Spectroscopy of Light Emission from a Scanning Tunneling Microscope in Air

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Abstract. — Light emission has been detected at the tip-sample junction of a Scanning Tunneling Microscope (S.T.M.) in air on noble metallic surfaces. A spectroscopic study of emitted photons for Au-Au and PtIr-Au tunneling junctions is presented. The general aspect of the spectra depends on the materials used in the junctions; a study of the spectra as a function of tunneling current and surface bias voltage reveals similar and reproducible characteristics.

Résumé. — Une émission de lumière a été détectée au niveau de la jonction pointe-surface d'un microscope à effet tunnel dans l'air sur des surfaces de métaux nobles. Une étude spectroscopique des photons émis par des jonctions tunnel Au-Au et PtIr-Au est présentée. L'aspect général des spectres dépend des matériaux utilisés ; une étude en fonction du courant tunnel et de la tension de polarisation de la jonction révèle des caractéristiques similaires et reproductibles.

Introduction

Since the pioneering work of Gimzewski *et al.* in 1988 [1], light emission stimulated by a Scanning Tunneling Microscope (S.T.M.) has proven to be a new way of investigating surface properties with a high lateral resolution. In addition, this technique allows excitations of solids to be studied at a subnanometric scale using a high-resolution imaging tool [2–6].

This phenomenon, previously by Lambe and McCarthy detected on polarized planar junctions [7], involves various theoretical interpretations depending on the nature of materials concerned. Light emission from noble metallic surfaces has been attributed to interface plasmon modes excited by inelastic tunneling electrons. These localized Tip Induced Plasmon (T.I.P.) modes are expected to radiate in photons if the translational invariance $k_{\parallel}$ of their momentum is broken by surface roughness or by the tip itself [8–10]. In the case of semiconductor samples, electron-hole recombinations are responsible for photon emission [3, 11].

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Using this light emission as an imaging technique, photonic mappings of scanned surfaces have been drawn up and a few interesting properties have been evidenced such as the control of light emission in air [12–14].

This paper presents a frequency spectroscopic study on Au-Au and PtIr-Au tunneling junctions in air. For a given Au surface and tip material, the wavelength components of the emitted light strongly depends on the tip used. However, reproducible phenomena can be observed when tunneling current or bias voltage are increased. The wavelength of the emitted photons is found to be independent of tunneling current but spectra depends on the materials of tunneling junctions and on applied bias voltage, *i.e.* energy of tunneling electrons. For each tunneling junction, the average spectrum at fixed bias voltage has been obtained from a set of recorded spectra.

1. Experimental Set-Up

The experimental set-up has already been described elsewhere [12–14]. A customized “pocket-size” STM operating in the constant current mode was adapted for photon detection. The emitted light was collected by five optic fibers with a core diameter of 1 mm each placed as close to the tip-sample junction as possible (about 1 mm) and oriented 45° relative to the normal of the sample surface. Two optic fibers were connected to photomultipliers and three to a spectrometer.

Photomultipliers (PM) (Hamamatsu R2949) operate in the pulse counting mode with a dark count rate of 1 count per second at 255 K in the 185–900 nm range, the complete range being used to draw up photon mappings of scanned areas.

The spectrometer consists of an Optic Multichannel Analyser (EG&G, O.M.A.1245) connected with a C.C.D. detector cooled at 173 K and operating in the 300–1050 nm range. The scattering system is a grating blazed at 750 nm. The effective spectral resolution of the spectrometer is of 2 nm. Spectra are integrated over 30 s to increase signal-to-noise ratio. The response curve of our measurement system (optic fibers, scattering system and C.C.D. detector) has been taken into account and recorded spectra were corrected at each wavelength by an appropriate function calculated from the expected black body spectrum of a carbon filament lamp.

This experimental set-up allows simultaneous acquisition of S.T.M. topography, related photon mapping and emission spectrum of the scanned area.

Samples were monocrystalline gold films evaporated to a thickness of 50 nm on freshly cleaved mica sheets heated at 623 K during 24 hours at 10^{-7} Torr [15]. A low deposition rate of 0.1 nm s^{-1} allowed quasi-epitaxy of the gold layer along the [111] direction on the hot mica substrate as demonstrated by X-ray diffraction experiments. These samples exhibited flat terraces typically $100 \times 100 \text{ nm}^2$ in size separated by 2 nm high steps. Tips were prepared by cutting 0.25 mm diameter Au or PtIr wires.

2. Experimental Results and Discussions

2.1. EMISSION SPECTRA AS A FUNCTION OF TUNNELING CURRENT. — Several spectra were recorded for Au-Au tunneling junctions in air in the 5 nA - 100 nA range, bias voltage being set to 1.8 V. These spectra are shown in Figure 1. The same study has been done for PtIr-Au tunneling junction and spectra were recorded in the 10 nA - 100 nA range at a surface bias voltage of 1.8 V, as shown in Figure 2. The overall emission rate of a PtIr-Au tunneling junction being weaker than that of an Au-Au junction, the spectra given in Figure 2 have been integrated over 60 s.

Fig. 1. — Emission spectra of an Au surface scanned by an Au-tip at various tunneling currents in the 5 nA - 100 nA range. Bias voltage has been set to 1.8 V. An increase in emission rate with tunneling current is observed.

Fig. 2. — Emission spectra of an Au surface scanned by a PtIr-tip at various tunneling currents in the 10 nA - 100 nA range. Bias voltage has been set to 1.8 V.

An increase in emission rate is clearly evidenced but emission wavelengths remain unchanged when the tunneling current is increased. The amplitude of each spectrum component is simply increased as the tunneling current. Then, the number of emitted photons increases proportionately with the number of injected electrons, thereby evidencing that the electron is the particle responsible for light emission in an S.T.M. This experimental result had already be

Fig. 3. — Emission spectra of an Au surface scanned by an Au-tip at various bias voltages in the 1.65 V - 2.05 V range. Tunneling current has been set to 10 nA. Cut-offs of each spectrum are indicated by arrows.

mentioned by Sivel *et al.* [14]. The basic working principle of a S.T.M. relies on the strong dependence of tunneling current I_t on tip-sample distance $d_{\text{tip-sample}}$. Thus, changes of I_t in the 5 nA - 100 nA range (at a fixed bias voltage of 1.8 V) are expected to cause important modifications of $d_{\text{tip-sample}}$: a variation of about 0.2 nm is expected in the one-dimension model of tunneling current [16]. Such a variation cannot be considered as a fluctuation around an average $d_{\text{tip-sample}}$ value: in the constant current mode, the feedback loop of the microscope does not allow such variations in the tip-sample distance. Emission wavelengths are thus found to be independent of $d_{\text{tip-sample}}$. Rendell *et al.* [17], predicted a dependence of frequencies of localized T.I.P. modes with $(d_{\text{tip-sample}})^{1/4}$. The energy of the emitted photons being equal to the energy of the excited electromagnetic modes [18], variations should be observed in the spectra positions. This model seems to be ill-suited when it comes to correctly describing the phenomenon.

2.2. EMISSION SPECTRA AS A FUNCTION OF BIAS VOLTAGE

2.2.1. Experimental Results. — Several spectra were recorded for Au-Au tunneling junctions in air in the 1.65 V - 2.05 V range, tunneling current being set to 10 nA. These spectra are shown in Figure 3. The overall emission rate of the tunneling junction is found to increase with applied bias voltage in this voltage range. New high-energy components appear in the spectrum when bias voltage is increased: a 700 nm-peak can easily be observed when bias voltage reaches 1.8 V and a shoulder centered at about 660 nm can be seen in the 2.05 V spectrum. An increase in the high energy component amplitude (the 770 nm-peak and, when bias voltage reaches 1.85 V, the 700 nm-peak) with bias voltage is also clearly shown: the 770 nm-peak becomes three times greater than the low-energy components when bias voltage increases from 1.65 V up to 2.05 V. Cut-offs of each spectrum are indicated in Figure 3 by arrows. In this voltage range, a blue shift of high-energy cut-offs is also evidenced when increasing bias voltage.

Fig. 4. — Emission spectra of an Au surface scanned by a PtIr-tip at various bias voltages in the 1.65 V - 2.15 V range. Tunneling current has been set to 20 nA. Cut-offs of each spectrum are indicated by arrows.

In the case of PtIr-Au tunneling junctions, several spectra were recorded in air in the 1.65 V - 2.15 V range, tunneling current being set to 20 nA owing to the weaker emission rate of PtIr-Au junctions. These spectra, shown in Figure 4, differ from those obtained for Au-Au tunneling junctions. The different components consist of bumps rather than sharp peaks, but the phenomena obtained in the case of Au-Au tunneling junctions when increasing bias voltage remain the same for PtIr-Au junctions. For a sample bias voltage of 1.65 V, the spectrum is centered at about 820 nm while it is located at about 750 nm when sample bias voltage reaches 2.15 V.

2.2.2. Discussion. — As the wavelengths of the different components of recorded spectra remain unchanged when bias voltage is increased, emission frequencies are independent of bias voltage. The fundamental mechanism of light emission is thus found to be independent of bias voltage. However, new spectral components appear in the 1.65 V - 2.05 V range. When bias voltage is increased, the potential barrier and thereby the Injected Electron Energy Distribution (I.E.E.D.) are modified. The presence (or absence) of given peaks is therefore closely linked to the I.E.E.D..

Experimental high-energy cut-offs are in good agreement with calculated ones ($\lambda_{\text{cut-off}} = \frac{hc}{eV_{\text{tip-surface}}}$) (discrepancies observed for low bias voltages cannot be explained by the spectral resolution of our spectrometer). Low-energy cut-offs are identical for a given tip-sample junction.

In the case of PtIr-Au tunneling junctions, the bumpiness observed on recorded spectra shows that at a given bias voltage the I.E.E.D. is different for an Au-tip and for a PtIr-tip. To account for this, two hypotheses can be put forward. The I.E.E.D. is expected to be different between an Au-tip and a PtIr one as energy levels are different in these two materials. Besides, injected electrons may lose part of their energy through a contaminant layer at the PtIr-tip apex and the low-energy tail of the I.E.E.D. can thereby be lengthened. A given tip-sample

Fig. 5. — Normalized spectra of the light emitted by a $200 \times 200 \text{ nm}^2$ Au area scanned with two different Au-tips at a surface bias voltage of 1.8 V, a tunneling current of 15 nA and a scan rate of 0.625 Hz. Two distinct peaks are visible at about 790 nm and 880 nm on spectrum (a), while spectrum (b) exhibits a sharp peak at 790 nm.

configuration therefore leads to a given I.E.E.D. and consequently a given spectrum.

These results have to be compared with spectra obtained by Berndt [18] in an U.H.V.-S.T.M.. In these experiments, Au samples were scanned by W-tips. Recorded spectra evidenced a main spectral peak located in the 600-700 nm region. A blue shift of this spectral peak was also observed in the 2.0 V - 4.0 V range. Differences observed in emission wavelengths may partially be due to the fact that our experiment is conducted in air: the presence of contaminants on the tip apex and on the sample surface may cause important modifications in the tunneling barrier particularly concerning the I.E.E.D. and Local Densities Of States (L.D.O.S.) of the sample surface.

3. Average Spectra at a Given Bias Voltage

Spectra shown in Figure 5 were recorded during scans of a $200 \times 200 \text{ nm}^2$ Au surface with two different Au-tips at a surface bias voltage of 1.8 V. The first spectrum (a) clearly evidences two discrete components centered at about 790 nm and 880 nm respectively while the second one (b) exhibits a sharp peak centered at 790 nm. Figure 5 clearly shows that two spectra obtained from the same sample surface scanned with two different tips made with the same material are different. The same remarks can be made concerning spectra taken from Figures 1 and 3 (these spectra have been obtained from two different tunneling junctions made with the same materials and under very close tunneling conditions). To average this, a large set of experimental spectra is required to study light emission from a given type of tunneling junction. 45 spectra were recorded for different areas scanned with different Au-tips on different Au-monocrystalline samples at a fixed bias voltage of 1.8 V and a fixed tunneling current of 10 nA. An average spectrum has been obtained by summing up these 45 spectra. This normalized average spectrum is shown in Figure 6a. A given spectrum of emitted light corresponds to

Fig. 6. — Normalized average spectra of light emitted by an Au-Au (a) and a PtIr-Au (b) tunneling junction at a fixed bias voltage of 1.8 V, tunneling current being set at 10 nA. These spectra have been obtained from 45 spectra recorded during scans of different Au surfaces with different Au and PtIr-tips.

a given tunneling configuration with a given tip geometry, tip apex oxidation state and contamination state of the scanned area (*i.e.* characteristics of a given spectrum do not depend only on the sample surface). These tunneling conditions impose a given I.E.E.D. and L.D.O.S. and consequently a given spectrum shape (the fine structure observed on emission spectra could be linked to these peculiar I.E.E.D. and L.D.O.S.). By summing up all these specific spectra, these characteristic effects are toned over and the average spectrum can better be described as a large peak in the near-infrared region than as the sum of two or three distinct components.

As for Au-Au tunneling junctions, 45 spectra have been recorded for different PtIr-Au tunneling junctions at a fixed bias voltage of 1.8 V and a tunneling current of 10 nA. These recorded spectra have been summed up to obtain the normalized average spectrum of Figure 6b. Two differences can be observed between the spectra of Figure 6. First of all, the low-energy sides of these average spectra are different. To account for this, the two hypotheses previously mentioned (modifications of I.E.E.D. due to a contaminant layer on the tip apex and differences in energy levels) can be proposed. The second difference between these two average spectra concerns their high-energy cut-offs: a difference of about 0.05 eV is observed. The transmission factor of the potential barrier being very strong for high-energy electrons, a slight difference in I.E.E.D. may be amplified by the transmission factor leading to such offsets in high-energy cut-offs.

Unfortunately, the average spectrum of light emitted by an AuAu tunneling junction at 2 V is very difficult to obtain. Indeed, a decrease in emission rate is observed when applying higher than usual bias voltages: light emission can be suppressed on a scanned light-emitting area by applying a bias voltage of typically 2 V for Au-Au tunneling junctions [13]. A possible interpretation of this phenomenon has already been given [14]: this decrease in emission rate can be attributed to the response of the molecules physisorbed on the gold surface to the high electric field applied in the tunneling junction. The bias voltage range available for the study

Fig. 7. — Normalized average spectra of light emitted by a PtIr-Au tunneling junction at fixed bias voltages of 1.8 V (a) and 2 V (b), tunneling current being set at 10 nA. These spectra have been obtained from 45 spectra recorded during scans of different Au surfaces with different PtIr-tips.

of light emission from an Au-Au junction is thus limited by this 2 V-threshold. To increase the available voltage range and obtain a 2V-average spectrum, the same study has been performed on PtIr-Au junctions. Indeed, the bias voltage threshold leading to a suppression of light emission in the case of PtIr-Au junctions has been found to be greater than the one needed for Au-Au tunneling junctions (typically 2.3 V in this case).

45 spectra of light emitted by PtIr-Au junctions have been recorded at a fixed bias voltage of 2 V and a tunneling current of 10 nA. The 1.8 V-normalized average spectrum (previously presented in Fig. 6b) is shown in Figure 7a with the 2 V-normalized average spectrum obtained using the same data treatment (Fig. 7b). An offset of 0.16 eV can be observed between the two high-energy cut-offs of these average spectra, their sides being roughly the same. When bias voltage is increased, the low-energy tail of the I.E.E.D. is not modified but its high-energy cut-off is blue-shifted. Average spectra given in Figure 7 are thus dependent on applied bias voltage, the distribution of emitted photons being closely linked to the I.E.E.D..

The presence of different components in individual spectra has also been observed by Ito *et al.* [19] with a different experimental set-up. The authors reported that polycrystalline Au samples scanned by PtIr tips in an U.H.V.-S.T.M. emitted two characteristic wavelengths (620 nm and 730 nm) at a fixed bias voltage of 2.5 V and a tunneling current of 5 nA. Here again, differences in emission wavelengths could partially be due to changes in the I.E.E.D. caused by the oxidation state of the tip apex and/or by the presence of contaminants in the tunneling barrier when the experiment is conducted in air.

Conclusion

Spectroscopy of light emission from a Scanning Tunneling Microscope in air on Au samples evidences different emission wavelengths in the near-infrared region. Even if the recorded spectra are found to be specific for a given tip-sample configuration, reproducible phenomena

can be observed. Emission wavelengths are found to be independent of tunneling current in the 5 nA – 100 nA range and thereby of tip-sample distance. The wavelengths of these different spectral components, closely linked to the basic emission mechanism, are found to be independent of bias voltage. However, new spectral components appear and high-energy cut-offs are blue-shifted when the Injected Electron Energy Distribution is modified *via* applied bias voltage. The results obtained in the case of Au-Au and PtIr-Au tunneling junctions show emission spectra to be dependent upon tip materials and applied bias voltage. Injected Electron Energy Distribution seems to play a major role in light emission from a S.T.M..

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