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Atomic-site-dependent light emission from Au(110)-(2×1) surface induced by scanning tunneling microscope

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We have investigated the scanning-tunneling microscope (STM) light-emission mechanism of the Au(110)-(2×1) surface. We found that the light stimulated by the STM is emitted through three different channels. The first channel is the emission through excitation of localized surface plasmons (LSP). The other two channels are through the recombination of *d*-band holes and *s-p* electrons in Au. When the sample bias voltage is positive (i.e., electrons are injected into the sample), *d*-band holes are created by impact ionization. The intensity due to this process is greater when the tip is located between the Au atomic rows than over the row. This process is the origin of the atomic-site-dependent spectra that we reported in a previous paper [Y. Uehara, T. Fujita, and S. Ushioda, Phys. Rev. Lett. **83**, 2445 (1999)]. When the bias voltage is negative, *d*-band holes are created by tunneling of *d* electrons from Au to the tip. The light-emission intensity due to the recombination of these *d* holes with *sp* electrons is about twice as strong as that emitted through the excitation of LSP.

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I. INTRODUCTION

The scanning-tunneling microscope (STM) has proven to be a very powerful tool for visualizing surface nanostructures with atomic spatial resolution. However, its ability to identify atomic species is limited. While an atom or a molecule adsorbed on a surface can be visualized by a STM, one cannot identify its species from the STM image alone. The recent development of STM light-emission spectroscopy (STM LES) originated by Coombs *et al.*[1] allows one to identify surface species from the emission spectrum. Indeed, hydrogen adsorbed on Si,[2] oxygen on Cu,[3,4] oxygen on Ni,[5] and C_{60} on Au (Refs. 6 and 7) have been identified by STM LES with atomic spatial resolution. From these investigations it is now clear that several STM light-emission channels are responsible for the characteristic emissions from atomic or molecular species. To establish a systematic methodology for identification of surface adsorbates by STM LES, it is important to understand different light-emission processes.

STM light emission from the Au surface has been investigated extensively, and it is generally understood that the emission is mediated by localized surface plasmons (LSP's) confined in the tip-sample gap.[8–12] The properties of LSP's confined in a nanometer scale region were first investigated by Rendell and Scalapino.[13] When one models the tip and the sample of the STM by a sphere with a radius a and a flat substrate with a semifinite thickness, the lateral extent of LSP confined in the gap is approximately given by $\sqrt{ad}$, where d is the distance between the bottom of the sphere and the substrate surface (i.e., the gap distance).[13] The numerical value of $\sqrt{ad}$ is a few nanometers even for a very sharp tip with $a\sim 5$ and $d=1$ nm. This value is larger than the lattice constant of Au (0.408 nm). Hence one expects that the STM light emission from the Au surface should not show any atomic-site dependence.

In contrast to this prediction, Berndt *et al.*[14] found that the STM light-emission intensity changes following the atomic corrugation along the $[\bar{1}10]$ direction on the Au(110)-(2×1) surface. We also found that the STM light-emission spectra of the Au(110)-(2×1) surface show atomic-scale tip-position dependence.[15] When the tip was located over an atomic row, the observed spectrum agrees well with that expected for the LSP-mediated emission. However, when the tip was located over the valley between the atomic rows, an extra spectral structure was superimposed on that of the LSP-mediated emission. In this paper we attempt to elucidate the mechanism of STM light emission whose spectra depend on atomic sites.

II. EXPERIMENT

The sample was a single crystal of Au with the (110) surface. The surface was cleaned by repeated cycles of argon ion sputtering (500 eV) and annealing (300 °C).[16] The reconstruction of the (2×1) surface structure[17] was confirmed by low-energy electron diffraction. No contamination was detected by Auger electron spectroscopy and (x-ray photoemission spectroscopy). Then the sample was loaded to a low-temperature STM housed in an ultrahigh vacuum chamber. The experiments described here were performed at 80 K. The STM tip was made of tungsten wire.

The STM light-emission measurements were made for bias voltages from 2.0 to 3.0 V and a constant tunneling current of 2 nA. The visible light emitted from the spot under the tip was passed through an infrared IR cut window of a liquid-nitrogen shield and then made into a parallel beam by a lens of focal length 150 mm. The beam was focused by a lens of 120-mm focal length into the entrance slit of a spectrograph. The solid angle of collection of the optical system was 0.05 sr. The IR-cut window had the pass band between

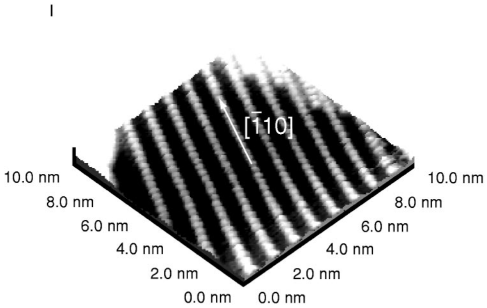

FIG. 1. Constant current image of Au(110)-(2×1) with an atomic-scale spatial resolution.

1.72 and 3.87 eV with transmission better than 10%. The spectra were detected by a one-dimensional charge-coupled device (CCD) with an intensifier. The exposure time was 200-s per spectrum. No change of the STM image was observed after each light-emission measurement; i.e., no damage was caused by the tunneling current during the optical measurement. The dark counts of the CCD detector have been subtracted from all the spectra shown here. The relative sensitivity of the light detection system had been calibrated by use of a standard lamp. The theoretical spectra shown here were multiplied by this relative sensitivity factor to allow direct comparison with the experimental results.

III. RESULTS

Figure 1 shows a typical constant current image of the Au(110)-(2×1) surface, showing the missing row atomic structure. Individual atoms along the [110] direction are well resolved. A clear atomic image is obtained only when the tip condition is optimal, and often the image did not show individual atoms on the row.

The solid curves in Fig. 2 show the STM light-emission spectra for a positive sample bias voltage of 2.3 V with respect to the tip (i.e., the electrons were injected from the tip to the sample) and a constant tunneling current of 2 nA. Figures 2(a) and 2(b) correspond to the spectra with the tip located over the atomic row and between the rows, respectively.[15] The dotted curves in Fig. 2 are the theoretical results discussed later.

The emission spectra for a negative bias voltage of 2.3 V with respect to the tip are shown in Fig. 3 by the solid curves. In this case the electrons were extracted from the sample. The dotted curves are the theoretical results discussed in the next section. Figures 3(a) and 3(b) correspond to the spectra for the tip positioned over the atomic row and between the rows, respectively.

IV. DISCUSSION

Let us first compare the experimental results shown in Figs. 2 and 3 with the dielectric theory that describes the light emission through LSP.[18,19] This theory assumes a two-step light-emission process. In the first step the tunneling current excites an oscillating dipole in the STM tip-sample gap. Then light is radiated by the oscillating dipole. The strength of dipole excitation and consequently the emission intensity are enhanced when the LSP resonance lies in the relevant energy range. The imaginary part of the dielectric constant of noble metals such as Au is small in the visible range. Thus they have strong LSP resonances that enhance light emission in the visible energy range.[20] Let us call the light emission due to the excitation of LSP resonances "LSP-mediated emission." The dielectric theory is a macroscopic description that only contains the LSP-mediated emission and does not involve the specific atomic structure of the Au(110) surface.

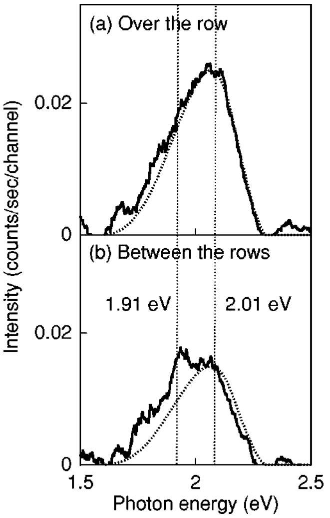

FIG. 2. STM light-emission spectra for a sample bias voltage of +2.3 V with respect to the tip. The tip was located over the atomic row in (a) and between the rows in (b). The solid curves correspond to the experimental results. The dotted curves were calculated by the dielectric theory. The two vertical dotted lines indicate the peak positions.

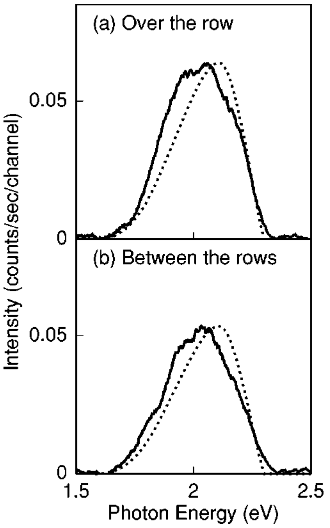

FIG. 3. STM light-emission spectra for a sample bias voltage of −2.3 V with respect to the tip. The tip was located over the atomic row in (a) and between the rows in (b). The solid curves correspond to the experimental results. The dotted curves were calculated by the dielectric theory. Note that the dielectric theory does not agree with the experiment.

The input parameters for the numerical calculation of the emission spectra are the radius of curvature of the tip, the tip-sample distance, the dielectric functions, and the work functions of the tip and the sample. The radius of curvature of the tip was determined to be ~50 nm by a scanning electron microscope. The STM gap distance was taken to be 1 nm.[21] The work functions and the dielectric functions of Au and W were taken from the literature.[22–25] The dotted curves in Figs. 2 and 3 show the theoretical curves normalized to each experimental curve. We note that several sets of dielectric functions are reported including those used in the present work.[26,27] The sensitivity of our optical detection system has a peak at 2.4 eV and decreases monotonically toward the lower-energy side. As a result the calculated spectra multiplied by the sensitivity factor have a single peak within the energy range of 50 meV for all choices of dielectric functions. The choice of the dielectric function does not significantly affect the following discussion. If the sensitivity of the low-energy side is improved in the future, it will be interesting to investigate which dielectric function gives the theoretical spectra that best fit the experimental data.

Let us first discuss the case of positive bias polarity. The theoretical spectrum due to the LSP-mediated emission (i.e., the theoretical result by the dielectric theory) agrees well with the experimental spectrum when the tip is located over the atomic row [Fig. 2(a)]. Hence we know that the spectrum shown in Fig. 2(a) is radiated by LSP's. On the other hand, the experimental spectrum for the tip located between the atomic rows does not agree with the theoretical spectrum in the spectral range around 1.9 eV [Fig. 2(b)]; there is an extra peak structure.

The lateral size of LSP's estimated by the dielectric theory[13] (i.e., $\sqrt{ad}$) is ~7 nm for the present geometry ($a=50$ and $d=1$ nm). This scale is much greater than the distance between the adjacent atomic rows lying in the [001] direction (~0.8 nm) on the Au(110)-(2×1) surface. Thus the difference between the spectra from the top of the atomic rows and the valley between the rows cannot be explained by the LSP-mediated emission mechanism or the dielectric theory. That is to say, this extra structure around 1.9 eV is not caused by LSP's but by local electronic states on the Au(110) surface.

The solid and the dotted curves in Fig. 4 show the experimental and calculated emission spectra, respectively, for bias voltages of 3.0 V [Fig. 4(a)] and 2.0 V [Fig. 4(b)]. Since the conditions of the tip used for these measurements were not good enough to achieve atomic resolution (STM images are not shown), these spectra were measured while the tip was being scanned over the surface. Thus the spectra here contain the emission detected over the rows as well as between the rows. In Fig. 4(a) we can find the extra structure (i.e., disagreement between the experimental and the theoretical spectra) around 1.9 eV. We recall that the extra peak appeared at 1.9 eV when the bias voltage was 2.3 V. This means that the peak energy of the extra structure is independent of the bias voltage. The observed spectrum of Fig. 4(b) for the bias voltage of 2.0 V agrees well with the theoretical curve. This agreement shows that the light is emitted only through the LSP-mediated emission channel independent of the tip position, and that the extra structure is not excited when the bias voltage is 2.0 V. Let us consider the light-emission mechanism that satisfies this bias voltage dependence.

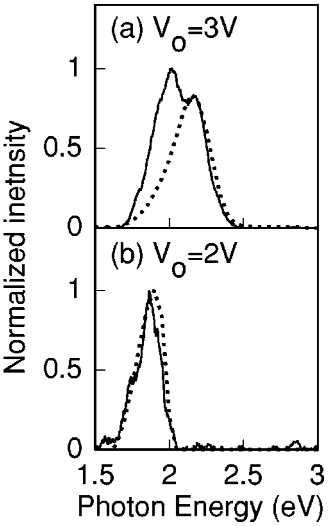

FIG. 4. STM light-emission spectra for sample bias voltage of +3.0 V (a) and +2.0 V (b). Both spectra were measured while the tip was being scanned over the surface. Hence the spectra contain the emission detected over the rows as well as between the rows. The solid curves are the experimental results, and the dotted curves were calculated by the dielectric theory.

The Au(110)-(2×1) surface has several surface electronic states above as well as below the Fermi level.[28–30] It is possible that the extra peak around 1.9 eV is excited by a transition of tunneling electrons to one of the unoccupied surface electronic states. If the energy difference between the Fermi level of the tip and one of the unoccupied surface electronic states is around 1.9 eV, one may expect the light emission excited by such a transition around 1.9 eV. The peak energy of the emission based on this mechanism should shift to the higher-energy side with increase of the bias voltage, because the Fermi level of the tip rises with respect to the surface electronic states as the bias voltage is increased. In contradiction to this picture, the extra peak was observed around 1.9 eV for both bias voltages of 2.3 and 3.0 V. Hence we exclude this process involving surface electronic states.

Mooradian[31] reported the photoluminescence (PL) of Au in the spectral range we are concerned with. This luminescence was explained by the emission arising from the recombination of *s*-*p*-band electrons and *d*-band holes created by the exciting light (Ar-ion laser). Thus if *d*-band holes can be created by the electrons injected from the STM tip (i.e., through impact ionization processes), light emission through the recombination process can be expected in the same spectral range as PL. Let us call the light emission based on this mechanism the "*d*-band impact ionization channel."

When the bias voltage is 2.3 V the maximum energy E_{injected}, of the injected electrons is 2.3-eV above the Fermi level of Au. Hence to create *d*-band holes by impact ionization, the energy difference $E_{d\ \mathrm{band}}$ between the Fermi level of Au and the top edge of the *d* band must be smaller than

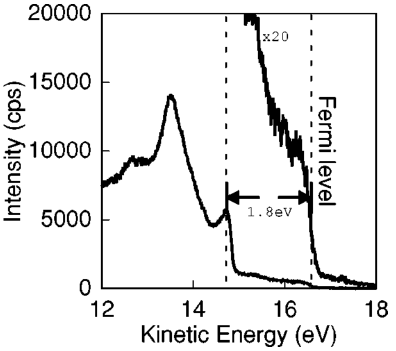

FIG. 5. UPS of Au(110)-(2×1) emitted along the surface normal.

E_{inject}. Figure 5 shows the ultraviolet photoemission spectrum (UPS) of the Au(110)-(2×1) surface measured along the surface normal. We see that $E_{d\ \mathrm{band}}$ is about 1.8 eV from this UPS. Thus the injected electrons with the bias voltage of 2.3 V can create *d*-band holes by impact ionization. We argue that these *d*-band holes and the *s-p*-band electrons recombine to emit the photons in the spectral range around 1.9 eV in Fig. 3(b).

STM light emission through impact ionization mechanisms is known for *n*-type GaAs and GaN samples.[32,33] In these cases the electrons injected from the STM tip create valence-band holes through impact ionization when the bias voltage is greater than a certain threshold value. Then light is emitted through the recombination of majority carriers (i.e., conduction-band electrons) with the holes. When this mechanism is operative, the light intensity increases with bias voltage above the threshold.

Based on the analogy with the GaAs and GaN cases, one predicts that the "*d*-band impact ionization channel" should have a threshold for impact ionization. It must be greater than $E_{d\ \mathrm{band}}$ and the emission intensity through this channel should increase with bias voltage above the threshold value. Indeed, the extra peak observed for the bias voltage of $V_0 = 2.3$ V was not seen at all for $V_0 = 2.0$ V. This result clearly indicates the existence of a threshold voltage. By comparing the spectra for the bias voltages of 2.3 V [Fig. 2(b)] and 3.0 V [Fig. 4(a)], we see that the extra structure (the difference between the experimental and the theoretical spectra) increases its intensity with bias voltage. Thus the trend predicted for the "*d*-band impact ionization channel" is consistent with the experimental results.

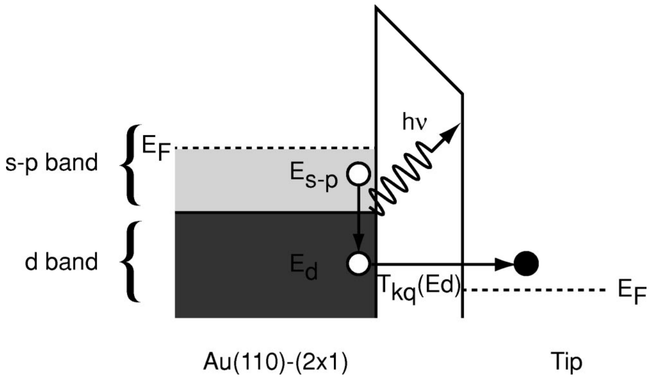

FIG. 6. Illustration explaining the *d*-electron tunneling emission (see text for details). Light is emitted by the recombination of the *s-p*-band electron with the *d*-band hole that is generated by tunneling of the *d* electron to the tip.

Ho and Bohnen calculated the density of states (DOS) of an Au slab structure of three atomic layers with (2×1) and (1×1) surfaces, and found that the density of states (DOS) of the *d* band is smaller for the (2×1) surface than for the (1×1) surface in the relevant energy range (i.e., around the top edge of the *d* band).[34] This decrease of the DOS for the (2×1) structure relative to that of the (1×1) structure must be caused by a large separation of Au atoms on the (2×1) surface. The distance between the adjacent atomic rows lying in the [001] direction of Au(110)-(2×1) is about 0.8 nm. Hence the overlap integral between the *d* electrons located in different rows must be small. As a result the local density of states of the *d* band on the row must be significantly smaller than that between the rows. This means that the "*d*-band impact ionization channel" becomes significant only when the tip is located between the rows as observed in Fig. 2(b).

Next let us discuss the spectra for negative bias polarity shown in Fig. 3. In this case the electrons are extracted from the sample surface. The dotted curves in Fig. 3 are the results obtained by the dielectric theory. The agreement between the experiment and theory is not as close as for the case of positive bias polarity shown in Fig. 2(a). Furthermore, we note that the intensity for negative bias polarity (Fig. 3) is about

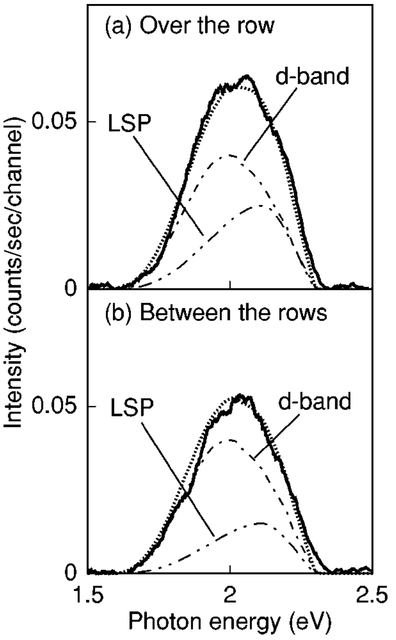

FIG. 7. STM light-emission spectra for a sample bias voltage of -2.3 V with respect to the tip. The tip was located over the row in (a) and between the rows in (b). The experimental results are shown by the solid curves (same as in Fig. 3). The calculated spectra through LSP-mediated emission and *d*-electron tunneling emission are shown by the dash-two-dotted curves and the dash-dotted curves, respectively. The dotted curves are the sum of the spectra due to the two processes.

three-times greater than that for positive polarity (Fig. 2). In the dielectric theory the change of bias polarity corresponds to the interchange of the work functions of the source and the counter electrodes. Since the difference in the work functions between Au and W is small, this theory predicts almost the same level of light intensity for both bias polarities. Thus the large intensity difference seen in Figs. 2 and 3 cannot be explained by the dielectric theory. The light-emission mechanism for negative bias polarity must be different from that for positive bias polarity. Now we consider the cause for this difference.

When the *d* electrons in Au(110) tunnel to the tip, holes are created in the *d* band. Then light is emitted through the recombination of the *d*-band holes with *s*-*p*-band electrons as indicated schematically in Fig. 6. Let us call the emission through this process ''*d*-band tunneling emission,'' and calculate the spectrum of emission from this process. The generation efficiency of *d* holes at energy E_d is proportional to the product of the DOS, $\rho_d(E_d)$ at E_d, and the tunneling-probability $T_{kq}(E_d)$ of *d* electrons at E_d to the tip. Here the subscripts *k* and *q* represent the electronic states of the source and the counter electrode (STM tip), respectively. The light-emission intensity $I(h\nu)$ for photon energy $h\nu$ can be written

$$I(h\nu)\propto\int \rho_{s\text{-}p}(E_d+h\nu)\,\theta(E_F-(E_d+h\nu)) \times M(E_d+h\nu;E_d)\rho_d(E_d)T_{kq}(E_d)dE_s, \qquad (1)$$

where $\rho_{s\text{-}p}(E)$ is the DOS of the *s*-*p* band at energy E; $M(E_d+h\nu;E_d)$ is the recombination probability of the *s*-*p* electron with energy $E_{s\text{-}p}=E_d+h\nu$ and the *d*-band hole with energy E_d. The Heaviside function θ in Eq. (1) represents the fact that the *s*-*p* band is occupied by electrons below the Fermi energy E_F.

In the numerical calculations of Eq. (1), $T_{kq}(E_d)$ was obtained by the WKB method for the gap distance $d=1$ nm to take into account the barrier height dependence of tunneling. The energy dependence of $\rho_d(E)$ and $\rho_{s\text{-}p}(E)$ was estimated from the UPS; and $M(E_d+h\nu;E_d)$ was assumed to be constant. The numerical results are shown in Fig. 7 by the dash-dotted curves. The dash-two-dotted curves in Fig. 7 are the spectra calculated by the dielectric theory. They are the same as those shown in Fig. 2. The dotted curves are the sum of the spectra from the two processes. The relative weight of the two contributions was adjusted to fit the data. We note that the contribution from the ''*d*-band tunneling channel'' is nearly twice as strong as the LSP-mediated emission for the negative bias case. The observed spectra for the negative bias polarity shown by the solid curves (same as in Fig. 3) agree well with the dotted curves for both tip positions. From these considerations we conclude that the spectra for negative bias polarity arise through two channels. One is through the LSP-mediated emission and the other is through the ''*d*-band tunneling emission.''

V. CONCLUSION

We have investigated the STM light-emission mechanisms from the Au(110)-(2×1) surface. We conclude that the STM light is emitted through three different light-emission channels. The first channel is the emission through the localized surface plasmons (LSP-mediated emission). The other two channels are the emission caused by the recombination of *d*-band holes and *s*-*p*-band electrons. When the electrons are injected into the sample (positive bias polarity), *d*-band holes are created by impact ionization. The experimental results show that the efficiency of *d*-band hole generation is higher for the tip located between the rows than the that located over the row. For negative bias polarity, *d*-band holes are created by tunneling of *d* electrons from Au to the tip. The light intensity due to the recombination of *d*-band holes and *s*-*p* electrons is about two-times greater than that through the localized surface plasmons.

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