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# PLASMON–INDUCED TUNNELING CURRENTS: THE INFLUENCE OF TIP MODES

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**Abstract.** The interaction of propagating surface plasmons (PSP) excited in a silver film with the tunneling junction of a scanning tunneling microscope has been investigated. Under particular conditions we find a strong plasmon–induced current (PIC) superimposed on the tunneling current. The generation of the PIC is in our view due to the rectification of the optical electric field by the nonlinearity of the tunneling junction. To obtain a PIC with detectable magnitude an enhancement of the optical field between tip and sample by several orders of magnitude is required. The observed dependence of the field enhancement (FE) on the tip material and the geometry of the tunneling junction will be discussed in terms of localized surface plasmons.

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## 1. Introduction

In 1973 Faris et. al. [1] observed an additional current across a metal-oxide-metal tunnel junction if the junction was exposed to near infrared radiation. Rectification of the light field at the tunnel junction was proposed as explanation of this effect. About 15 years later similar experiments have been performed with a scanning tunneling microscope (STM) [2]. Arnold and Krieger [3] demonstrated the mixing of two laser beams at an STM tunnel junction. They also observed a dc current at zero bias. Möller et. al. [4] and Kroo et. al. [5] used propagating surface plasmons (PSP) to couple the light to the tunnel junction. Beside the usual dc tunnel current, an additional plasmon–induced current (PIC) was found. They proposed that also this current is due to the rectification of the electromagnetic field related to the PSP. S. Ushioda et. al. [6] investigated the excitation of PSP by tunneling electrons. In their experiment the tunneling current drives localized surface plasmons (LSP) which in turn are converted into PSP. The optical radiation emitted by the decaying PSP was detected. The LSP are well-known from light emission from a tunnel junction as investigated by Gimzewski et. al. [7] and Berndt et. al. [8]. Specht et. al. [9] examined the electromagnetic coupling of the tip modes with PSP. They used the distance dependence of the coupling to control the tip–sample separation without tunneling. Unfortunately, they did not examine the dependence of the tip modes on the tip material and the tip radius.

In early investigations of the PIC [10] we assumed, that the electromagnetic coupling of STM tip and sample causes an additional field enhancement by LSP (tip modes). The aim of the present work was to gain more insight into the nature of the tip modes, mainly the dependence of the plasmon–induced current on the tip material was investigated.

## 2. Experimental

### 2.1. SETUP

All our experiments were carried out under well defined conditions under ultra high vacuum (UHV) at a base pressure of $5 * 10^{-11}$ mbar.

To excite the PSP the method of Kretschmann [11] was used but modified to match the requirements of an experiment in UHV (Fig 1). The beam of an $Ar^+Kr^+$ ion or a HeNe laser enters the vacuum chamber through a viewport and is then incident on the hypotenuse face of a glass prism. The beam is reflected at the two other faces one of which is covered by a silver film. The reflected beam leaves the prism antiparallel to the incident beam. Thus, a single viewport is sufficient for both the incident and the reflected light. A further advantage of this arrangement is that the prism is the

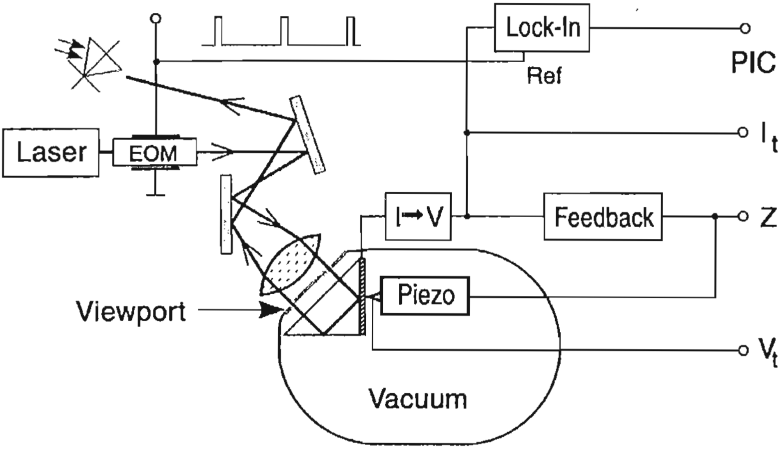


*Figure 1.* Scheme of the experimental setup combining the STM and the excitation of the surface plasmons.

only optical device inside the vacuum chamber. The surface plasmons are excited by matching the momentum of the p polarized light parallel to the silver film to the momentum of the PSP. Since energy has to be conserved the excitation of the plasmons leads to a reduction of the total reflection (to almost 10 %). There is no excitation of surface plasmons for s polarized light. In our experiment an electro-optical modulator (EOM) switches between p and s polarization to control the excitation of the plasmons. A photo diode detecting the reflected light monitors the plasmon excitation. A lens is used to focus the laser beam for increasing the light intensity. The lens is mounted on an XYZ-stage which allows to position the laser spot within a few mm. The UHV system consists of two chambers. The preparation chamber is equipped with tungsten boats for thermal evaporation of silver and copper. An oven enables the sublimation of the metal organic dye copper phthalocyanine (CuPc). The samples can be heated up to 300°C with a resistive heater. A quartz microbalance allows to measure the evaporation rate. The other chamber contains the homebuilt STM. For early experiments we used a pocket size STM with a spring reduction system for the coarse approach as described in [12]. The recent measurements have been performed with a new STM which has an improved coarse approach.

## 2.2. PREPARATION OF THE TIP AND THE SAMPLES

For the preparation of the tungsten tips for tunneling we use a dc drop-off method as described by J.P. Ibe et. al. [13]. During the etching process in a NaOH solution a viscous layer of higher density is formed flowing down the immersed wire and shielding its lower portion. This lowers the etching rate at this part, and a waist is formed at the top. Finally, the wire breaks off, and a control circuit switches off the power supply. Thus, the etching process stops immediately.

Prior to the measurement all STM tips were cleaned and sharpened in situ by field–emission [14]. An emission current (10 $\mu$A) is passed through the tip for about half an hour (tantalum counter electrode). The clean state of the tips was checked determining the height of the tunneling barrier. The barrier height should be comparable to the average of the workfunctions for tantalum and tungsten. Surface contamination leads to lower values [15].

The metal films have been prepared by evaporating silver ($\approx 400$Å) onto BK7 glass prisms (substrate not heated).

## 3. Early experiments

Fig. 2 shows a time record of the tunneling current and of the signal at the photo diode. When the electro–optical modulator switches to p polarization the total reflection is reduced leading to the dips in the photo diode signal. Simultaneously, sharp peaks appear in the tunneling current. For a tunneling bias of 10 mV the current reverses its sign, excluding the possibility that the PIC results from thermal expansion. According to the rectification model [3] the rectified current can be calculated by the Taylor expansion of the non–linear I–V curve. The linear term vanishes by time averaging. For the simplest approach the rectified current is proportional to the square of the ac bias, independent of the frequency. The data plotted in Fig. 3 allow comparison of the PIC (at $\approx 10^{14}$Hz) to the rectification of a low frequency bias (1kHz). For a low frequency bias of $0.1V_{pp}$ the PIC and the rectified low frequency current are expected to have the same magnitude. We estimate the field enhancement assuming:

- The optical field is constant in the tunneling region (this will be justified later).
- The tip–sample separation is 10Å for the given tunneling resistance [16].
- The 5mW laser beam was focused to about 50$\mu$m (field amplitude 60kV/m).
- The field enhancement due to propagating surface plasmons is about 5 [17].

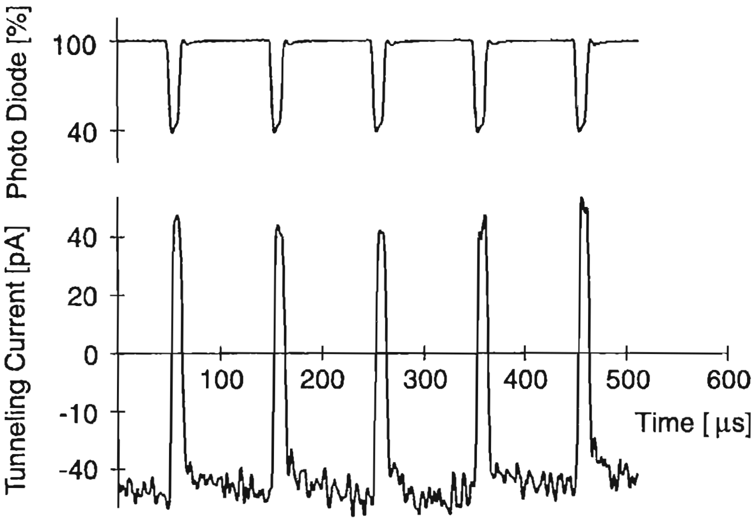


*Figure 2.* Time record of the tunneling current and the signal at the photo diode. The dips in the diode signal indicate the excitation of surface plasmons.

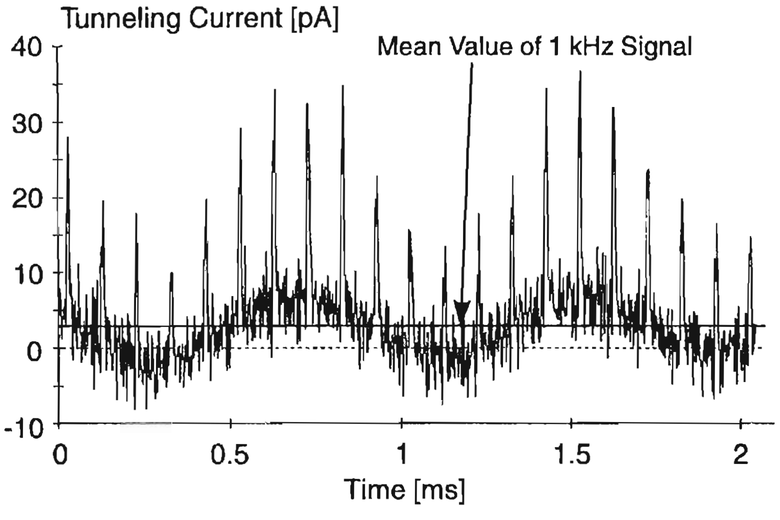


*Figure 3.* Comparison of the plasmon–induced current with a low frequency signal. ac bias of $40\mathrm{mV}_{pp}$ at 1kHz was applied to the tunnel junction.

Under these circumstances the additional field enhancement must be about 150. In several experiments we were, however, not able to observe any PIC. It turned out that a non-linear I–V curve is necessary but not sufficient for a PIC generation.

Since we did not account for the influence of the tunneling tip (geometry and optical properties) we suggested that the extra FE is due to the tip. The preparation of the tunneling tip is not very reproducible which might account for the observed variation of the results (range of the PIC from undetectable to 100pA).

We concluded:

- The tip geometry must be determined.
- The tip material might be important.
- A non-linear I–V curve caused by adsorbates might enhance PIC generation.

## 4. Recent Experiments

For direct comparison all data shown here refer to an experiment performed on one sample using one tip. The experiment was reproduced reliably.

### 4.1. DETERMINATION OF THE TIP RADIUS

To determine the tip radius we applied the Fowler Nordheim (FN) analysis [18]. In this experiment the tip–sample separation is measured as a function of the field–emission voltage while the field–emission current (100 pA) is kept constant by the feedback loop of the STM. Consequently, the electrostatic field at the tip apex is constant [19]. Solving the electrostatic problem [20] yields the tip radius.

The results of the field–emission measurement are plotted in Fig. 4. For a bias below 18V theory and measured data do not agree. In this voltage range tunneling occurs in addition to the field–emission [18] effectively increasing the tip–sample separation. A value of 49nm for the tip radius has been determined for the fit to the Fowler Nordheim line. Also the field at the tip apex (second fit parameter) of 0.34 V/Å is in good agreement with other measurements [18].

### 4.2. COVERAGE OF THE TUNGSTEN TIP WITH SILVER

The tungsten tip was covered with silver by pushing it gently into a flat silver film. The silver film was prepared by baking a mica substrate at 300°C for several hours and depositing 1000Å of silver at a rate of 5Å/s (substrate temperature 270-280°C) [21]. Then, the sample was annealed at

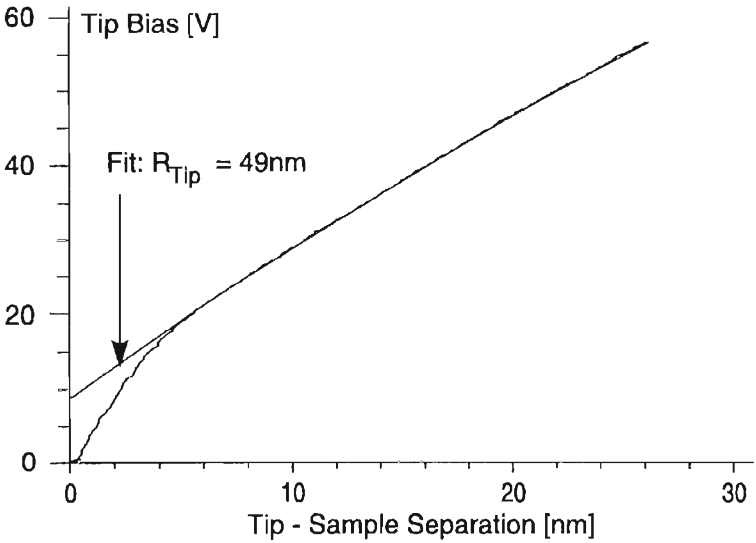


*Figure 4.* Fowler Nordheim measurement. The field–emission current is kept constant at 100pA by the feedback loop. The deviation at low tip bias is due to the tunneling current.

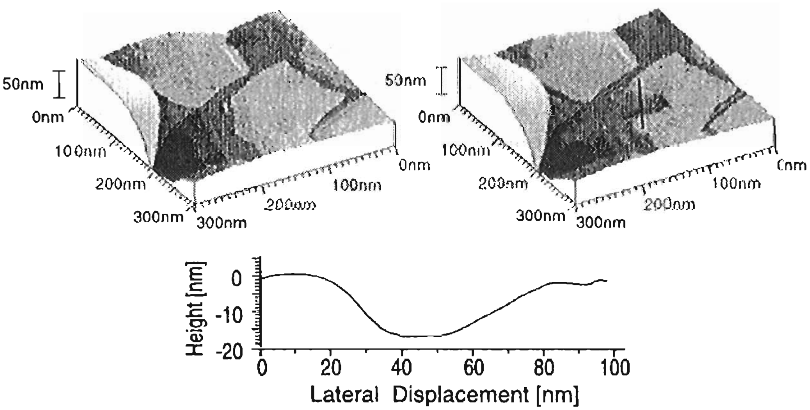


*Figure 5.* Indentation by the tip. Top: Three dimensional representation (shaded) of the data acquired before (left) and after (right) the indentation. Bottom: cross-section as marked in the right image.

270-280°C for 15min before the tungsten tip was indented 200Å into the film.

STM images of the silver film were acquired before and after the indentation (Fig. 5). One can clearly identify flat, (111)-oriented areas. Apart from the mark of indentation (right), the images differ only slightly. The diameter of the imprint of the tip is about 100nm, which is in good agreement with the tip diameter derived from the Fowler Nordheim data (see cross section).

We did not repeat the Fowler-Nordheim measurement with the covered tip because we expected a strong electro-migration of the silver.

### 4.3. OBSERVATION OF PLASMON-INDUCED CURRENT

In spite of many trials we were never able to detect a PIC using a pure tungsten tip. The experiments have been performed at different wavelengths and with different tunneling tips, never showing any generation of a PIC. After covering the tip with silver we only found a PIC if the PSP were excited with light of the wavelength 568nm. We did not observe a PIC when exciting the PSP at 633nm or 488nm. This will become clear when discussing Fig. 7.

A PIC was detected at few locations showing a non-linear I-V curve. After absorbing CuPc on the film at almost any point of the sample a PIC and a non-linear I-V curve was found. Fig. 6 shows a Z-V curve and the simultaneously acquired PIC in such an area. During the bias sweep the feedback loop was kept in operation maintaining the absolute value of the tunneling current. Thus, the gap width is altered by the feedback loop.

The data shown in Fig. 6 prove that the PIC is not due to thermal expansion of the tip or the sample. Since the tunneling current depends exponentially on the gap width, a thermal expansion would give rise to a signal proportional to the tunneling current.

## 5. Model

In our model to be discussed here the propagating surface plasmons are scattered at the tunneling tip and partially converted into localized surface plasmons introducing a strong field enhancement. The enhanced electric field modulates the tunneling voltage at optical frequencies leading to a tunneling current which contains a rectified dc component detected as a PIC.

The coupling between the propagating and localized surface plasmons is still under investigation. Holland and Hall [22] studied a sandwich structure made of silver/lithium fluorid/silver islands. A change of the matching angle for PSP excitation with respect to the silver-LiF system was observed.

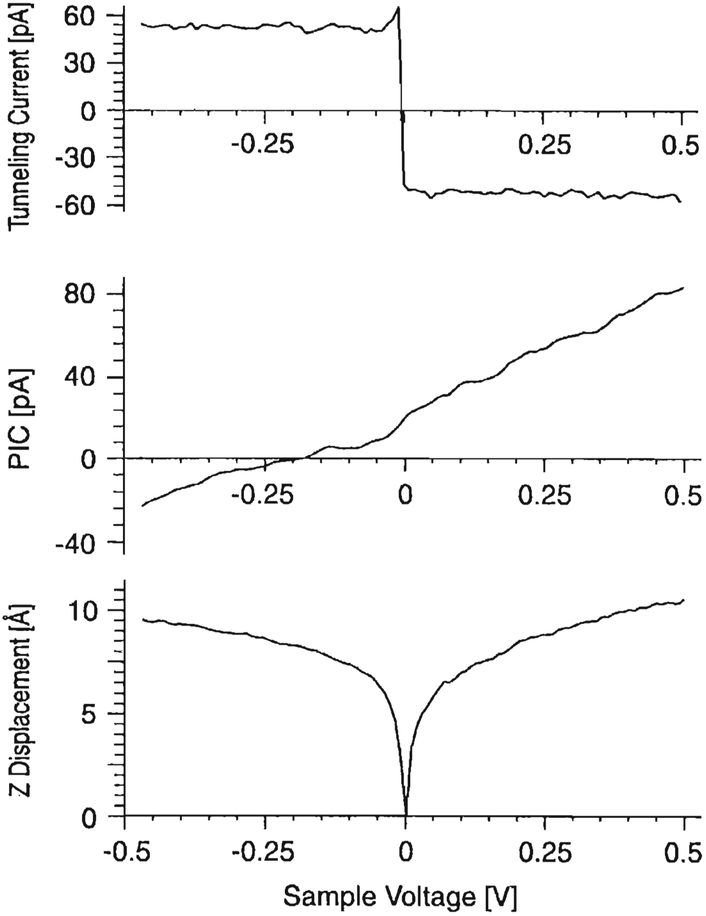


*Figure 6.* Tunneling current, plasmon-induced current (PIC), and Z displacement as a function of the bias voltage. The feedback loop is operating during the sweep of the tunneling voltage.

Agarwal and Dutta Gupta [23] explained this change by the coupling of PSP at the silver film to LSP of the silver islands. This theory does not apply to STM experiments because a change of the matching angle was not observed neither in our experiment [4] nor by Takeuchi et. al. [24].

Schollwöck et. al. [25] investigated the scattering of PSP at a tunneling tip employing perturbation theory. However, the approximation is valid only for a large tip–sample separation. Specht et. al [9] approximated the LSP by an oscillating damped dipole. This model has already been used to explain the energy transfer from excited dye molecules to PSP [26]. The coupling was estimated by Sommerfeld's theory [27] of a radiating dipole close to a conducting plane. If the dipole is 20 to 150nm apart from and oriented perpendicular to the surface, there is a strong coupling to the PSP. These results support a strong coupling of the LSP to the PSP which, indeed, is needed to explain our data.

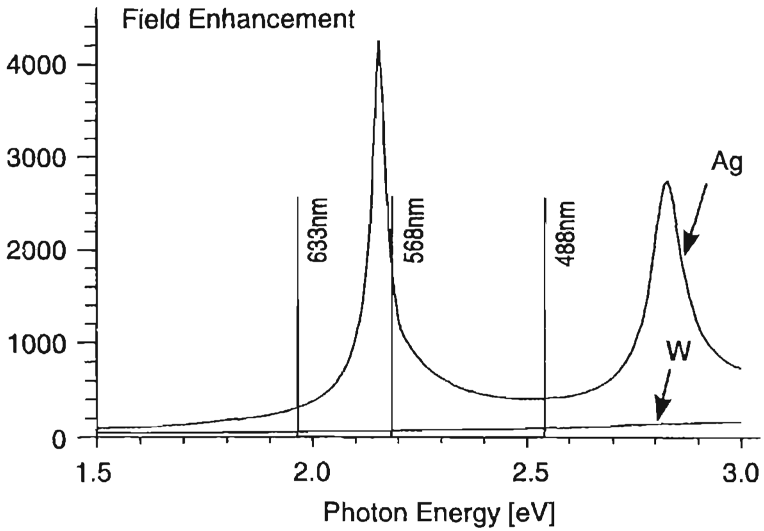
The electromagnetic field related to the LSP can be calculated solving Maxwell's equations. However, due to the complex geometry (tip, silver film, and glass support) it is very difficult to solve the Maxwell equations under these boundary conditions. Therefore, we have to adopt the following simplifications:

- An unretarded calculation is used.
  Since the size of our system is smaller than $\lambda/2\pi$ of the light the resulting errors should be small.
- Bulk values are used for the dielectric constants of the metals.
  (The dielectric constants of thin films deviate from bulk materials.)
- The silver film and the glass prism are replaced by a semi–space of silver.
  The glass prism is needed to excite the PSP and has little influence on the optical field in the area of interest.
- We approximate the tip geometry by a sphere using the tip–sample separation and the tip radius of curvature to determine the dimension of the model geometry. The field of the LSP is mostly confined to the film–tip interface. Neglecting the shaft of the tip should have little influence on the result.
- The exponential decay of the driving PSP perpendicular to the surface is neglected.
  The decay length of the surface plasmons perpendicular to the surface is $\lambda/(2\pi) * \sqrt{\epsilon_{Ag}+1}$ which is much larger then the diameter of the sphere.

Due to the host of approximations we do not expect exact results. Instead, we get the possibility of qualitative comparison between the behavior of pure tungsten tips and tips with silver coverage.

The Laplace equation for the above problem has already been solved [28, 29]. Similar calculations were carried out by W. Denk and D.W. Pohl [30] for a hyperboloid tip leading to similar results.

Fig. 7 shows the dependence of field enhancement on the photon energy calculated for a silver and a tungsten tip (tip radius 500Å, tip–sample sepa-



igure 7. Field enhancement as function of the wavelength of the light for a silver phere (radius 500Å) close to silver film (separation 10Å). The wavelengths used for the xperiment are marked. The left maximum shows a fundamental plasmon mode and the ight peak corresponds to a higher collective mode.

ation 10Å, tunneling region). The photon energies used in our experiment re marked. The FE for a silver tip exhibits pronounced resonances and trongly exceeds for all photon energies the small FE for tungsten. Since he PIC is proportional to the square of the field in the tunneling gap the ariation of the PIC is even stronger.

The field distribution is shown in Fig. 8. On the left side the magnitude f the field is shown on a logarithmic scale in units of the driving field. n the right side the direction of the field is plotted. The field distribution ustifies some of the above approximations because the field is well confined o the tunneling region. Additionally, the model holds even though the tip s only covered with silver. The field in the tunneling gap (Fig. 9) is of articular interest. The magnitude of the field is almost constant in the unneling volume as assumed in section 3.

As last step we calculated the dependence of the FE on the geometry f the tunnel junction. Fig. 10 shows the dependence on the tip radius, nd Fig. 11 shows the dependence on the tip–sample separation. Since the E varies strongly with the tip radius, and since the radius of curvature of

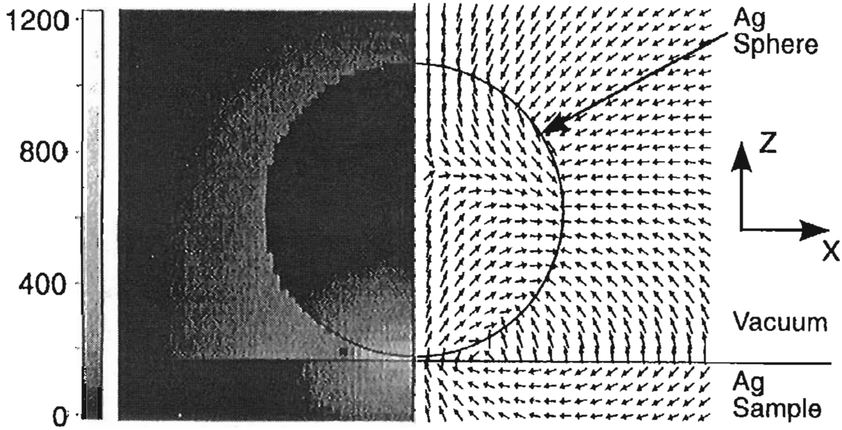


*Figure 8.* Optical electric field in the XZ plane. Left: magnitude of the field in units of the driving field (log. scale); Right: direction of the field ($\lambda$ 568nm, sphere radius 500Å, separation 10Å).

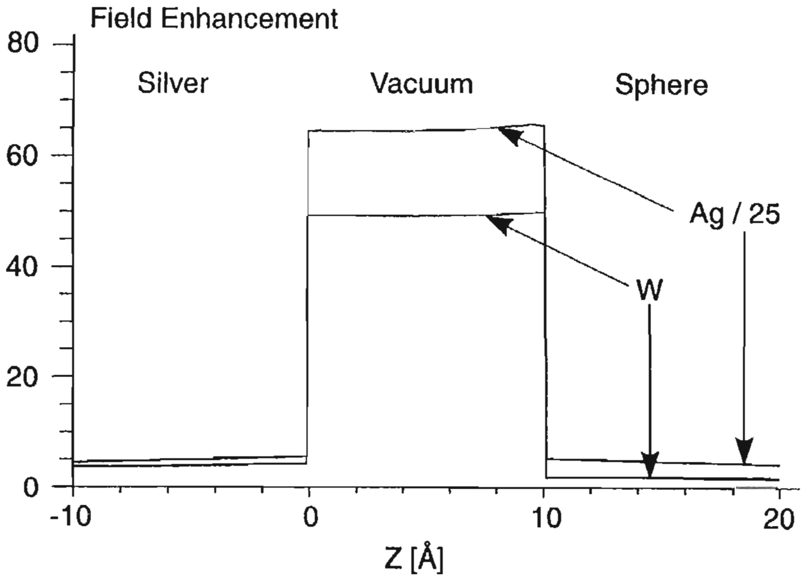


*Figure 9.* Field in the tunneling gap ($\lambda$ 568nm, radius 500Å).

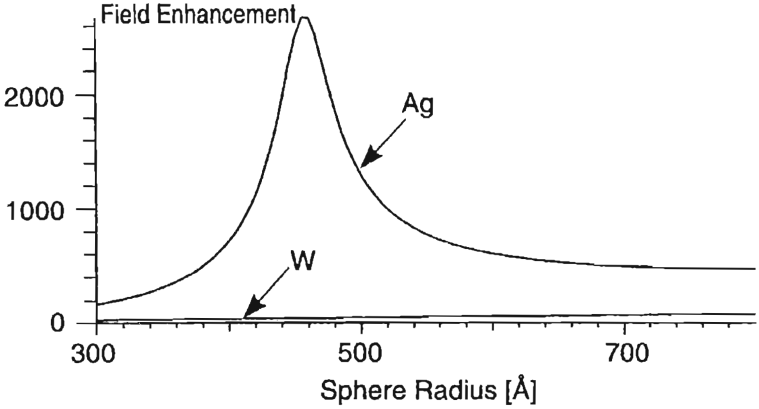


*Figure 10.* Field enhancement as function of the sphere radius ($\lambda$ 568nm, separation 10Å).

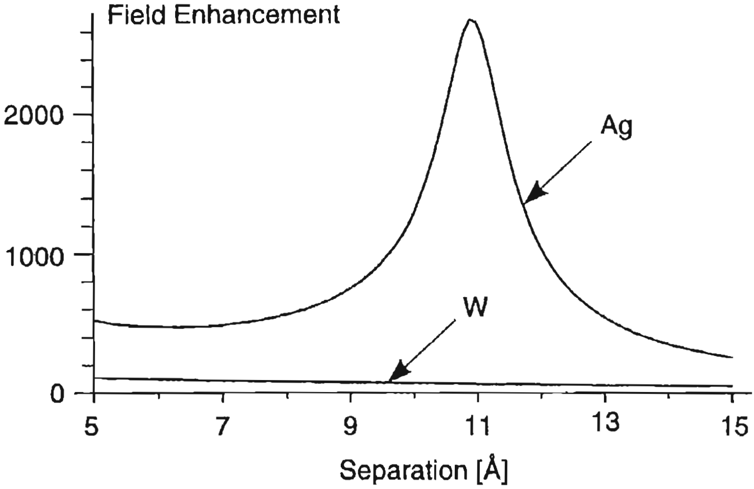


*Figure 11.* Field enhancement as function of the sphere-sample separation ($\lambda$ 568nm, sphere radius 500Å). The resonance peak corresponds to the fundamental plasma mode in Fig. 7.

tunneling tips is hard to control a strong variation of the PIC for different tips can be expected.

The dependence of the PIC on the gap width has been proposed to yield information about time effects for tunneling electrons (See for example [31, 32, 33]). Since the FE can change significantly if the tip–sample separation is altered the measurement of the PIC as a function of the gap width can only be used if one considers the contribution of both effects.

## 6. Conclusion

We coupled light to the tunneling junction of an STM via propagating surface plasmons excited at a silver film. The plasmons can generate an additional current which is superimposed on the tunneling current. It is found that a non–linear I–V curve is necessary for the generation of the plasmon–induced current (PIC).

We detected a PIC only if the tungsten tip was covered with silver and if the tunneling junction was illuminated with an optical frequency close to the plasma resonance of the tip–sample system. The comparison of the current induced by plasmons ($\approx 10^{14}$Hz) with low frequency fields ($10^3$Hz) supports the model of rectification of the optical field at the tunnel junction. The field amplitude depends crucially on the tip material and is enhanced by a factor of several hundreds for a silver tip. The field enhancement is due to a localized plasma oscillation of the tunneling tip and the sample.

## 7. Acknowledgements

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