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Photon emission stimulated by scanning tunneling microscopy in air

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Photon emission from gold surfaces stimulated by electron tunneling under application of scanning tunneling microscopy has been detected in air. At low voltages, a correlation between the light emitted and the topographic features could be observed. The influence of various parameters on the light emission has been investigated. As a secondary phenomenon, the light emission was observed to decay in an irreversible way, at high voltages (2 V).

INTRODUCTION

Lambe and McCarthy[1] have detected light emission from tunnel junctions stimulated by electron tunneling, at low voltages. Later Reihl, Coombs, and Gimzewski[2] detected such photon emissions from various materials; because they worked with an UHV chamber, they successfully investigated noble metals such as Ag, Cu, and Au, as well as semiconductors like GaAs. To account for this phenomenon the following interpretation[1–3] has been made: electrons pass through the tunnel barrier, inelastically interacting with interface plasmon modes; these plasmons decay, sending out photons on a roughened surface.[4]

Our experiment is a local method of surface investigation, complementing the scanning tunneling microscopy (STM) information. The emission depends upon the nature of the surface and tip.[5] Since the plasmon energy is an intrinsic property of the material, the emitted light contains spectroscopic information. As the emission is also correlated with surface roughness, a map of the emitted light can be established.

In this paper, experiments performed in air at room temperature are reported. A spatial map of the emission and an STM topography were successfully carried out simultaneously, showing a correlation in the relief. The influence of the tunneling conditions on the emitted light was also surveyed.

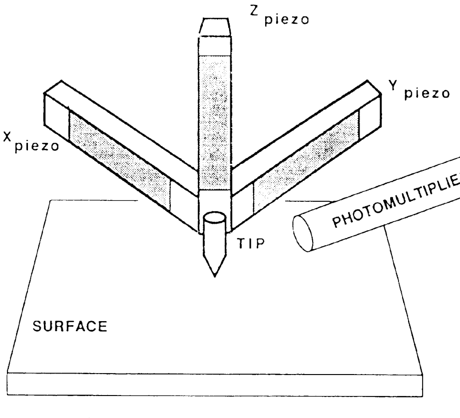

FIG. 1. Schema of the experimental setup. The PM is placed as close to the end of the tip as possible, in order to collect photons in a large solid angle.

EXPERIMENTAL SETUP

A "pocket-size" type STM built in the laboratory[6,7] was adapted for photon detection. Measurements were obtained from the STM operating in the constant current mode. The tips were prepared by cutting a 0.2-mm gold wire.

A photomultiplier (Hamamatsu R2949), operating in the pulse counting mode, with a dark count rate of 130 counts/s, was placed as close to the tip (5 mm) as possible, in order to have the larger light-acceptance angle, as shown in Fig. 1. Photons emitted between 5° and 65° relative to the surface were collected. The position of the photomultiplier could be adjusted so as not to obstruct the view of the tip coming close to the surface.

The lowest cutoff photomultiplier (PM) was chosen: our PM operated in the wavelength range $\lambda = 185-900$ nm. The complete range was used for drawing up a photon map.

Acquisition involved a double electronic system. On the one hand, the STM signal was measured with an analog-to-digital converter (ADC). On the other hand, a pulse counter was employed to evaluate photon emission; the photon count was integrated between two successive acquisitions and a single computer controlled both systems. The STM signal along with the photon count were simultaneously recorded as a spatial function. A program processed the information in order to show both maps side by side in gray scale. For all the following images the light-intensity scale ranges from minimum photon count (i.e., zero photon count) to maximum photon count. A histogram of the photon count was also used.

RESULTS

As a preliminary problem for the investigation of this type of photoemission, the tip and sample have to be selected. So far the STM has been operating with tungsten tips. However, at the voltage ranges involved (up to -2.5 V), no light emission could be achieved with this kind of tip. Tips made of Ag or Pt which emit photons were tested, but the tunneling current was too unsteady to record a reproducible topography by STM. A gold tip was therefore preferred because it is not oxidized in air and gives a good yield of emission.

Then gold samples were chosen for the same reason. The tested Ag, Cu, or Cr samples did not provide a sufficiently stable current to search for a significant photon emission.

Comparison between the STM topography and the associated emitted-light intensity

The spatial variations in photon intensity were investigated by simultaneously recording the light emission and the STM surface image at low bias voltage, in order to work in direct tunneling: tip voltage always remained less than -2.5 V. Typical measurement time was 2–4 min to achieve a contrasted photon map.

Two different types of gold samples were surveyed, that is, a gold ball, obtained by heating a gold wire and a gold film evaporated on glass to a depth of 500 Å.

As expected, the gold ball exhibited (by STM) flat surfaces separated by steps of 30 Å. A tunneling current of 30 nA was required to record a sufficient light emission, at an applied tip voltage of -1.7 V. A close relation was noted between the emitted light and the topographic features. The different steps could be made out on both maps. For example, Figs. 2(a) and 2(b) show an area of the gold ball surface, with a step and small islands. The right-hand surface emitted light strongly, with a high count rate (a factor of 30 was noted between the photon rates of the no-emission zone and the emitting step). However, the left-hand area did not emit light and the other islands emitted either more or less light.

The gold film also gave satisfactory results. STM topography displayed an array of clusters spread out on the surface. A more or less regularly roughened surface, with a grain size of about 150 Å and a corrugation of 100 Å, was observed. Unlike the gold ball, this sample was polycrystalline. The photon intensity was recorded with a tip voltage of -1.75 V, but a tunneling current of 8 nA sufficed to achieve the required contrast. The photon map showed the same contrasting clusters as on the corresponding topography [Figs. 3(a) and 3(b)]; some of them emitted light strongly, and others emitted no light at all. During subsequent scans, the emitting clusters remained the same. The drift has to be taken into consideration, while tracking the clusters.

Role of tunneling current

In air, the emission seemed to behave anomalously relative to the current. Different ranges of tunneling current, from 5 and 100 nA, were used for establishing a photon map. Use of the gold film allowed us to achieve a good contrast at tunneling currents, ranging from 5 to 10 nA, while the gold ball required currents from 30 to 100 nA, depending on the considered area. Since the noise increases with the tunneling current, the lowest possible current was always preferred to achieve a sharp contrast. With our apparatus, an optimum current seemed to exist for each emitting surface, offering the best local informa-

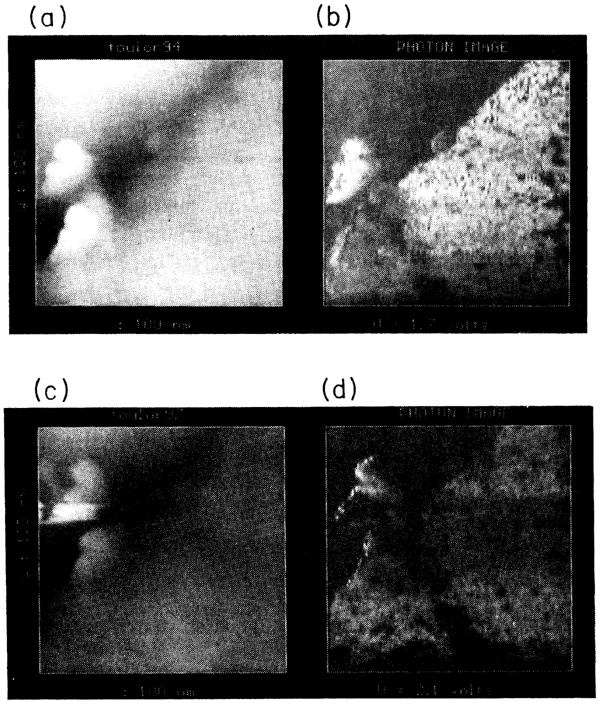

FIG. 2. Gold ball images ($I=30$ nA; area, 100×100 nm^2). (a) The topography by STM exhibits flat surfaces separated by a step of 3 nm, and small islands. (b) Corresponding spatial map of the light emission. A correlation exists between emission and topographic features. The right-hand part of the area emits light strongly, whereas the other does not. Islands emit more or less frequently ($V=-1.7$ V, maximum photon count, 20 000 counts/s). (c) and (d) STM and the corresponding photonic image of the same area, at a different tip voltage ($V=-2.10$ V, maximum photon count, 8000 counts/s). The black area corresponds to zero photon count.

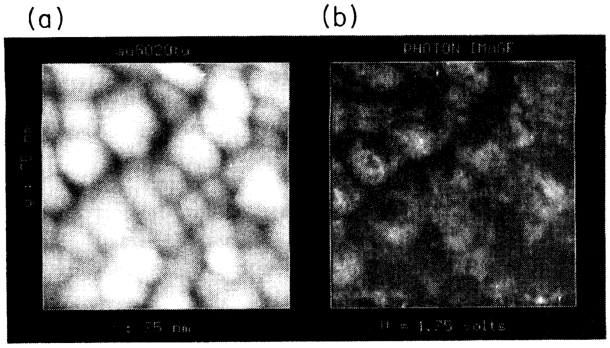

FIG. 3. Gold film evaporated to a depth of 500 Å on a glass surface ($I=8$ nA; $V=-1.75$ V; area, 75×75 nm^2). (a) The tunnel image shows gold clusters spread out on the surface with a grain size of about 150 Å. The corrugation of the clusters is 10 nm. (b) The photonic image shows the same clusters. Some of them emit photons, while others do not. Light intensity scale ranges from dark count rate (i.e., zero photon count) to 9000 counts/s.

tion. This could be accounted for as follows: the different surfaces emitted varying amounts of light, depending, for example, on surface roughness. A highly light-emitting surface only required a low tunneling current to yield a sufficient photon emission.

Strangely enough, the rate of photon emission does not increase linearly with the tunneling current, whereas theoretical calculations give a constant photon creation efficiency (about 10^{-4} photons per electron, at the resonance energy of 2.5 eV, for a silver sample).[3] This is probably due to the tunneling current noise.

Role of applied bias voltage

Our experiments involved tip bias voltages ranging from -1.4 to -2.5 V; below -1.4 V the photomultiplier did not permit any measurements because of its low-energy cutoff (therefore, no photon was detected up to -1.6 V). As we operated in the air, microstrains were present above -2.5 V. The tunneling current became unsteady and the topography was disturbed resulting in no significant emission possible.

Some authors have already suggested that plasmon frequency depends upon the nature of the tip and the surface, following the relation $\omega=[(\omega_1^2+\omega_2^2)/2]^{1/2}$, where ω_1 and ω_2 are the bulk plasma frequencies of both materials. Smolyaninov, Khaikin, and Edelman[5] showed that a Au-Au couple provides the lowest interface plasmon energy. Given the difficulties encountered at high bias voltages in air and with our apparatus, this couple is definitely the best choice.

An investigation of the evolution of the photon emission as a function of the applied voltage gives the following results: during the observation of the gold ball, the first significant emission was observed at a voltage of -1.65 V. When the bias voltage increased, the surface still emitted up to -2.10 V, with an optimum emission around -1.70 V. This range of energy corresponds to the results concerning gold, already reported in earlier works.[5] Figures 2(a)–2(d) illustrate this evolution. Figures 2(b) and 2(d) are both taken on the same area of the surface, but at a voltage of -1.7 V [Fig. 2(b), where a high emission is observed] and at -2.10 V [Fig. 2(d), where the emission begins to decay] at -2.20 V there is no longer emission. A surprising phenomenon can also be noticed: if a voltage of -1.8 V is again applied, the surface no longer emits light. Attention must be paid to the drift, which can easily be observed on the corresponding STM images.

Finally, if the tip polarity is inverted, an emission decay occurs at positive tip voltages.

Like the gold ball, the gold film surface emitted at tip voltages ranges from -1.60 to -2 V, with an optimum around 1.8 V (Fig. 4). However, when a higher bias voltage was applied between tip and sample (higher than -2 V), an "inversion" occurred; clusters no longer emitted light, whereas their edges did [Fig. 4(f)]. With respect to the gold ball, the phenomenon became irreversible when the voltage decreased. Again, clusters did not emit light below -2 V. If a larger area was scanned, centered at the same place, at a voltage of -1.75 V, a black square could be seen in the middle of the image [Figs. 5(a) and 5(b)], corresponding to the area just scanned before at a higher voltage. The rest of the surface showed clusters emitting light normally. Also a little black tail could be noted in the upper right-hand corner of the black square, corresponding to the position of the tip before scanning. This tail exceeded a spot in size because of the drift. This phenomenon was reproducible and irreversible for 30 min.

As the electrons tunnel through a barrier, they inelastically interact with plasmons from the tip-sample inter-

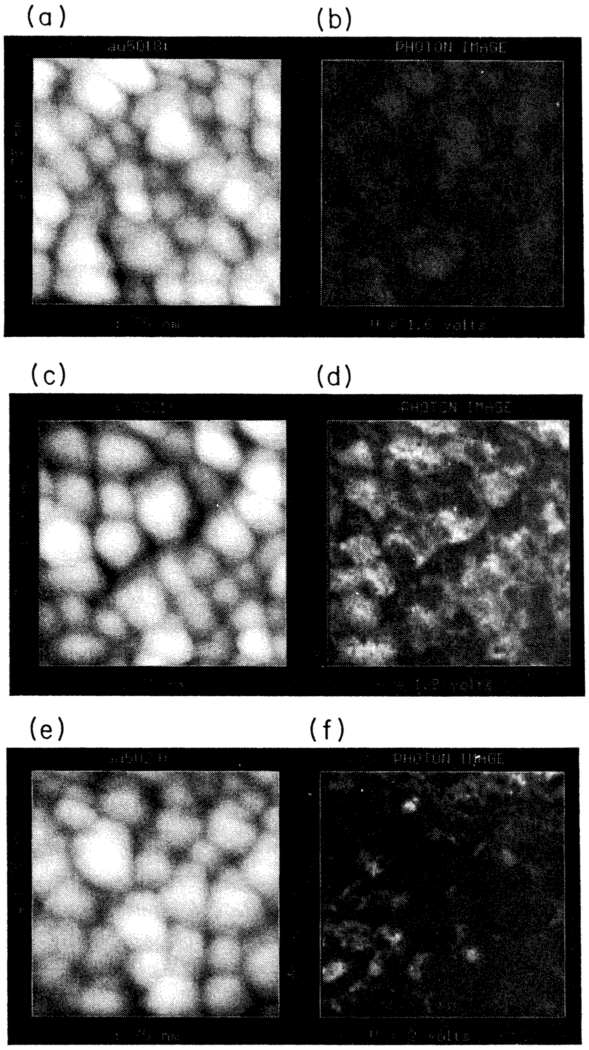

FIG. 4. Images of a gold evaporated film, showing the evolution of an emitting surface relative to the applied bias voltage ($I=5$ nA; area, 850×850 nm^2). (a) and (b) $V=-1.6$ V; maximum photon count, 4000 counts/s (c) and (d) $V=-1.8$ V; maximum photon count, 9000 counts/s, (e) and (f) $V=-2$ V; maximum photon count, 13 000 counts/s (minimum photon count, 0 counts/s). (a), (c), and (e) are the STM topographies (the corrugation of the clusters is about 10 nm), while (b), (d), and (f) are the corresponding photonic images. (f) shows an inversion of the emission; clusters no longer emit, whereas their edges do.

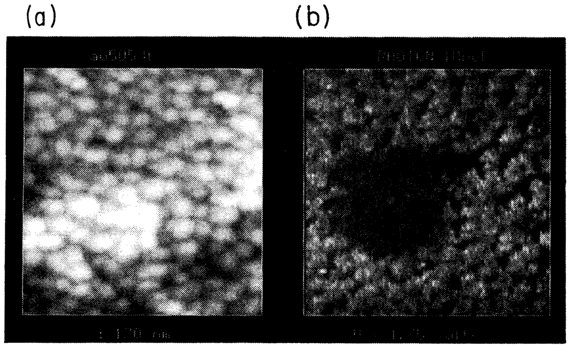

FIG. 5. Image of a large area of a gold film, evaporated on glass to a depth of 400 Å ($I=5$ nA; $V=-1.7$ V; area, 170×170 nm^2). (a) Topography by STM (the corrugation of the clusters is 10 nm). (b) Photonic image (minimum photon count, 0 counts/s). The black square in the middle of the image corresponds to an area just scanned before, at a voltage of -2.1 V; this area still does not emit. The black array on the lower right-hand corner corresponds to the position of the tip before scanning.

face. Due to the conservation of parallel momentum, surface plasmons cannot radiate on perfectly smooth surfaces. However, if the translational invariance along the surface is disrupted by roughness, the interface plasmon, localized between the tip and the surface, can emit light. This is why only some clusters emit light, while others do not. We suggest that the emission decay, at high bias voltages, could be due to any kind of surface deformation (e.g., local contamination, cleaning, or rearrangement of the surface). The tip seems to "disrupt" the surface faster at high bias voltages. The contamination assumption coincides with the following experiment: if a gold film surface has remained exposed to the air for a long time (a month), the light emission decreases. Further, a bias voltage of -1.85 V suffices for the observation of a black square with no emission, while with a clean surface, -2 V is necessary to achieve the same result. Thus photon detection confirms an expected result, which is invisible with the STM: that the scan of the tip disrupts the surface.

CONCLUSION

In this paper, the influence of certain parameters on photon emission from gold surfaces, stimulated by the STM, has been observed in air. After optimizing the tunneling current for each surface, a voltage range has been found in which light emission is enhanced, which is the same for all the surfaces.

This work demonstrates the correlation between photon emission and topographic features. This experiment can be operated in air, but at such high bias voltages and tunneling currents, a surface disruption is induced that can only be noted by photon detection. In addition to these preliminary results, further tests are being performed in our laboratory to improve our knowledge and understanding of these phenomena.

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