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Photon emission by scanning tunneling microscopy in air

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Résumé. — Une expérience d'émission de photons par microscopie à effet tunnel a été effectuée dans l'air. Les photons émis par une surface d'or sont collectés de manière à obtenir côte à côte une topographie STM et la cartographie photonique correspondante. Des correlations évidentes sont observées entre les deux images. Des spectres d'émission sont collectés simultanément en balayant la surface, donnant un troisième type d'information sur la surface. Les résultats sont un peu différents de ceux obtenus dans l'ultra vide.

Abstract. — A photon emission experiment has been done by Scanning Tunneling Microscopy in air. The emitted photons from a gold surface are collected in order to print side by side the STM topography and the corresponding photoemission mapping. Significant correlations can be observed between both images. The emission spectra are also collected while scanning the surface, thus yielding simultaneously a third piece of information. The results are markedly different from those obtained in ultra high vacuum.

1. Introduction.

Since 1976 and Lambe and McCathy's work [1] it is known that photon emission can be detected from a polarized tunnel junction. This emission was attributed to the excitation of surface plasmon modes by tunneling electrons, radiating in photons due to surface roughness [1, 2].

In 1988, Gimzewski *et al.* [3] successfully tried to detect this emission from a surface observed by STM in UHV (Ultra High Vacuum) and acquired photonic images of evaporated Ag surface [4] showing a good correlation with the STM topography. The process involved in the emission of metallic surfaces is attributed to the excitation of interface plasmon modes by inelastic tunneling electrons [5]. These local modes should be created between tip and sample by the high electric field applied. These plasmons could then radiate in photons. This process has been studied by Persson and Baratoff [6] and also by Johansson *et al.* [7] who calculated the emitted spectrum. Berndt *et al.* [8] carried out further experiments with semiconductors as well. However the latter seem to involve a different process: electron hole recombination rather than plasmon excitation [8, 9].

The study of metallic surfaces by photon emission with STM was done in air by Sivel *et al.* [10], and allowed the introduction of very fast experimental modifications. However we cannot work at a bias voltage higher than 2.50 V because of the strains due to the high field in air. Also this voltage does not allow observations of field states but is high enough to see the photon emission from metallic surfaces, thus providing a wealth of information.

A triple collecting system has been created in order to reconstruct tunneling and the corresponding photonic images, and the spectra of the number of emitted photons versus the photon wavelength.

2. Experimental set up.

The description of the experimental set up has already been given elsewhere [11, 10]. A homemade "pocket size" scanning tunneling microscope was used in air. A photomultiplier (PM Hamamatsu R2949) operating in counting mode was mounted over the tip, as close as possible to the tip apex, to collect as many photons as possible. The photomultiplier was sensitive in the 185 to 930 nm range with an attenuation in the high wavelengths. This photomultiplier is used for photonic mapping purposes. When the PM is cooled, noise decreases, but the set up requires optic fibers which may attenuate the signal. The STM signal along with the photon count were simultaneously recorded as a spatial function. A program processed the information to show both maps side by side in gray scale levels. The light intensity scale ranged from zero photon to maximum photon count. On one side of the sample a glass fiber drove photons to an Optical Multichanel Analyzer operating efficiently from 300 to 1050 nm. This spectrometer operated with gratings and a CCD detector cooled at – 110 °C. The photons were counted *versus* their wavelength. The whole set up was naturally isolated from the light. Thus we were able to collect simultaneously three different kinds of information from the same area: tunneling topography, the corresponding photonic mapping and the emission spectra during at least 30 seconds.

Due to the absence of UHV, only non oxydized samples could be observed with our microscope. This is why only gold samples were considered in this paper. Also gold emits light at a low energy range that can easily be reached in air. Two different samples were successfully utilized: - a 80 nm thick gold film evaporated on glass, and - an 80 nm gold film evaporated on heated cleaved mica.

The tips were produced by cutting a 0.2 mm diameter gold wire.

3. Comparison between tunneling topography and photonic mapping.

The gold film surface evaporated on glass was scanned by STM and showed regular clusters of about 10 nm in diameter with a 2 nm high corrugation. For emitting light the clusters were scanned by the microscope tip with a tunneling current ranging from 5 to 14 nA, and for bias voltages from 1.50 to 2.30 V. Down to 1.85 V, the photonic image showed clusters emitting light on their top (Fig. 1 with $V = 1.70$ V, $I = 14$ nA). However below 1.90 V, the light was emitted between the clusters (Fig. 2, with $V = 1.90$ V, $I = 14$ nA) (note that the scale is different between the two images). If the voltage decreased on the same area, the light still emitted between the clusters. The definition was as good in the photonic image as in the tunneling image. However the contrast between an emissive and a non emissive region in a photonic mapping was sharper than in the neighbourhood of a grain boundary. Thus, some details were better defined in the photonic image.

The second sample (gold film evaporated on heated mica) exhibited large flat areas, separated by small steps. The same features could be observed on the tunneling and photonic images. Some of these areas emitted photons while others did not (Fig. 3 was obtained at a voltage of 1.75 V and

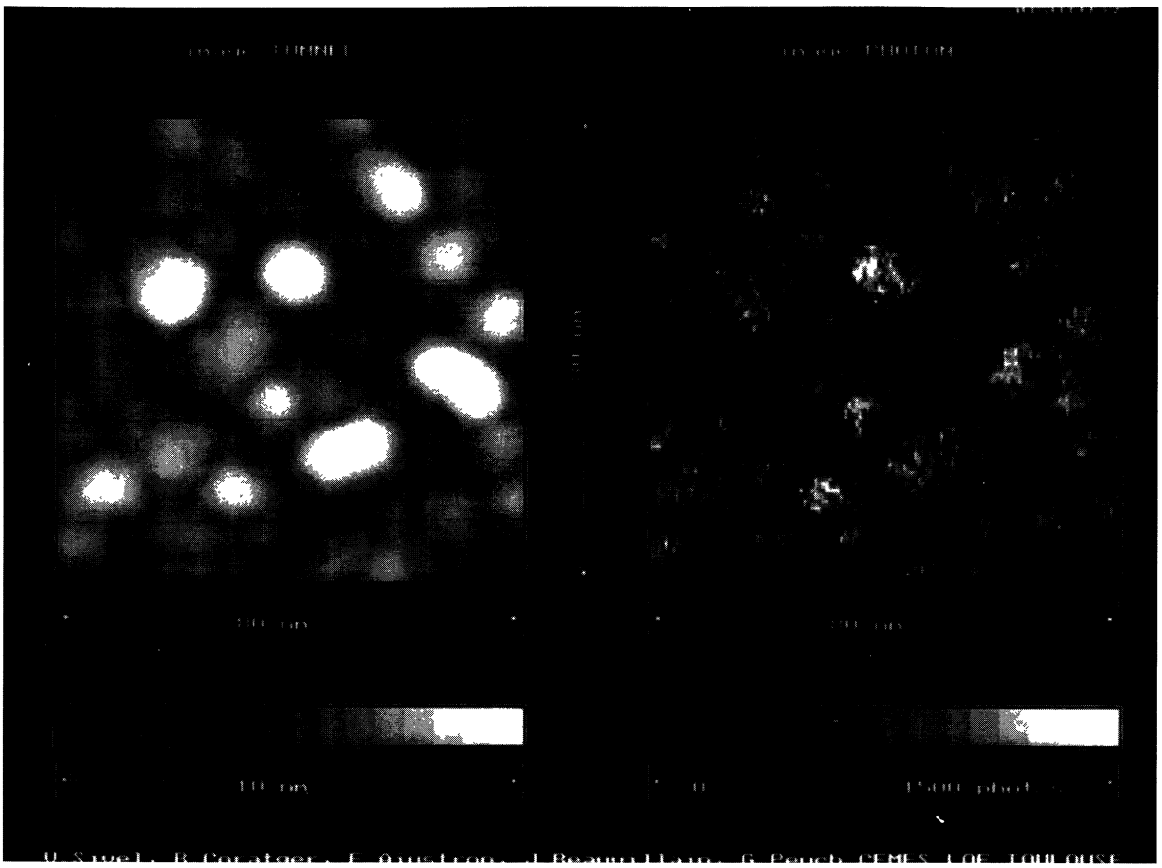

Fig. 1. — A 80 nm thick gold film evaporated on glass. (the scanned area is 80*80 nm^2, It = 14 nA, Vs = 1.70 V). a) the tunneling topography shows clusters spread out on the surface with a diameter of about 15 nm. b) The photonic image shows the same clusters emitting light on their top. Light intensity scale ranges from dark count rate (i.e. zero count) to 1200 cps.

a tunneling current of 5 nA). Photonic emission perfectly followed the steps and small topographic features. Figure 4 shows a flat low emitting surface with two small clusters on it. Emission was sharply enhanced on one of them, while the second did not emit. This can be accounted for as follows [12] an amount of gold deposited on the surface with an enhanced density of states could locally increase the emission probability for the first one, while contamination deposited on the surface could prevent emission for the second. Another likely explanation would involve cluster crystallography. Emission was expected to differ with surface orientations. A cluster with a more or less emitting crystallographic orientation could be deposited on the surface, thereby exhibiting this contrast. Also, the boundary of the the photonic feature was very well defined.

By increasing bias voltage, the emission became more intense but less uniform. If the applied bias voltage was reversed (negative bias voltage on the surface) no emission could be detected, the phenomenon was then unsymmetrical.

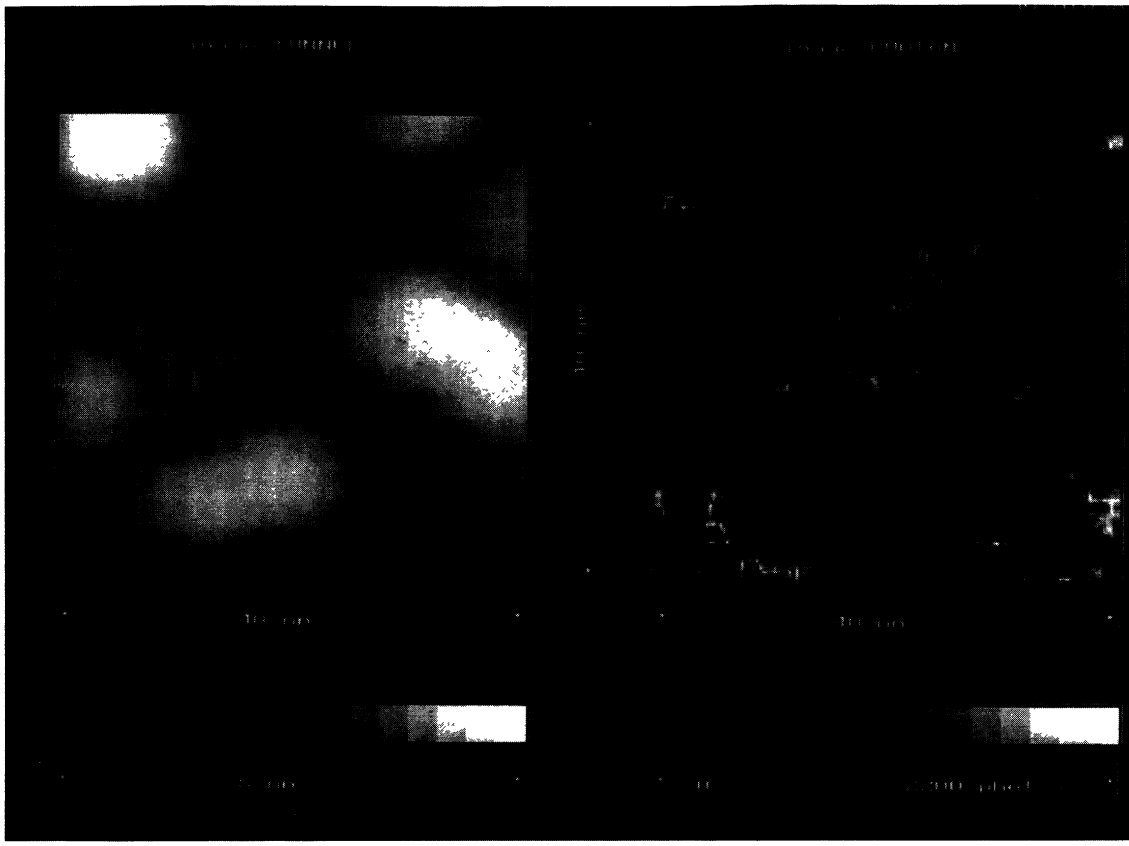

Fig. 2. — A 80 nm thick gold film evaporated on glass. (scanned area = 40*40 nm^2, It = 14 nA, Vs = 1.90 V). a) topographic image of the gold surface. b) the photonic image shows that the cluster tops no longer emit light while the interfaces between the clusters emit photons. This phenomenon appears when the bias voltage increases. The maximum count rate is 2000 cps.

4. Photon emission spectroscopy.

Three different types of surface information can be simultaneously recorded; while drawing the tunneling and photonic images, the spectra of the emitted photons can be recorded, presenting a large peak from 700 to 1000 nm (Fig. 5), for a gold film evaporated on heated mica. This peak is centred at a lower energy than those observed by Gimzewski *et al.* [12]. Two parameters differ from the latter results: firstly the surface bias voltage was low in our experiments (less than 2.10 V rather than in excess of 2.50 V), and it has been shown that the wavelength decreases when the bias voltage rises. Secondly surface contamination due to the exposure in air may shift the emission. The plasmon energy is indeed translated by the adsorbats on the surface.

Depending on the tip, the surface or sometimes the different scans, the spectrum shape varied from a single sharp peak to a larger double peak. A study of the spectra according to the bias

Fig. 3. — A 80 nm thick gold film evaporated on heated mica. (scanned are = 80*80 nm^2, I = 5 nA, V = 1.75 V). a) Three flat areas separated by steps are evidenced in the tunneling topography. Some clusters can be observed on the surface. b) the photonic image shows that only one of the three areas emits light. The large cluster in the right-hand part of the area and the small other one do not emit light at all. The maximum count rate is about 1800 cps.

voltage failed to show any variation: the spectra remained unchanged between 1.5 and 2.5 V. Only the onset of the peak was shifted to the lower wavelengths with increasing bias voltages.

Several features could be noticed in the peaks. They always occurred at the same wave-length but their respective intensities differed from one to another. Worthy of note is the fact that the spectra were recorded while scanning the surface. The different features can then be attributed to the different topographic features, the different contaminants, or different cristallographic orientations on the surface.

A study has been done with a flat gold film, by recording simultaneously the topography, photon emission and spectrum (Fig. 6a, b and c). Changes in the emission seemed to involve changes in spectra; at the beginning of the image, the emission was uniform. The spectrum exhibited a single peak centred at 800 nm. Then the emission worsened and another peak appeared at 960 nm, enlarging while the 800 nm one was vanishing. It may therefore be thought that two different emissions are involved in our surfaces, depending on the surface states.

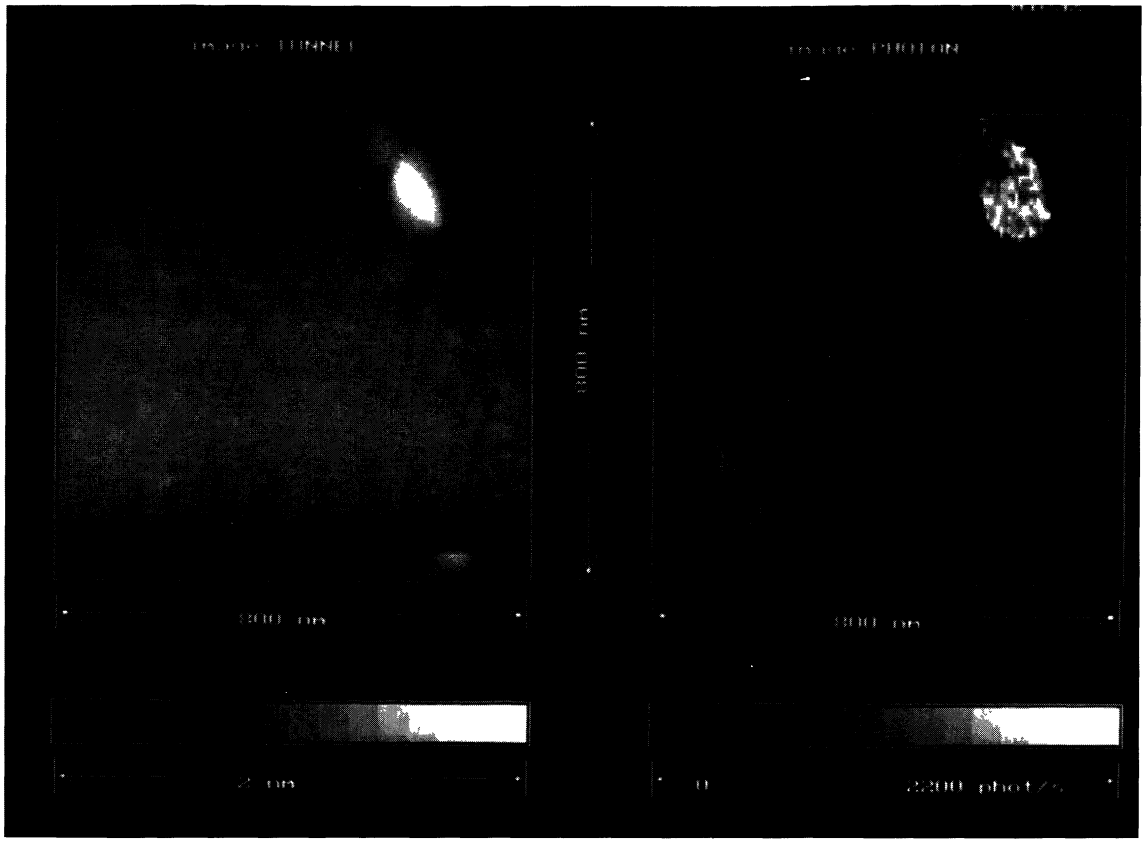

Fig. 4. — Gold film evaporated on heated mica. (scanned area = 80*80 nm^2, It = 5 nA, Vs = 1.75 V). a) the tunneling image shows a flat area with some clusters. b) the big cluster has the strongest emission. The maximum count rate is about 1800 cps, the black area corresponds to the zero photon count.

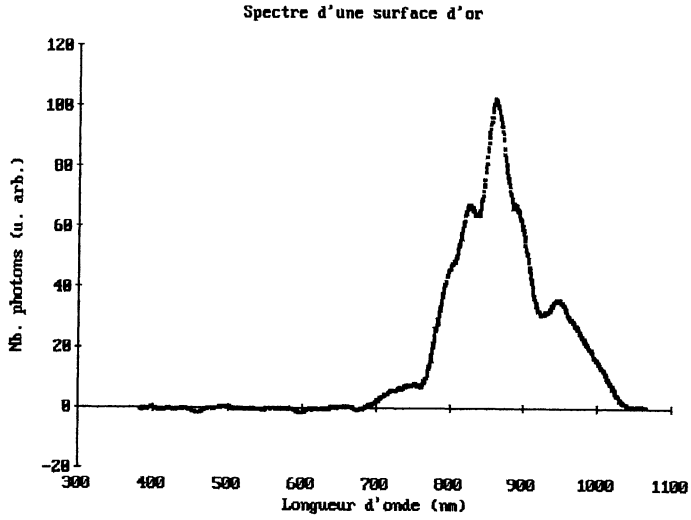

Fig. 5. — This spectrum has been recorded while scanning the surface of a gold film evaporated on heated mica, with a tunneling current of 10 nA and a bias voltage of 1.80 V, during 30 s. Several features appear in this peak.

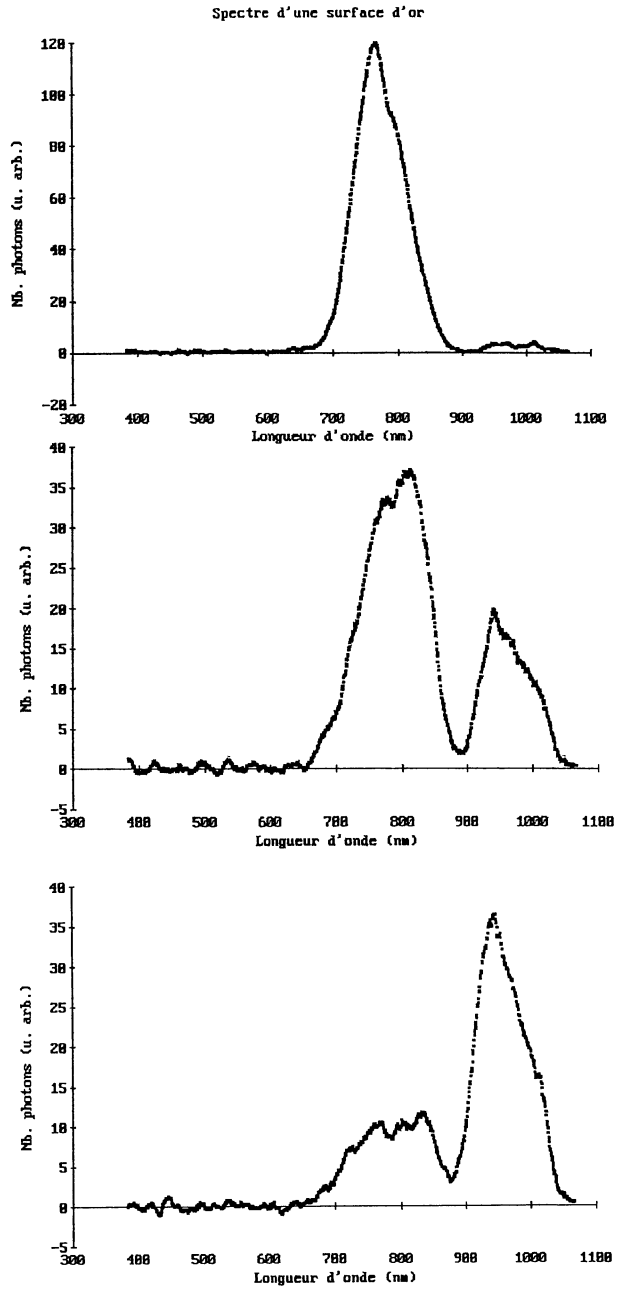

Fig. 6a. — Spectrum evolution while scanning the surface of a 80 nm thick gold film evaporated on heated mica. The first peak at 800 nm decreases while the second at 960 nm increases. b) Tunneling corresponding topography (scanned area = 40*40 nm^2, It = 10 nA, Vs = 1.90 V). b) Photonic corresponding image (maximum count rate = 1800 cps); the emission worsens during the scan.

Fig. 6b, c.

5. Conclusion.

In this paper it has been shown that by adapting the photoemission technique in air the studied samples and the bias voltage are limited but it gives rise to further interesting observations. Surface contamination seems to greatly modify the emission, but its part in the observed phenomena is still unknown. It has also been shown that the experiment is feasible in air with a significant signal correlated to the topography. This paper gives some possible explanations.

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References

[1] LAMBE J. and MCCARTHY S.L., *Phys. Rew. Lett.* **37** (1976) 923.
[2] KIRTLEY J.R., THEIS T.N. and TSANG J.C., *Appl. Phys. Lett.* **37**(5) (1980) 435-437.
[3] GIMZEWSKI J.K., REIHL B., COOMBS J.H. and SCHITTLER R.R., *Z. Phys. B Cond. Mat.* **72** (1988) 497.
[4] BERNDT R., BARATOFF A. and GIMZEWSKI J.K., *Scanning Tunneling Microscopy Related Methods* (1990) 269-280.
[5] BERNDT R., GIMZEWSKI J.K. and JOHANSSON P., *Phys. Rev. Lett.* **67** (1991) 3796-3799.
[6] PERSSON B.N.J. and BARATOFF A., to be published.
[7] JOHANSSON P. and MONREAL R., *Z. Phys. B, Cond. Mat.* **84** (1991) 269-275.
[8] BERNDT R., SCHITTLER R.R. and GIMZEWSKI J.K., *J. Vac. Sc. Techn.* **9** n°2, part 2 (1991).
[9] BERNDT R. and GIMZEWSKI J.K., *Phys. Rev. B* **45** (1992) 14096-14099.
[10] SIVEL V., CORATGER R., AJUSTRON F. and BEAUVILLAIN J., *Phys. Rev. B* **45** (1992) 8634.
[11] CORATGER R., BEAUVILLAIN J., AJUSTRON F., LACAZE J.C. and TREMOLLIERES C., *Rev. Sc. Instrum.* **62** (1991) 830.
[12] BERNDT R. and GIMZEWSKI J.K., *Surf. Sc.* **269/270** (1992) 556-559.