Localized plasmon enhanced optical response : harmonic generation and polarization effects.

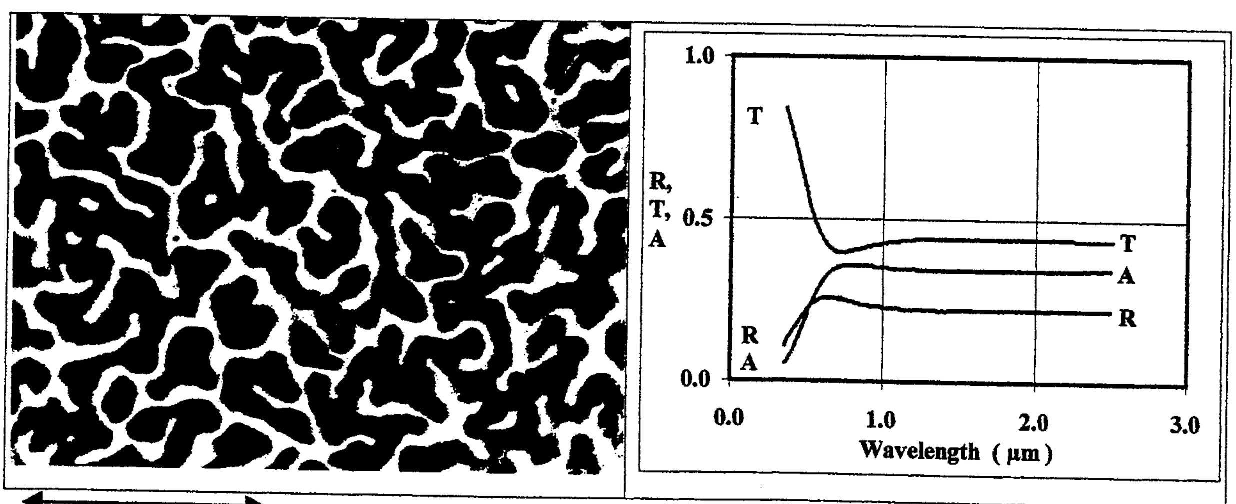
P. Gadenne * [a], B. Berini [a], S. Buil [a], X. Quelin [a], C. Anceau [a], S. Gresillon [b,c], S. Ducourtieux [b], J. C. Rivoal [b], M. Breit [c], A. Bourdon [d], A. K. Sarychev [e], V. M. Shalaev [e].

ABSTRACT

It is now known that plasmon oscillations supported by nanostructured metal thin films of fractal morphology, can result in large local fields and strong enhancement of optical phenomena, for example Raman scattering [1]. The localized plasmons, acting like nano-antennas, can concentrate very large electromagnetic energy in nanometer-sized areas, "hot spots" and provide particularly strong enhancement of optical responses, in a very broad spectral range. Our new experimental results show up position dependence of the hot spots on the polarization state of the light. Moreover, as expected from recent theoretical predictions [2], on this kind of thin percolating films, there is a dramatic enhancement of the second harmonic generation (2ω) out of the specular directions. This unusual diffuse SHG could be connected to possible chirality of the percolating metallic films, which is expected to manifest itself as change in the hot-spot distribution for the left- and right circularly polarized incident light.

INTRODUCTION

The 2D metal-dielectric films consist in a planar distribution of nanometer sized metal grains randomly distributed on the surface of an insulating substrate. When increasing the filling factor p (ratio of metal to total volume), the coalescence between initially isolated metallic grains occurs at the percolation threshold p_c, resulting in formation of very irregularly-shaped fractal clusters.



200 nm. 1.a : TEM 1.b : Linear optical properties

Figure 1 : Granular 2D silver film close to the percolation threshold. "Mass thickness" is d_m = 6.5 nm.

*: Patrice.Gadenne@physique.uvsq.fr , phone (33)1 3925 4494 ; a : Laboratoire de Magnetisme et d'Optique de Versailles, UMR 8634, Universite de Versailles Saint Quentin, 45 ave. des Etats Unis, F-78035 Versailles Cedex, France ;
b : Laboratoire d'Optique Physique, L.O.P. - ESPCI Universite Pierre et Marie Curie, 10 rue Vauquelin, F-75231 Paris Cedex 05, France ;
c : Photonik und Optoelektronik, Ludwig-Maximilians-Universität München, Amalienstr. 54, Munich, Germany.
d : Laboratoire des Milieux Desordonnes Heterogenes , Universite Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France.
e : Department of Physics, New Mexico State University, Las Cruces, NM 88003, USA..

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In a significantly wide range close to p_c, these granular metal thin films manifest electromagnetic properties that are absent for both components : bulk metal and dielectric [3]. Figure 1.a shows the transmission electron micrograph (TEM) of a silver percolating metal-dielectric thin film, and figure 1.b the corresponding linear optical transmittance T, reflectance R and absorption A. The main point is the presence of unexpected very high nearly wavelength-independent absorption, which is not due to the components (metal and vacuum or silica), but due to the morphology of the metallic nanoparticules. "Mass thickness" is the thickness that would have an homogeneous bulk metallic film of the same weight. It is continuously measured in situ by using a quartz micro-balance of very high sensitivity. The actual thickness of the grains of the film is always bigger. It can be calculated by taking into account the filling factor p, which is determined by Transmission Electron Microscopy (TEM), or measured by using an atomic force microscope (AFM) working in appropriate mode.

The presence of high absorption was not physically well understood before pointing out the possibility of exciting Surface-Plasmons (SP) at every frequency below the original resonance frequency of one isolated metal grain. Because of fractal structure (see figure 2) at the percolation threshold, every size and shape of metallic clusters is present in the 2D percolating film, and then every SP frequency find some special clusters able to resonate. Moreover, the disorder allows the SP to be localized, resulting in large local fields and then strong enhancement of optical surface phenomena, for example Raman scattering [1]. The localized plasmons, acting like nano-antennas, can concentrate very large electromagnetic energy in nanometer-sized areas ("hot spots"), and provide particularly strong enhancement of local linear and non linear optical responses, in a very broad spectral range.

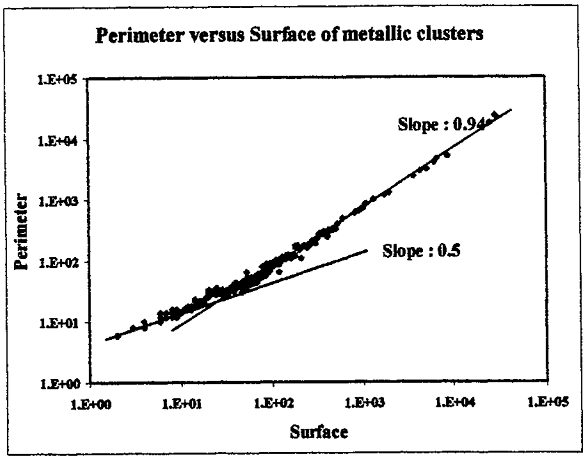

Figure 2 : Perimeter versus surface [4] of the metallic clusters in a granular gold 2D percolating film. These two quantities are measured on electron micrograph. For big metallic clusters, the shape is tortuous, and the perimeter increases as the power 0.94 (close to 1) of their surface, showing up a fractal behavior. On the contrary, smaller cluster perimeters are showing up an Euclidean behavior (0.5 exponent).

The theory modeling the electromagnetic properties of such 2D granular metal films has been extensively studied and published [2]. We illustrate here the recent experimental results in the field, referring to the theory through common sense remarks rather than through calculations.

"HOT SPOTS" OBSERVATION

The high (X,Y) resolution SNOM Setup.

The localized high intensity enhanced electromagnetic fields can be observed in the near field region, by using a Scanning Near-Field Optical Microscope (SNOM) of very high lateral resolution [5], lighted in both transmission and reflection modes. Our SNOM is simultaneously working as an Atomic Force Microscope (AFM) in tapping mode, and gives [6] both signals together. The probe tip of extremely sharp end is a tungsten wire cantilever, vibrating close to its own resonant frequency (~5kHz) in the Z direction, perpendicularly to the sample. A feedback system keeps the amplitude of vibration constant. Scanning of the sample surface is obtained by attaching it an 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 the 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, while a second microscope objective collects the optical signal. The detector can be either a photodiode or a photomultiplier. The vibration of the tip in AFM tapping mode, scatters the local electromagnetic field in all directions, the modulation of which is detected by a lock-in amplifier after collection in the far zone.

Enhanced field peaks linear direct observation.

The samples are prepared by evaporating the metal onto the silica substrates at room temperature under ultra high vacuum (10^{-9} Torr). The elementary gold grain size a_o ranges from 10 to 40 nm in diameter, depending on the deposition conditions. On figure 3a, we show a near-field 3D optical image of the electromagnetic field scattered close to the sample surface of a percolating gold film. The (X,Y) resolution of one pixel is 10 nm. Because of very sensitive mechanical and thermal controls, it is now possible to collect several SNOM images of the same area, which is established by comparing the simultaneously recorded AFM images. The vertical scale is the ratio of the measured intensity (I) to the mean value of the noise taken on the entire image (Io).

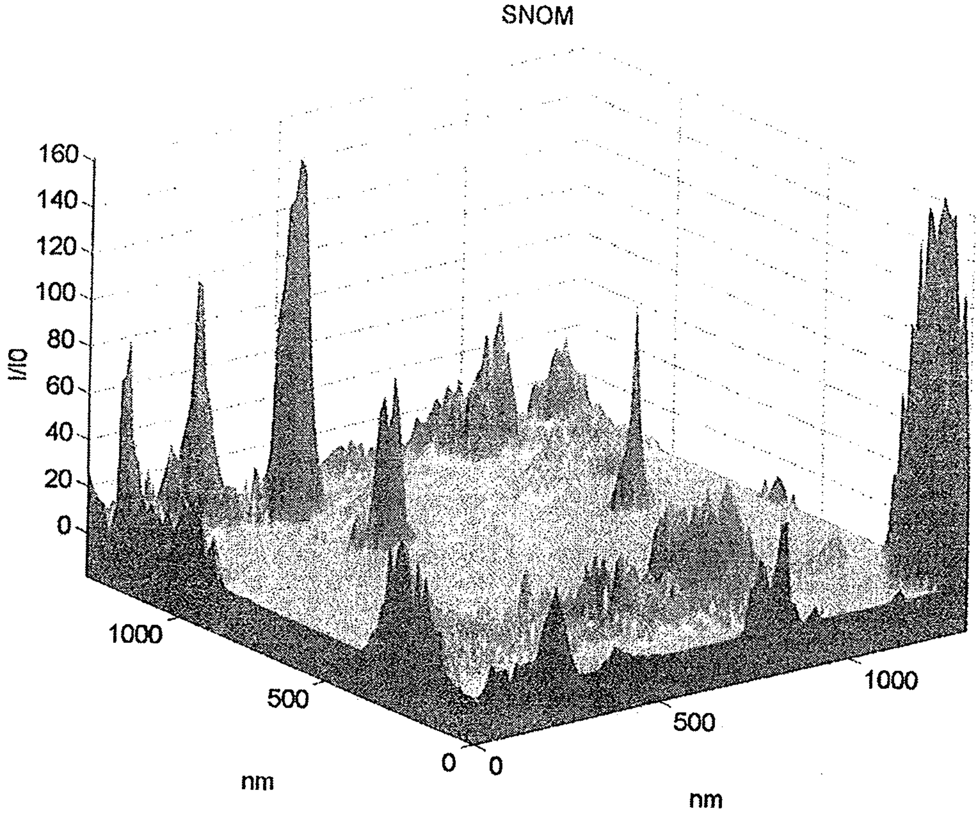

Figure 3, Repartition of electromagnetic field intensity at the surface of a gold on silica granular film. Note that the resolution of the finest peaks is one 10x10 nm pixel.

Spectral dependence of the location of the peaks.

As expected from the theoretical point of view, the position of hot spots should depend on the lighting wavelength, simply because the clusters which resonate are different for each wavelength. Surface Plasmons (SP) are localized by the disorder and give constructive interference only in certain regions distributed at random on the sample surface. Moreover, because the metal is dispersive, both real and imaginary parts of the dielectric function $\varepsilon = \varepsilon' + i\varepsilon''$ vary versus frequency (or wavelength). The field enhancement also varies following [2] the ratio $\varepsilon' / \varepsilon''$. This is the reason why enhancement is low for gold granular films in the visible inter-band transitions region, where ε'' is quite large.

We have studied the spectral dependence of the field peaks in two complementary ways : first by recording (figure 4) the spectral variations on several fixed points, second by taking the field intensity images (figure 5) of the same area at two different wavelengths. In the first experiment, we park the tip at one point where we expect some field enhancement, and we record the spectral intensities in the range open by Ti-Sapphire laser modulation. Recording the same spectrum at a second point, 100 nm apart from the first, shows up clear differences in the intensities spectral distribution at distance much shorter than the wavelength. This gives a good idea of the spectral sensitivity of the energy localization in the hot spots.

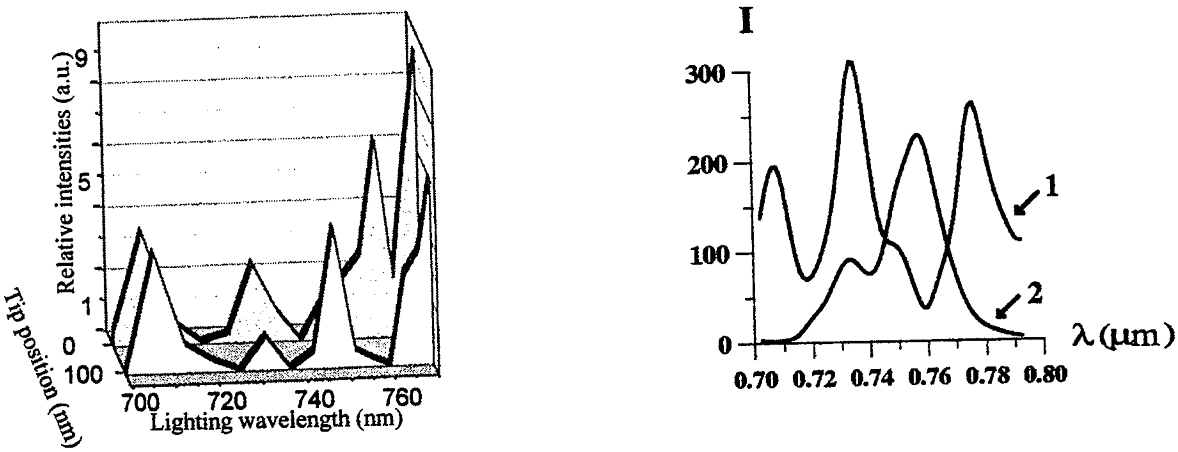

Figure 4, Experimental (left), tip of the SNOM is parked, and theoretical (right) spectra at two different points 100 nm apart (much smaller than the wavelength). Note the good agreement in the general shape of the experimental and theoretical curves.

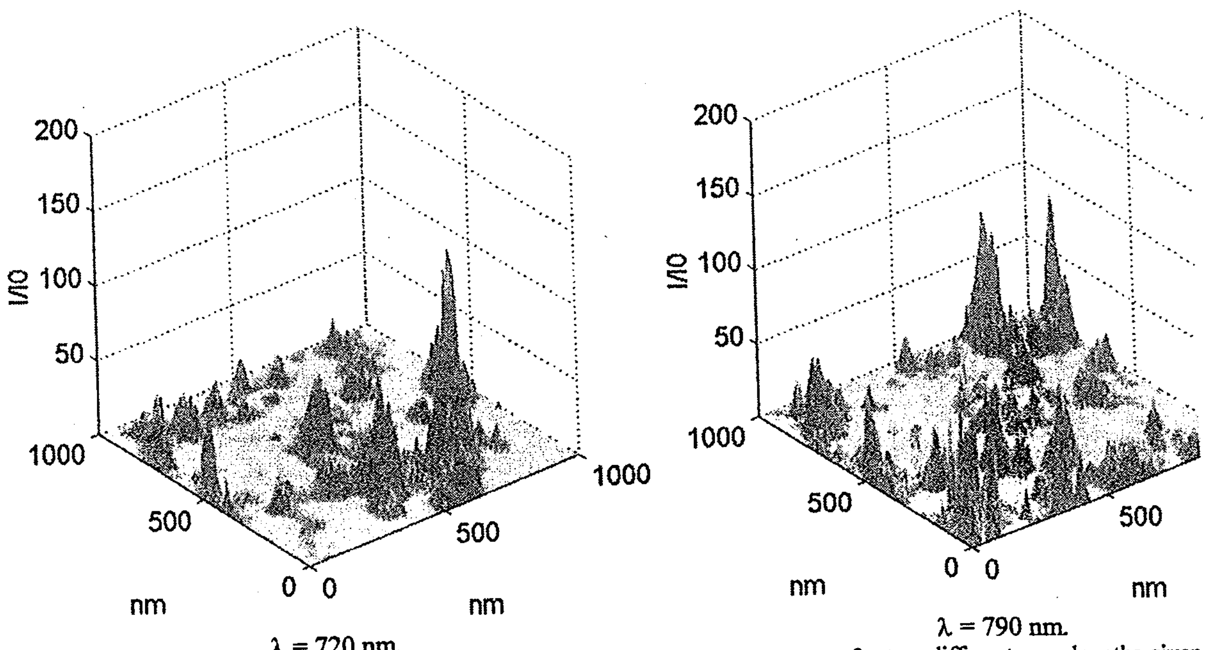

Figure 5. "Hot Spots" position wavelength dependence measured on the same film area for two different wavelengths given by the Ti-Sapphire laser. Position matching is achieved through AFM images.

By using very high quality piezo-translators, and by increasing the signal to noise ratio, we have been recently able to scan several times the same sample area with very high reproducibility. This new ability will also be used in the next paragraph on polarization dependence.

In these kind of experiment, exact matching of the scanned areas is then checked by superimposing the successive AFM images recorded during the same scan of the sample. This allows us to compare at different times the field distribution on the same region in different conditions. The two parts (left and right) of the figure 5 give the field intensity distribution for two different wavelengths 720 and 790 nm.), on the same area of the sample. The general shape of very few peaks of small enhancement are visible in the same place on both images (for example at the bottom left edge of the image close to the position "500 nm"), but the main point is given by the differences (position, shape and value) in high enhancement intensity peaks, that have not to be better described as they are unambiguously visible on the two images.

Polarization dependence of the location of the peaks.

The plasmon resonance excitation is well known to be dependent on the nature of the metal, and on size and shape of the metallic clusters. After analyzing the influence of the incoming frequency, we did vary the direction of the incident electric field, which gives the direction of polarization of the light. As the 2D granular metal films are made of fractal disordered clusters, close to the percolation threshold, they are expected to differently resonate when changing the probing direction of the electric field. This experiment is achieved by introducing a polarizer perpendicular to the lightning beam between the source and the sample, and by rotating it in the wave plane. Figure 6 gives the two images corresponding to two directions of linear polarization perpendicular to each other

Here again, the AFM and SNOM images are taken at the same time, during the same single scan of the sample. This allows us to establish that successive images are taken on the same sample area without any doubt : shift of the region scanned by the tip is of order of few nanometers.

First look at the SNOM images taken for two different polarization directions (figure 6), shows that they are mainly different, even if they look of the same kind. First to be pointed out is that the peak positions are totally different. The size of the field peak clusters (in the sample plane) is approximately of the same order of magnitude for both polarization directions.

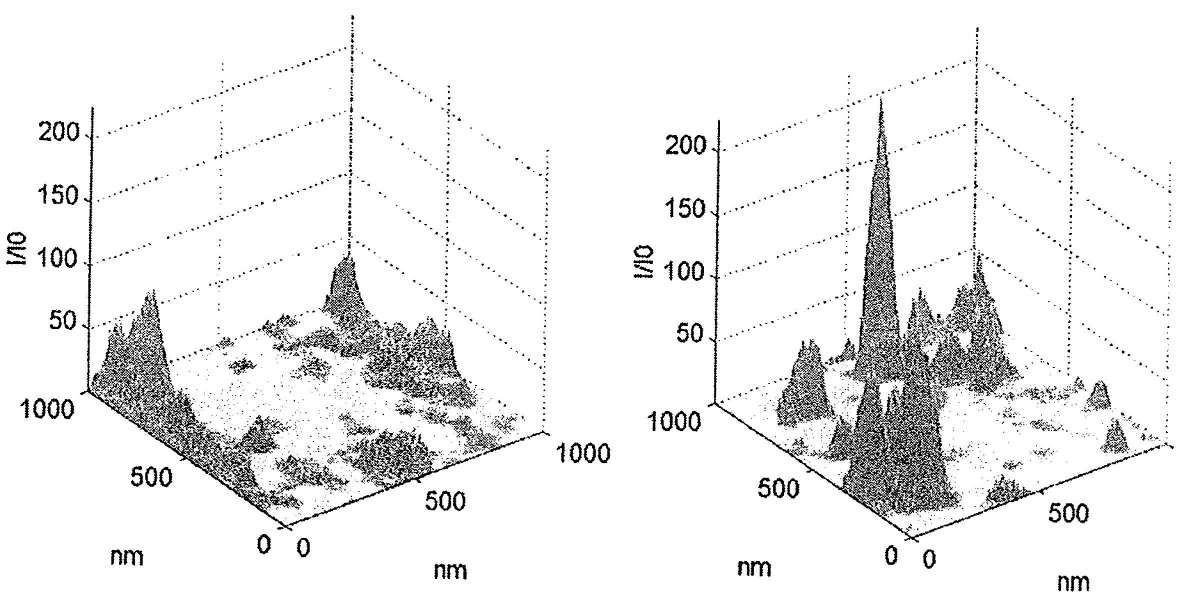

Figure 6, Two images of the same 2D percolating film in the same area, for two different linear polarizations (field directions) perpendicular to each other.

Moreover, in one of the images (right hand side), there exist a giant field intensity peak, enhanced up to 200 times, ending with a one by one pixel size. This statement allows us to expect to be able to fill the sample surface by small micro-sized squares, each of them supporting a giant field intensity peak for one special polarization direction. In other words, whatever the micro-sized area of the 2D percolating film, one could find one direction of the incident field giving rise to a giant enhancement peak. This is a powerful possibility for single molecule or single cluster physics. Other possibilities of varying the polarization of the incoming light have to be studied, and could give new interesting applicable results, for example by using circularly polarized light [7].

NON-LINEAR EXPERIMENTAL RESULS.

As it was already the case for Surface Enhanced Raman Scattering (SERS), this kind of thin granular metallic films are expected to give rise to rough surface (or fractal surface) enhanced phenomena [8]. Moreover, because of involving the electric field risen to higher powers, nonlinear optical properties should be of special interest on this kind of thin films. For example, 2ω generation and scattering have been studied using granular gold percolating films. Second Harmonic Generation (SHG) have been already achieved years ago on rough silver surfaces [9].

Percolation Enhanced Nonlinear Scattering and Super-Continuum Generation.

The new point we can emphasize here is that we have experimentally found nearly isotropic Percolation-Enhanced Nonlinar Scattering (PENS) of high intensity at 2ω, out of the specular directions. This was already predicted by theory [10]. Because the percolation films are seen as mostly homogeneous at the micrometer scales (order of magnitude of λ), the diffuse component in linear scattering (at frequency ω) is negligible compared to the collimated specular beams. In the case of nonlinear scattering, the sources for the light are the hot spots, where the plasmons are localized and then the electromagnetic local intensity is dramatically enhanced. The hot spots can be thought as nano-antennas radiating at 2ω (or *n*ω for higher orders) frequency.

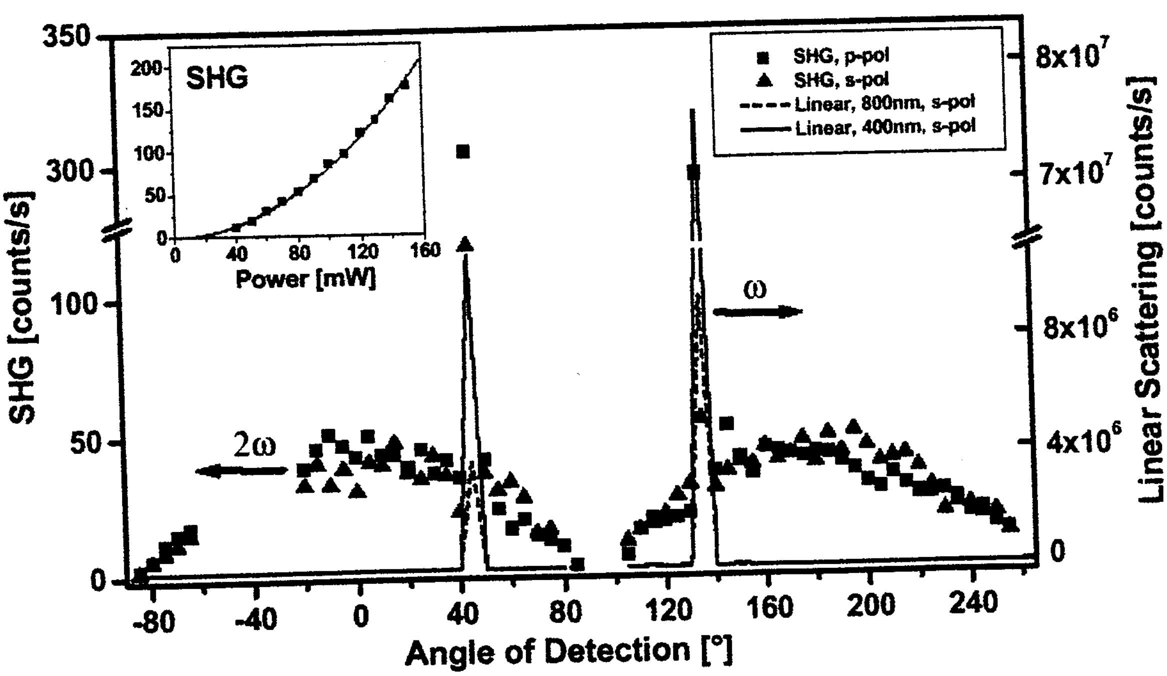

Figure 7, Scattered light intensities for P and S polarization as a function of the direction of detection. 0° is the normal to the plane of the substrate. Incident P polarized beam comes from –45°, specular reflected and transmitted beams are respectively at +45° and 135°. Linear light at ω is referenced on the right scale and nonlinear light at 2ω on the left hand scale. The insert gives the experimental parabolic variation of the 2ω signal as a function of incident light power, as expected from theory.

In this experiment [11], the p-polarized light source is a Ti-sapphire laser (pulse duration 150 fs at 76 MHz repetition rate, angle of incidence 45°). The beam is focussed on a 4×10^3 μm^2 area of the film, and scattered light at 2ω is filtered and detected by a photomultiplier in photon-counting mode. The photomultiplier can be moved around the sample for angular dependence measurements. Same measurements have been done for comparison as well on continuous and semi-continuous gold films. As expected on continuous film, both linear (w) and nonlinear (2ω) energies are concentrated in the specular reflection and transmission directions. In contrast, in the case of percolating gold films (figure 7), the 2ω generated light is mostly diffuse-like, giving a signal comparable to the one of continuous gold film in the specular directions, but two orders of magnitude larger when integrating it over all the angles. Moreover, for frequencies different from ω, at low incoming energy (below 10^8 W/cm^2), only 2ω signal is readily detected, but at higher lightning energy level, the background continuum radiation become also detectable [7], and can be related to White Light Generation (WLG), which can be interpreted as a third order non linear effect and is then also strongly enhanced by the localized plasmons on the hot spots. This last WLG lightning energy threshold has been found of about five to six orders of magnitude lower than the intensity typically needed for WLG in other media.

2ω generation on 3D cermets.

Another experimental work on 2ω generation is at present time under work in a different way. The goal is to determine all the coefficients of the second order polarization tensor $\chi^{(2)}$, which requires many measurements at different angles of incidence for different incident and outgoing beams polarizations. Moreover the calculation of the coefficients is a difficult task for each of the studied samples.

The samples used in that experiment are no longer 2D granular thin films, but 3D cermets as mixtures of small gold grains dispersed in an alumna matrix. This kind of samples also present optical absorption by plasmons. They already have been used for third order nonlinear optical experiment, using Z Scan technique [12], and have been proved to enhance absorption by optical phonons [13] in the IR regime. These first results show a maximum of nonlinear third order optical response in the percolation region.

Our experimental setup is simply shown on figure 8, giving the definitions of the different measurement angles. Some of the first results are shown on figure 9, but do not yet lead to definitive conclusions about enhancement of all the coefficients of the $\chi^{(2)}$ tensor. We just have good reasons for expecting enhancement of some of these coefficients.

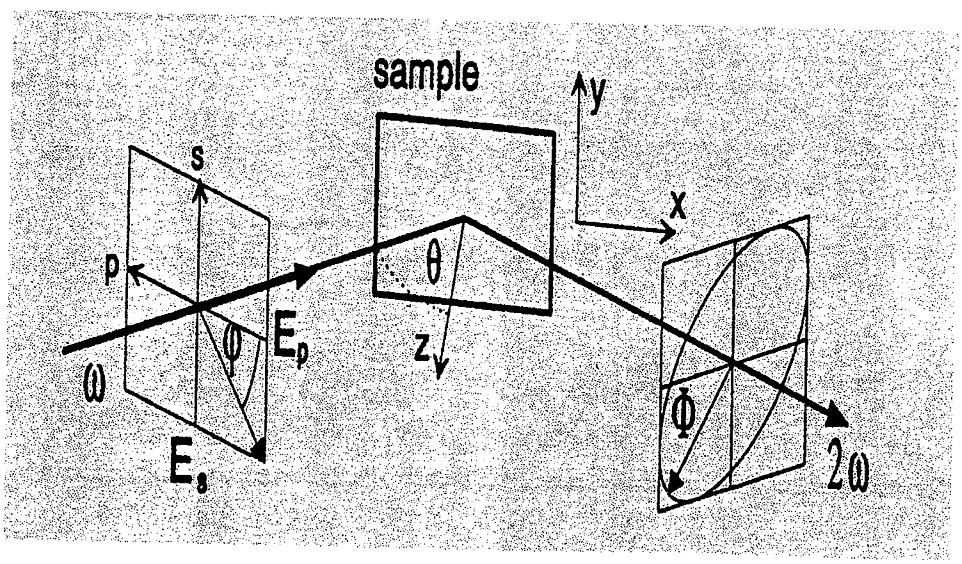

Figure 8, Experimental setup for measuring non linear reflection. The incidence and polarization angles are defined on the figure

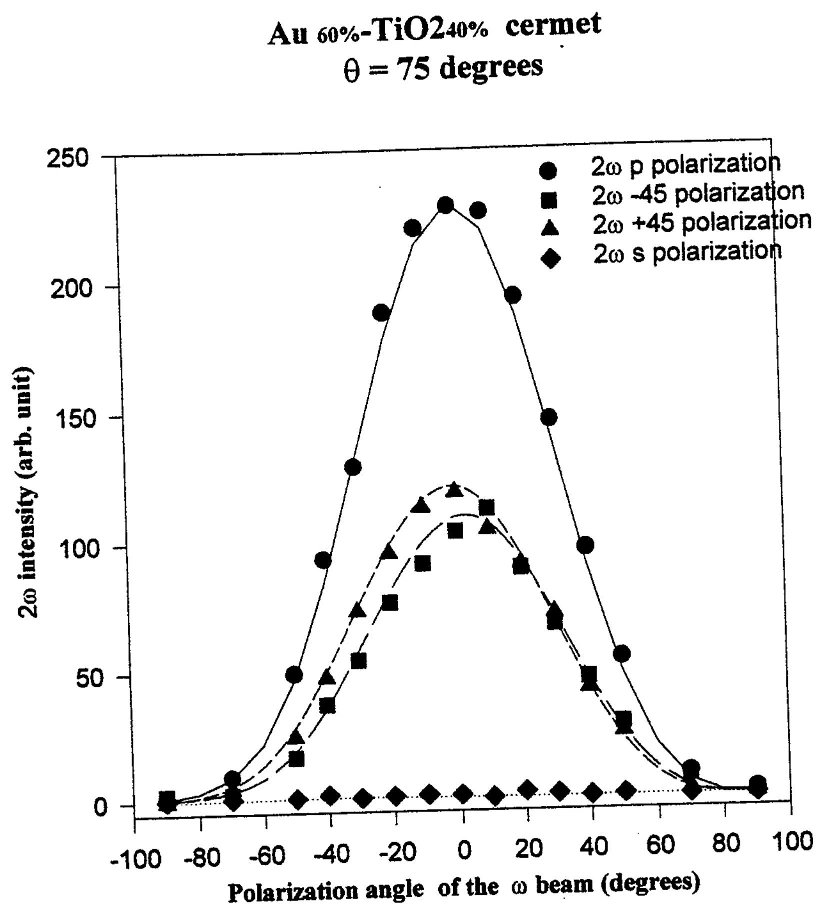

Figure 9, Intensities measured at 2ω, for one angle of incidence of p-polarized beam and for several polarization outgoing states.

CONCLUSIONS.

This paper have been mostly devoted to experimental results and does contain only intuitive theoretical arguments without any theoretical development, which are extensively published in other papers. We have shown that percolating metal-dielectric composites have linear optical properties, which are absent from the components and depend on the fractal structure of the percolating tortuous metal clusters. The plasmon resonance presence is wavelength independent in the IR regime, and leads to enhanced local electromagnetic fields, which have been observed and studied in the near field region.

The agreement of experiments with theoretical predictions can be summarized as follows :

- The hot spots are localized in areas, which are much smaller than the wavelength, and can be compared to the elementary grain size a_0.
- The experimental enhancement of the local field intensity is increasing with the wavelength, as does the ratio $\varepsilon'_m/\varepsilon''_m$, and is of order of 10^2 as expected for $\lambda = 770$ nm.
- The near-field images are very much wavelength dependent : even shifts in wavelength as small as shown in figure 5 can result in very different images.
- According to the theoretical model, the hot spots spatial separation has to increase with the wavelength. This is not visible on figure 5 due to the too small wavelength shifts.

The hot spots, acting as antennas, are able to enhance, by a giant factor, the local optical non linear response of the metallic nano-sized structure. New nonlinear effects can then be seen even in the far field. Moreover, in the next future it is reasonably expected that the local fields enhancement could give some new applications in very different ways, as it is already the case in single molecule or nano-cluster observation.

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