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Direct observation of locally enhanced electromagnetic field

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Abstract

Surface enhanced Raman scattering and other nonlinear enhanced optical effects are well known to be induced by the surface of discontinuous or rough metal thin films. In the percolating range of concentration, theoretical calculations lead to locally enhanced field distributions at the surface of the films, due to huge fluctuations close to the phase transition threshold. 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 discontinuous gold films in both transmission and reflection modes. We report here the direct observations, at a scale much shorter than the wavelength, of the giant field peaks, the so-called "hot spots". Their intensities and spatial distribution are found in good agreement with the theoretical predictions.

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1. Introduction

Rough or discontinuous metallic surfaces have been shown to be able to produce giant optical responses, like surface enhanced Raman scattering (SERS) [1]. By checking other surface optical properties, it was found that surface second harmonic generation (SSHG) [2] could also be significantly enhanced. We report here near-field direct observation of giant field fluctuations at the surface of gold granular films, in the visible and near infrared range. These fluctuations lead to a few giant field peaks, the so-called "hot spots", which are responsible for the enhanced optical responses. The height and the position of the hot spots are found to be strongly dependent on the wavelength.

2. Sample preparation

The optically active surfaces are obtained by depositing very thin silver or gold granular 2D films onto an amorphous glass substrate. In the first stage of the growing process, small metallic grains are formed on the surface. As the film grows, the metal concentration p increases, and the grains, of elementary size a_o, start to coalesce and to form very irregularly shaped ("tortuous") conducting paths. The morphology of the clusters is well known to be fractal at the percolation threshold. Gold is evaporated from a tungsten crucible, under ultra high vacuum (10^{-9} Torr), keeping the substrate at room temperature. The elementary gold grain mean size a_o,

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determined by TEM measurements, is about 10–30 nm in diameter, depending on the deposition rate. In order to determine the closeness to the percolation threshold concentration p_c, 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 [3–5]. We then use the same gold granular films for SERS and SNOM experiments.

3. Localized giant field peaks distribution

The optical properties of the thin inhomogeneous metallic films close to the percolation threshold, while being extensively studied since the beginning of the century, have only been well understood in the last 10 years in terms of scaling models [4,5] and field fluctuations [6,7]. As is well known, a phase transition is accompanied by strong long-range fluctuations [8,9] so that one anticipates that the local field at the percolation threshold can be very large. At optical frequency 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, and therefore be especially large. For example, for a 2D system, the sp resonance of non interacting metal spheres 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, respectively.

At the percolation threshold, metal particles are combined into fractal clusters, and cannot be treated as independent. However, it has been shown [10] 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. Then, the corresponding local field distribution consists of sharp field peaks, the "hot spots", the intensity of which is, on average, enhanced by a factor given by $\varepsilon'_m/\varepsilon''_m \gg 1$ 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 [11–13]. Recently, using a SNOM in transmission, we reported the first direct observation [10] of the predicted localized giant field peaks. We compare here the direct observation of the hot spots in both transmission and reflection modes at normal incidence. Because the lateral size of the giant field fluctuation areas is of order of a few tens of nanometers and may content several different field peaks, the lateral resolution of the SNOM has to be better or of order of 10 nm, in order to be able to separate the peaks.

4. The experimental setups

Our SNOM is depicted in Fig. 1, in both reflection and transmission aperture-less modes [14–16]. A tungsten tip, vibrating above the sample in the tapping mode, probes the local electromagnetic field onto the surface and radiates it in the far field. In the present work we use as sources either a laser diode in reflection or a Ti/Sapphire laser in transmission. The probe tips are made of a tungsten wire (125 μm in diameter) bent on one end and etched by electrochemical erosion. The typical tip-end radius of curvature is of the order of 15 nm (sometimes less than 10 nm). The tungsten wire is sealed on its other end to a twin piezoelectric ceramic, that can excite it close to its resonant frequency ($\sim$5 kHz) in the Z-direction. Moreover it acts as a cantilever and is attached to a piezoelectric translator (Z-motion).

The incident beam is focused on the surface of the sample, via a first microscope objective located either above or below the sample depending on the set-up. Collection of the light is axially symmetric above the sample and is made by a second microscope objective in transmission mode or by the same objective in reflection mode. The detector is a photodiode or a photomultiplier (Fig. 1).

The sample is attached to a horizontal (X, Y) piezoelectric stage. During the scan a feedback system keeps the Z-amplitude of vibration of the tip constant and gives the atomic force microscope topographical signal (AFM tapping mode [14–16]).

The vibration of the tip, on top of the sample surface, modulates the scattered fields. Keeping constant the tip amplitude vibration, and thus the average distance between the tip and the sample, gives a constant modulation of the scattered signal when scanning an uniform surface. The electromagnetic field (X, Y) local variations close to the sample surface, are collected in the far zone at the tip vibration frequency. Our SNOM setup is directly sensitive to the local electromagnetic field amplitude. The optical (X, Y) resolution is the one of the tip's end as

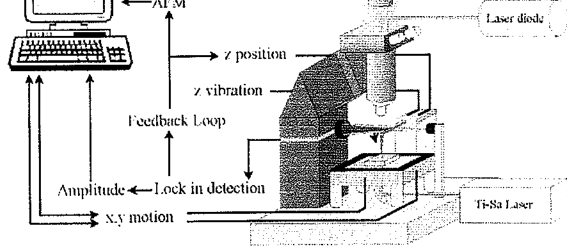

Fig. 1. SNOM reflection mode (laser diode) or transmission mode (Ti/Sapphire) setups.

previously shown [14–17]. The AFM and SNOM signals are recorded simultaneously [17].

5. Experimental results

Note that in the following images the background signal was subtracted and the incident intensity taken as unity. We show in Fig. 2 the raw near-field optical image of a granular gold film obtained at normal incidence in reflection mode. The light source is a laser diode at 670 nm. The (X, Y) resolution of one pixel is 15 nm. While the AFM signal (not shown here) recorded at the same time in the same (X, Y) range ($0.8\ \mu m \times 1.6\ \mu m$) depicts a very flat surface, where the metallic grains can only be seen as "orange skin noise" in the AFM signal, the SNOM image shows several field peaks. These peaks are seen as belonging to enhanced field clusters and are averaged by the 10 nm tip resolution. These clusters are localized in 100 nanometer sized areas, which shows that the hot spots imply an area significantly bigger than the elementary grain size.

Fig. 3 shows up a SNOM image of the same film recorded in transmission mode for two different wavelengths, using a Ti/Sapphire laser at low incident power. The field enhancements gains are very comparable for both reflection and transmission modes at short wavelengths (Figs. 2 and 3a). As expected for the longer wavelengths, the field enhancement (Fig. 3b) is much larger (about 20 times) for $\lambda = 770$ nm.

The observed enhancements are, of course, less than the 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, in both reflection and transmission modes, less enhanced than the predicted ones. In accordance with the theoretical model, the hot spot spatial separation (>300 nm) is much bigger than the elementary grain size (≈ 20 nm). This spatial separation is theoretically expected to increase with increasing wavelength, but it cannot be seen here because the difference in wavelength is too small.

On the granular metal film, for the incident frequency ω, we have determined the local resonances of areas, which size is of order of tens of nanometers. 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. It would not be the case for longer wavelengths in the middle infrared range. The tip then becomes more and more metallic, and another effect needs to be taken into account: it is well known that, when the tip is irradiated, the electromagnetic field at the apex of the tip can be enhanced by several orders of magnitude [18]. This well known static effect leads to spurious effects on the detection of the local field at higher incident power in reflection mode. Moreover, it can cause local damage on the sample, even in transmission mode in the wavelength range of the Ti/Sapphire laser, if the incident power is raised.

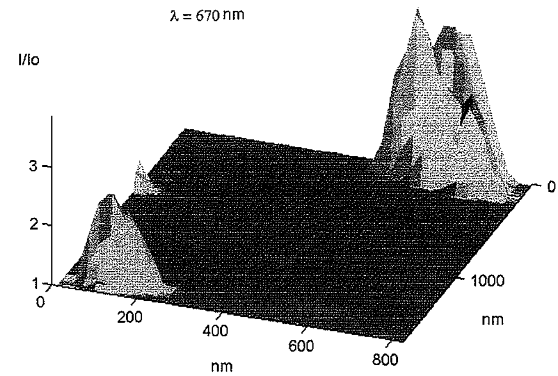

Fig. 2. Experimental reflection mode SNOM 2D image of the local fields of a percolating gold on glass film. Incident wavelength is 670 nm of a laser diode.

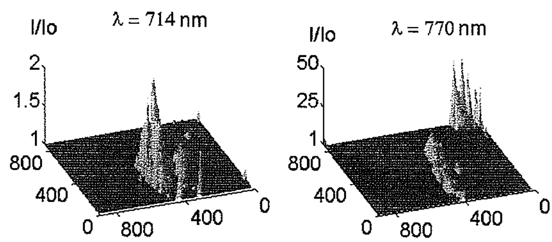

Fig. 3. Experimental transmission mode SNOM 2D image of the local fields of a percolating gold on glass film. Incident light is from a Ti-Sapphire tuned laser; (a) wavelength is 714 nm; (b) wavelength is 770 nm.

6. Conclusions

By performing near-field high-resolution imaging, we have experimentally analyzed the localized optical excitations of random metal-dielectric thin films close to the percolation threshold in both reflection and transmission modes. Both modes of investigation show the presence of areas with enhanced field peaks, even when there can exist standing waves in the far field of the reflection mode. The "hot spots" on the films represent the 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 nonlinear optical signals are proportional to the field raised to some power, the large local fields should induce very much enhanced nonlinear local responses.

References

[1] M. Moskovits, J. Chem. Phys. 69 (1978) 4159.
[2] C.K. Chen, A.R.B. de Castro, Y.R. Shen, Phys. Rev. Lett. 46 (1981) 145.
[3] P. Gadenne, Thin Solid films 57 (1979) 77.
[4] Y. Yagil et al., Phys. Rev. B 46 (1992) 2503.
[5] P. Gadenne et al., J. Appl. Phys. 66 (1989) 3019.
[6] A.K. Sarychev, D. Bergman, Y. Yagil, Phys. Rev. B 46 (1997) 2503.
[7] V.M. Shalaev, A.K. Sarychev, Phys. Rev. B 20 (1998) 13265.
[8] L.D. Landau, E.M. Lifshitz, Electrodynamics of Continuous Media, Vol. 8 of the Course of Theoretical Physics, Pergamon Press, Oxford, 1963.
[9] H.E. Stanley, Introduction to Phase Transitions and Critical Phenomena, Oxford press, Oxford, 1981.
[10] S. Gresillon et al., Phys. Rev. Lett. 82 (1999) 4520.
[11] P. Gadenne et al., Physica A 241 (1997) 161.
[12] F. Brouers et al., Phys. Rev. B 55 (1997) 13234.
[13] P. Gadenne et al., J.O.S.A. B 15 (1998) 68.
[14] R. Bachelot et al., Appl. Opt. 36 (1997) 2160.
[15] A. Lahrech et al., Opt. Lett. 21 (1996) 1315.
[16] P. Gleyzes et al., Appl. Phys. Lett. 58 (1991) 2989.
[17] S. Gresillon, H. Cory, J.C. Rivoal, A.C. Boccara, J. Opt. A: Pure Appl. Opt. 1 (1999) 178.
[18] H. Cory, A.C. Boccara, J.C. Rivoal, A. Lahrech, Microwave Opt. Technol. Lett. 18 (2) (1998) 120.