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Nanoscale Observation of Enhanced Electromagnetic Field

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The surface of nanosized discontinuous or rough metal thin films is able to induce Raman scattering enhanced by several orders of magnitude. This effect has been theoretically attributed to the local field distribution at the surface of the films. As for the relevant parameter in phase transitions, the fields experience here huge fluctuations, leading to localized giant peaks so called "hot spots". Using a Scanning Near-Field Optical Microscope (SNOM) of extremely high lateral resolution (10 nm), we have been able to record the field distribution close to the surface of gold films. We report here the first direct observation of the hot spots with such lateral resolution. Their intensities and spatial distribution are found in good agreement with the theoretical predictions. We also have performed local spectroscopy, which shows up sharp variations at nanometric scale (much smaller than the wavelength).

1. Introduction

Since the late 70's, rough or discontinuous metallic surfaces are known to be able to induce giant optical responses, like Surface Enhanced Raman Scattering (SERS) [1]. Checking other surface optical properties, it was found that Surface Second Harmonic Generation (SSHG) [2] could also be significantly enhanced.

The active surfaces can be obtained by depositing very thin silver or gold films onto a glass substrate. These films are known to be made of a planar (2D) nanosized particle distribution. By increasing the amount of deposited metal, the particles touch each other and start to coalesce. Their shape becomes then tortuous and fractal when crossing the percolation threshold.

2. Localized Giant Field Peak Distribution

The optical properties of inhomogeneous metallic films have been extensively studied since the beginning of the century. However, close to the percolation threshold, they have only been well understood within the last ten years in terms of scaling models [3] and field fluctuations [4]. As well known, a phase transition is accompanied by strong

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long-range fluctuations [5] so that one anticipates that the local field at the percolation threshold can be very large. At the optical frequencies ω of the applied field E_0 , metal particles possess a strong surface plasmon (sp) resonance, so that the field fluctuations that accompany the percolation transition can experience the resonant enhancement in the optical spectral range, and therefore be especially large. For a 2D system, the sp resonance of non-interacting metal particles occurs for $\varepsilon_d = -\varepsilon'_m$, where ε_d and $\varepsilon_m \equiv \varepsilon'_m + i\varepsilon''_m$ are the dielectric permittivity of the insulating and metallic components. At the percolation threshold, metal particles are combined to fractal clusters, and cannot be treated as independent. However, it has been shown [6] that the problem of sp resonance in random metal–dielectric films maps the Anderson transition theorem. Therefore, it has been concluded that the collective plasmon resonance modes are localized, and found that the corresponding local field distribution consists of sharp field peaks so called “hot spots”, which intensity is, in average, enhanced by a factor $\varepsilon'_m/\varepsilon''_m \gg 1$, compared to the applied field intensity. The field peaks are separated by the field correlation length, which has been found to be much larger than the metal elementary grain size a_0 . Moreover, the theoretical model has been proved to well represent the variations of the SERS intensities, when varying the metal surface morphology and concentration [7].

We report here the first direct observation [6] of the predicted localized giant field peaks. Our experimental study includes the dependence of the intensity of the peaks on the wavelength as well as local spectroscopy for given points few tens of nanometers apart, which is much smaller than the wavelength. This study has been made feasible by using a Scanning Near-Field Optical Microscope (SNOM) of very high in plane lateral (x, y) resolution, which is directly sensitive to the local electromagnetic field amplitude.

3. The High (x, y) Resolution SNOM Set-Up

As our previous set-ups [8], our new transmission mode SNOM (Fig. 1) works simultaneously as an Atomic Force Microscope (AFM), and gives both signals together [9]. The probe tip is made with a tungsten wire (125 μm in diameter) etched by electrochemical erosion. We obtain a typical tip-end radius of curvature of 20 nm, and sometimes less than 10 nm. The tip is the end of a cantilever attached to a piezoelectric translator that can excite it close to its resonant frequency (≈ 5 kHz) in the z direction, perpendicular to the sample (AFM tapping-mode [8]). A feedback system keeps the amplitude of vibration constant during a scan of the sample surface, and gives the AFM topographical signal of the sample. The sample is attached to a horizontal (x, y) piezoelectric stage.

The tip and the sample are set below a commercial microscope (Olympus BH). In the present work, the light source is mostly a tuned Ti–sapphire laser in the near IR range, but we also used various visible wavelengths of the He–Ne, Ar⁺ and Kr⁺ lasers. The beam is focused on the surface of the sample, via a first microscope objective. The collection of the transmitted light passing through the microscope is axially symmetric above the sample and is made by a second microscope objective. The detector is a photodiode or a photomultiplier.

The vibration of the tip, on top of the sample surface, modulates the transmitted and scattered fields. As the tip scatters the near-field optical signal of the sample

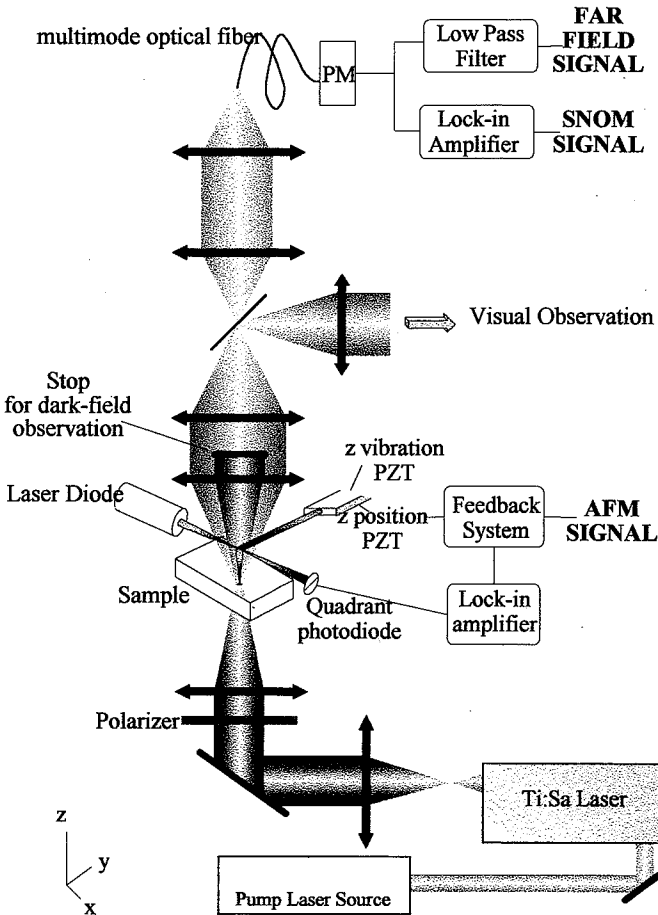


Fig. 1. New SNOM set-up (mostly described in text)

surface in all directions, it is an apertureless set-up. Keeping the tip amplitude vibration constant, and thus the average distance between the tip and the sample, gives a constant modulation of the scattered signal when scanning a uniform surface. The modulation of the radiated field allows us to follow the local electromagnetic field (x, y) variations close to the sample surface. A lock-in detection of the light collected in the far zone at the tip vibration frequency gives the electromagnetic field locally scattered in the near-field region. As we have shown in previous papers [8], this near-field optical signal, the SNOM signal, has the optical (x, y) resolution of the tip end.

The light transmitted from the source may produce a strong dc signal, and the cantilever itself gives a residual modulation. Rejecting both unwanted signals improves the dynamic of the detector. We then work in a dark field configuration by putting a black screen before collecting the flux.

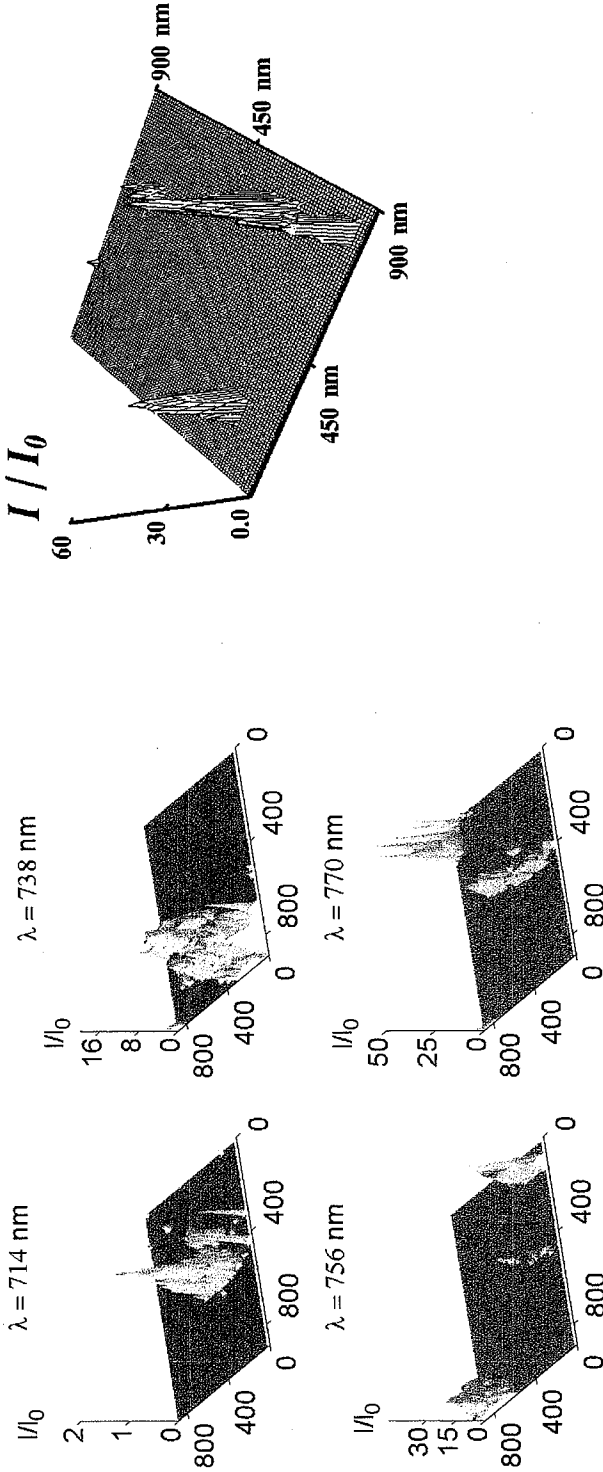


Fig. 2. Left part: experimental SNOM images of the local fields of a percolating gold on glass film for the different wavelengths set on the Fig. (nm units are used for the x, y coordinates). Right part: calculated distribution of the local electromagnetic field intensities at the surface of a percolating semicontinuous gold film. The incident wavelength (780 nm) has been kept very close to the highest one in the left part of this figure

4. Experimental Results

The samples were prepared by depositing the metal on glass substrates at room temperature under ultra high vacuum (10^{-9} Torr). The elementary gold grain size a_0 , determined by TEM measurements, is about 10 to 30 nm in diameter, depending on the deposition rate. In order to determine the closeness to the percolation threshold, dc resistance and mass thickness were measured all along the deposition process. Optical reflection and transmission in the visible and near IR range were measured afterward, and compared with the well-known optical properties of percolating samples [3, 10].

We show in Fig. 2 (left part) four near-field optical images, recorded in the same (x, y) area ($900 \times 900 \text{ nm}^2$), on the same percolating gold on glass film, for four different wavelengths in the near infrared range. The (x, y) resolution of one pixel is 10 nm. Due to this extreme lateral resolution, the images cannot be anymore exactly reproducible in space, because of very small mechanical or thermal drifts. The vertical scale is the ratio of the measured intensity (I) to the mean value of the noise taken on the entire image (I_0). We then take, in the figure the maximum of the noise background as the basal plane of these images. These four near-field images clearly have the same appearance as the typical simulated image shown in Fig. 2 (right part).

The agreement with theoretical predictions can be summarized as follows. (i) The hot spots are localized in areas, which are much smaller than the wavelength, and can be as small as the elementary grain size a_0 . (ii) The experimental enhancement of the local field intensity is increasing with wavelength, as does the ratio ϵ'_m/ϵ''_m , and is of order of 10^2 as expected for $\lambda = 770 \text{ nm}$. Note that the intensity scales are not the same for the four experimental images. The observed enhancements are, of course, less than the

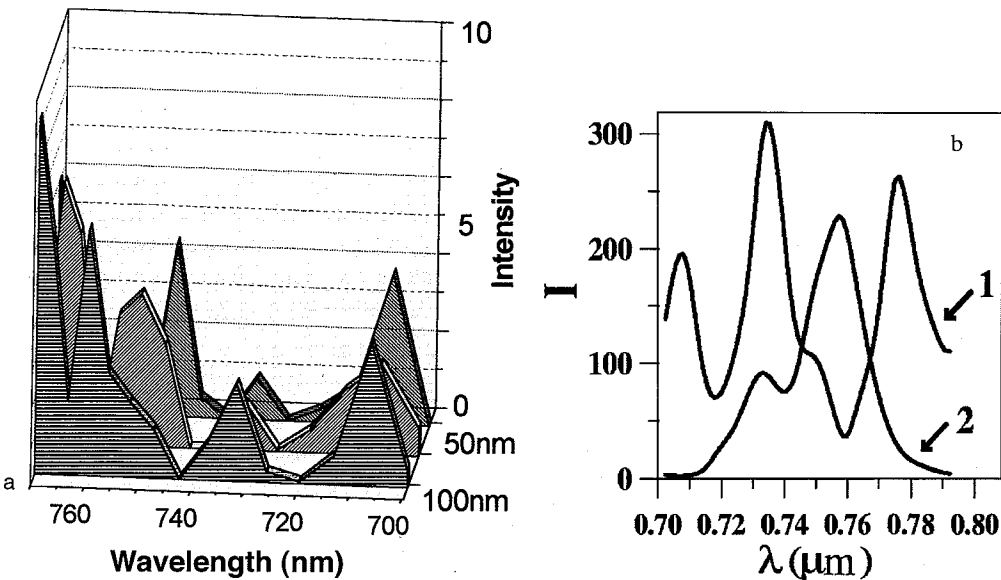


Fig. 3. a) Experimental near-field spectra for three points, separated by a distance of 50 nm. The spectral range is given by the Ti-sapphire laser, without changing any optical component. b) Calculated near-field spectra, for the same range as in a) and two points separated by a distance of 5 elementary grains ($5a_0$)

actual largest enhancements occurring in the peak, due to some averaging at the scale of the finite spatial resolution. For the same reason, the experimental peaks also appear less enhanced than the predicted ones. (iii) The near-field images are very much wavelength dependent: even shifts in wavelength as small as shown in Fig. 2 (left part) can result in very different images. (iv) In accordance with the theoretical model, the hot spot spatial separation has to increase with the wavelength. This is barely visible on Fig. 2 (left part) due to the too small wavelength shifts.

We have also performed near-field nano-spectroscopy on percolating samples, in the optical allowed range of the Ti-sapphire laser. We first park the SNOM tip at one place, and then vary the incident wavelength. We thus can determine the local resonance frequencies of nm-size areas of the film. The experimental results are depicted in Fig. 3a, which shows three spectra recorded at three different points of the same sample, only separated by a distance of 50 nm. Even at this small scale, the areas located underneath the tip have different local structure, and therefore resonate at different wavelengths, leading to different local spectra. These local spectral variations are due to differences in the field distribution for the modes involved at each wavelength. The tip acts as a nano-detector of the near-field electromagnetic wave existing at its location in space. The local field is due to the simultaneous presence of the surface and the tip, and is excited by the incident field. In fact, because the tip does not resonate in the used wavelength range, the images and the spectra represent mostly the fields that would have existed in the absence of the tip, and then represent the normal modes of the percolating gold film. The experimental local spectra are in very good agreement (amplitudes, shape and distances between peaks) with the theoretically predicted ones shown in Fig. 3b.

5. Conclusions

By performing near-field high resolution imaging and local spectroscopy, we have experimentally analyzed the localized optical excitations of random metal dielectric thin films close to the percolation threshold. The "hot spots" of the films strongly depend on the incident wavelength, and represent very large localized fields due to excitation of the different modes. All these features are only observable in the near zone. In the far zone, the images and spectra are all averaged, and the fluctuations are no longer visible.

Since non-linear optical signals are proportional to the field raised to some power, the large local fields should induce very much enhanced non-linear local responses.

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