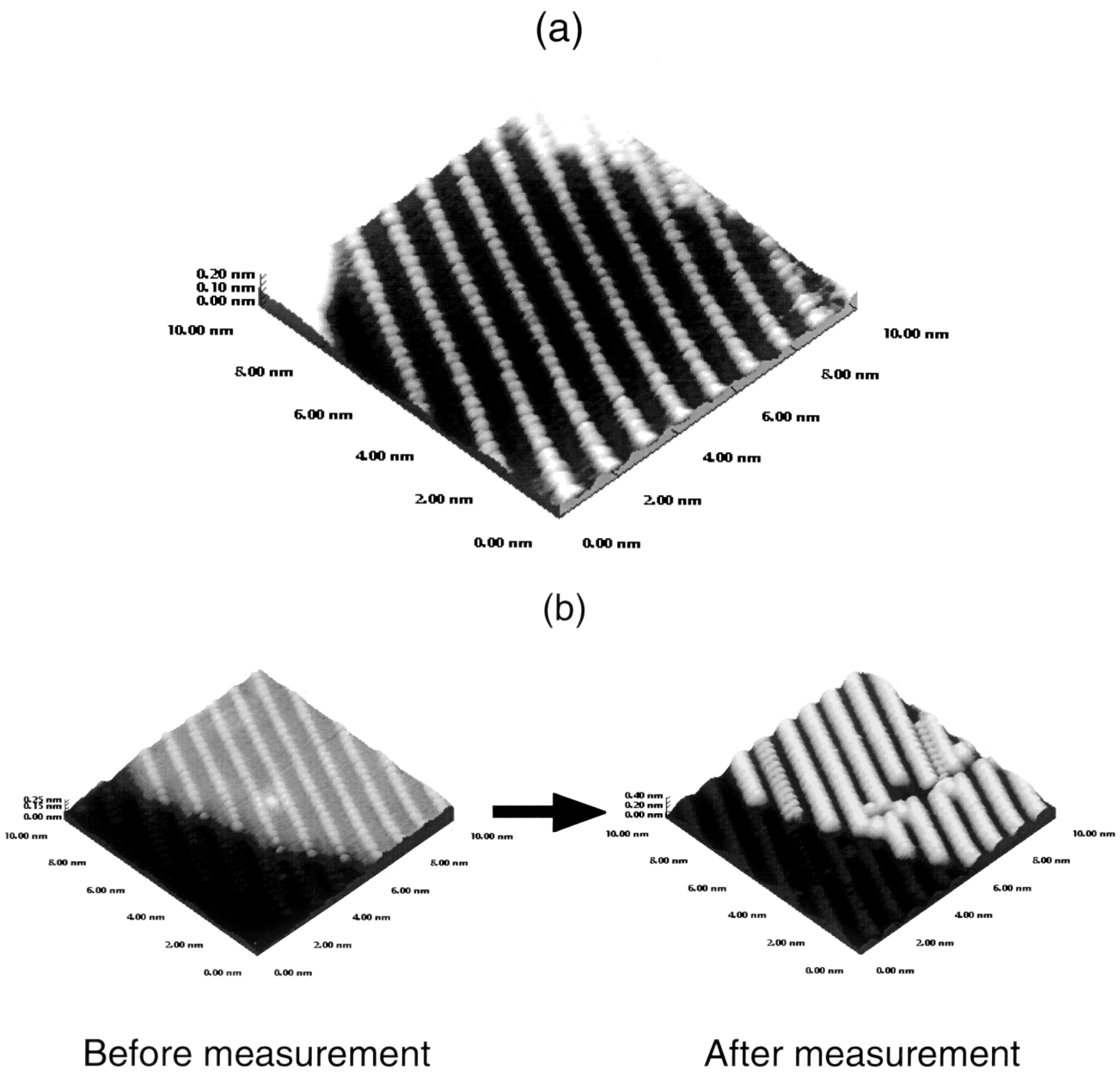

FIG. 1. (a) STM image of the Au(110)-(2 × 1) surface with an atomic resolution. The atoms along the rows can be clearly seen. (b) Atomic scale damage caused during an optical measurement when the bias voltage was 2.5 V.

constant. When the tip is over the row [Fig. 2(a)], the spectrum has a single broad peak at 2.09 eV. When the tip is located over the valley between the rows, the spectrum shows a peak at 1.91 eV in addition to the peak at 2.09 eV as seen in Fig. 2(b).

When the bias voltage was 2.5 V, the spectra in Figs. 2(c) and 2(d) were observed. Under this bias condition the topographic image did not change before and after spectral measurements when the tip was located over the valley between the rows. On the other hand, when the tip was located over the row, several atoms under the tip were missing after the spectral measurement as seen in Fig. 1(b). The damage occurs at a random time during the spectral measurement. Thus the measured spectrum varies depending on when the atomic modification occurred. For this reason we did not use averaging of the spectra for this bias voltage. Figures 2(c) and 2(d) are the raw results of spectrum collection for 200 s.

The cutoff photon energy satisfies the relation, $h\nu_{\max} = eV_0$, as seen in Fig. 2(c). When the tip is located over the row [Fig. 2(c)], a broad peak is seen centered between 1.91 eV [peak position found in Fig. 2(b)] and 2.14 eV which is the peak position predicted by the theory described below. When the tip is over the valley between the rows [Fig. 2(d)], there is a strong peak at 1.91 eV and a weak shoulder at 2.14 eV.

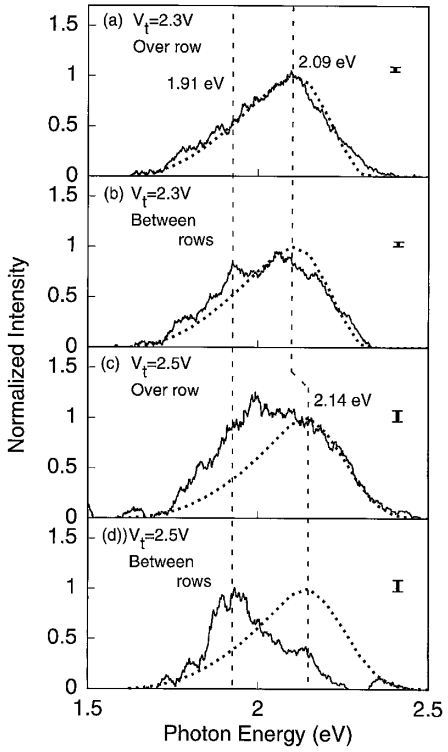

FIG. 2. Visible emission spectra measured with the tip fixed over the atomic row and over the valley between the rows, for two different bias voltages, 2.3 and 2.5 V. The current was fixed at 2 nA for all the optical measurements. The vertical error bars indicate the size of statistical uncertainties in the photon counts. The vertical dashed lines are drawn at 1.91, 2.09, and 2.14 eV corresponding to the three peak positions. The dotted curves are the calculated curves based on the macroscopic dielectric theory: (a) With the tip fixed over the atomic row for the bias voltage of 2.3 V. (b) With the tip fixed over the valley between the rows for the bias voltage of 2.3 V. (c) With the tip fixed over the atomic row for the bias voltage of 2.5. The atomic scale modification shown in Fig. 1(b) was caused during this spectral measurement. (d) With the tip fixed over the valley between the rows for the bias voltage of 2.5 V. No damage was caused when the tip was over the valley.

To understand the emission mechanism for the observed spectra, we make comparisons with a theoretical calculation based on the macroscopic dielectric functions of the metals involved [10]. Basically similar treatments to ours were reported by other authors as well [11,12]. The only elementary excitation that emerges from this theory is the localized surface plasmon defined by the geometry of the tip-sample gap region. The input parameters to the calculation are the radius of the tip, the tip-sample distance, the work functions of Au and W, and their dielectric functions. We used the radius of the tip ($\sim$50 nm) measured by a SEM. The gap distance was taken to be 1 nm. This value is a rough estimate, but the specific value does not affect the result significantly. The dielectric functions of Au and W as well as the work functions of Au(110) and polycrystalline tungsten were obtained from the literature [13–16]. The actual experimental values were used for the bias voltage and the tunneling current.

The dotted curves in Fig. 2 are the calculated spectra for the corresponding bias voltages. The theoretical curves include the correction for the wavelength dependent sensitivity of the spectrometer system that had been determined previously. The calculated curves are normalized separately for the two bias voltages shown in Figs. 2(a) and 2(c). As clearly seen in Fig. 2(a) the calculated spectrum reproduces the measured spectrum very well when the tip is located over the atomic row. From this agreement we conclude that the spectrum observed over the row arises from the localized surface plasmons between the sample and the tip.

The lateral extent of the localized surface plasmon is much greater than the distance between the top and the valley of the rows ($\approx$4 Å). Thus one does not expect the emission spectrum originating from the localized surface plasmons to depend on the spatial difference between the top of the row and the valley between the rows. Hence the peak at 1.91 eV observed only when the tip is over the valley [Figs. 2(b) and 2(d)] cannot be due to the localized surface plasmons.

When the bias voltage is 2.5 V and the tip is located over the valley [Fig. 2(d)], the shoulder at 2.14 eV agrees with the position of the peak predicted by the calculation (dotted curve) for this bias voltage. Thus the spectrum of Fig. 2(d) can be understood to be a superposition of the strong peak at 1.91 eV and a weak peak at 2.14 eV that arises from the localized surface plasmons.

Next let us try to understand the spectrum of Fig. 2(c) that was obtained over the atomic row for the bias voltage of 2.5 V. Recall that an atomic scale depression was created during the optical measurement for this bias voltage when the tip was over the row [see Fig. 1(b)]. The dotted curve in Fig. 3 is the difference spectrum obtained by subtracting the calculated spectrum (due to the localized surface plasmons as discussed above) from the spectrum of Fig. 2(c). The solid curve is the spectrum from the valley between the rows for the bias voltage of 2.5 V [same as Fig. 2(d)]. We see that the two spectra essentially agree with each other. This result indicates that the spectrum seen in Fig. 2(c) is a superposition of the spectrum from the top of the row and from the atomic scale depression created during the spectral measurement. Note that no peak was observed at 1.91 eV when the tip was located over the row and the bias voltage was 2.3 V [Fig. 1(a)]; i.e., when an atomic depression was not created. Hence, we conclude that an atomic scale depression, either an existing valley or a depression created during the optical measurement, produces the peak at 1.91 eV seen in Figs. 2(b) and 2(d).

Summarizing the above considerations, we see that a peak appears at 2.09 or 2.14 eV depending on the bias voltage but independent of the location of the tip. From

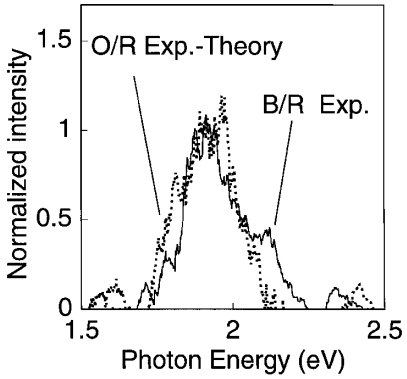

FIG. 3. Comparison of the measured spectrum of Fig. 2(d) (solid curve) with the difference spectrum (dotted curve) obtained by subtracting the calculated spectrum for $V_0 = 2.5$ V from the spectrum of Fig. 2(c).

the comparison with theory this peak is seen to arise from the localized surface plasmons between the tip and the sample surface. When there is a depression of the atomic scale under the tip like the valley between the rows or an atomic scale depression created by the tip, the peak at 1.91 eV appears independent of the bias voltage. This peak must arise from a microscopic electronic excitation whose wave function is localized in a depression of the atomic scale. The exact origin of this emission peak is not clear at present. It would be extremely interesting to identify the electronic transition that corresponds to this emission.

To conclude, we have succeeded in observing the STM light emission spectra that depend on the position difference on the order of atomic distances in solids. We have demonstrated that the STM light emission spectroscopy can achieve an atomic scale spatial resolution.

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