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Influence of metal nanoparticles on electromagnetic surface waves and laser light scattering

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Abstract. We show that metallic nanoparticles (NP) deposited upon a surface modify its optical properties. Light scattering and its energy level under conditions of surface plasmon resonance are strongly affected by the presence of NP. The results of angle resolved scattering (ARS) measurements of light and scattered light in the configuration of attenuated total reflection by surface plasmon resonance (ATRSPR) are presented. We show that ATRSPR is more sensitive to the presence of NP than ARS.

PACS. 61.46.+w Clusters, nanoparticles, and nanocrystalline materials – 78.20.Ci Optical constants (including refractive index, complex dielectric constant, absorption, reflection and transmission coefficients, emissivity) – 78.35.+c Brillouin and Rayleigh scattering; other light scattering

1 Introduction

In recent years, nanoparticles (NP) have been the object of increasing interest among physicists. We intend to show that NP deposited upon a surface scatter light whose wavelength is several orders of magnitude larger [1]. Both the techniques of attenuated total reflection by surface plasmon resonance (ATRSPR) and angle resolved scattering (ARS) have been applied on samples devised for scattering measurements with and without NP.

The main purpose of this paper is to show that NP influence the propagation of surface plasmon-polaritons and elastic scattering of light in such conditions. However, light scattering and surface plasmons by themselves are not the subject of the paper but rather are used to demonstrate, through a comparison of the obtained results, the influence of NP deposited on a surface.

In the first part of this paper, the sample and the principles of our experiments are described. In the second part, we present the experimental results obtained with both techniques. In the last part, a tentative interpretation and a conclusion will be given.

2 Principles of the experiments

NP are made by evaporation–condensation in an ultrahigh vacuum; they are deposited upon a sapphire prism specifically designed for ATR [2]. The largest face of the prism is first covered with a 52-nm-thick layer of silver. A 4-nm-thick layer of SiO_x covers Ag; then the material forming NP is evaporated. It condenses on the substrate maintained at a temperature which ensures the growth of the NP in the liquid state; hence NP are shaped as truncated spheres determined by their contact angle with SiO_x (the material used for NP does not wet SiO_x). The final SiO_x 10-nm-thick layer is deposited at low temperature so that NP are in the solid state, and any oxidation or further evolution is prevented. The embedding SiO_x matrix is dielectric, amorphous, and transparent in our wavelength range.

The experiment uses two optical configurations. ATR is performed in Kretschmann's configuration (see [3] and inset in Fig. 1) and extends to a wide range of angles of incidence α. A pronounced minimum $R_{p\,\min}$ of the reflectance $R_p\ (\alpha)$ occurs when the electromagnetic field of the incident p-polarized light of a laser couples with the collective oscillations of the free electrons of the silver layer. In other words, the coupling condition corresponds to a given angle of incidence $\alpha_{\min}$ which makes the parallel component of the light wave vector equal to the one associated with the collective oscillation of the electrons. Then, a surface electromagnetic wave (SEW) propagates along the Ag$-$$\mathrm{SiO}_x$ interface, with an attenuation, which depends on Joule's losses and surface roughness. The energy transferred to the system is located entirely on both sides of this interface.

Concerning ARS, the sample is illuminated at normal incidence with a laser beam, and the normalized intensity of the scattered light is characterized [4] by the bidirectional reflection distribution function BRDF(θ,φ), depend-

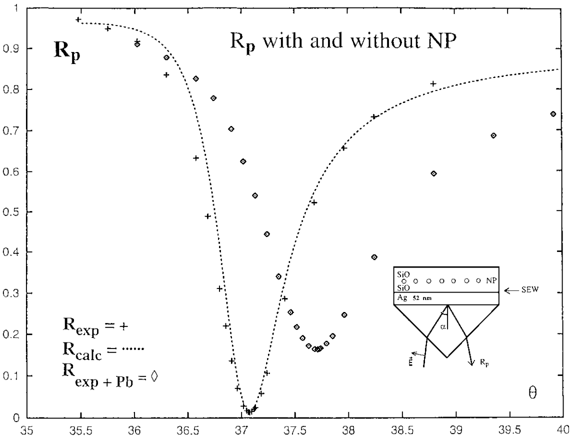

Fig. 1. Experimental reflectances R_{exp} of a sample with lead NP (with mean size 5 nm), and without NP measured in ATR conditions, and calculated one R_{calc}. The inset describes the structure of the sample. Without lead NP, $R_{\min} = 0.0135$ and $\alpha_c = 37.08°$. With lead NP, $R_{\min} = 0.1630$ and $\alpha_c = 37.71°$.

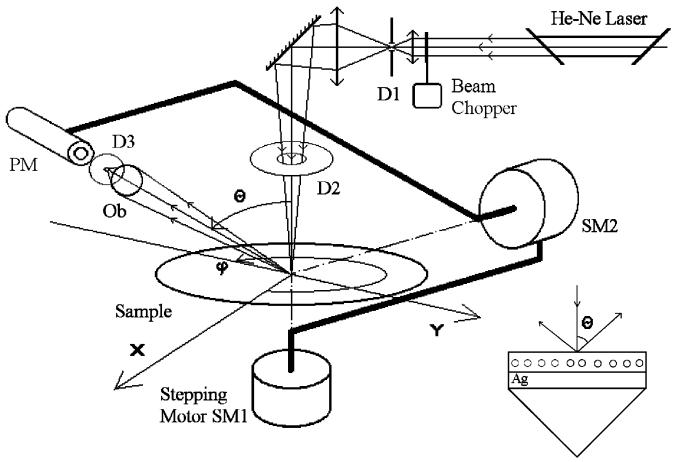

Fig. 2. ARS apparatus: PM is a photomultiplier, D_i are diaphragms, and Ob is an objective. The inset describes the sample.

ing on both angles θ and φ. Conditions of measurements are shown in Fig. 2.

The results will demonstrate that, in the configuration of ATRSPR, i.e., with p-polarized light impinging on the prism with the internal incidence angle $\alpha_{\min}$ associated with SPR, scattered light still exists. In this configuration the space distribution of scattered light is characterized by the bidirectional scattering distribution function (BSDF) BSDF(θ, φ). Although BSDF resembles BRDF, the physical processes involved are different.

3 Experimental results

A typical result obtained by ATR performed on lead NP has been given in Fig. 1. The accuracy allowed by the apparatus is better than 10^{-2} degree for α and 10^{-3} for R_p.

For both samples and for a 632.8 nm wavelength, the reflectances $R_p(\alpha)$ without and with NP at room temperature are presented. These results show a measurable variation of $\alpha_{\min}$ and $\mathrm{R}_{p\,\min}$ [5]. The high sensitivity of ATRSPR to any change is demonstrated.

In the following, we present measurements of ARS in both configurations described above. They have been realized on samples containing NP of gallium instead of lead for the following reason: Gallium is liquid at room temperature, thanks to the thermodynamic size effect, i.e., the lowering of the melting point of NP with their size. This ensures that a possible crystallographic anisotropy of NP in their solid state, which could influence the measured optical properties, is avoided.

The sample is illuminated at normal incidence and 632.8 nm wavelength as shown in Fig. 2. The logarithm of BRDF(θ,φ) of a sample without NP is given in Fig. 3a while Fig. 3b gives the corresponding result when the NP are present.

One observes a maximum of the scattered intensity along the normal to the sample, decreasing when θ increases. When the sample contains NP, the angular distribution of the scattered intensity is more uniform than it is without NP.

Turning back to ATRSPR illumination conditions of the sample: Some scattered light outside the prism has been detected; this is BSDF (θ,φ).

The results are presented in Fig. 4. The dark left part of the pictures comes from some unavoidable shadow caused by the holder of an optical component. Here again we observe that light is more uniform when the sample contains NP than when it does not.

4 Interpretation and conclusion

Our interpretation is given on a semi-quantitative level. Regarding ATR measurements: Without NP, $R_p(\alpha)$ is at a minimum and close to zero when α gets the value $\alpha_{\min}$ that corresponds to ATRSPR. This comes from an adequate choice of the thicknesses of both the Ag and SiO_x layers. The main point to notice is that the presence of the NP leads to a shift of $\alpha_{\min}$ by 0.63°, and an increase of R_p ($\alpha_{\min}$); also, the minimum of R_p (α) is not as sharp as in the case without NP. The calculated curve R_{calc} is given by a Fresnel combination of the various indices and layer thicknesses. Both the shift and broadening of the resonance peak are clearly due to the presence of NP [5,6]. They can be explained by the modification of the index of SiO_x to an effective index of SiO_x + embedded lead NP.

We can describe the same process in other words: When NP are placed near the silver layer, the NP's electrons can participate in the collective oscillations of the silver electrons. The change in the electron gas density and spatial configuration (spheres in front of a continuous layer) lead to a change in the SPR conditions. The resulting oscillating system modifies its way of dissipating the energy.

With regard to ARS, notice in Fig. 3 first that most of the scattering is concentrated at low θ. In Fig. 3a, the angu-

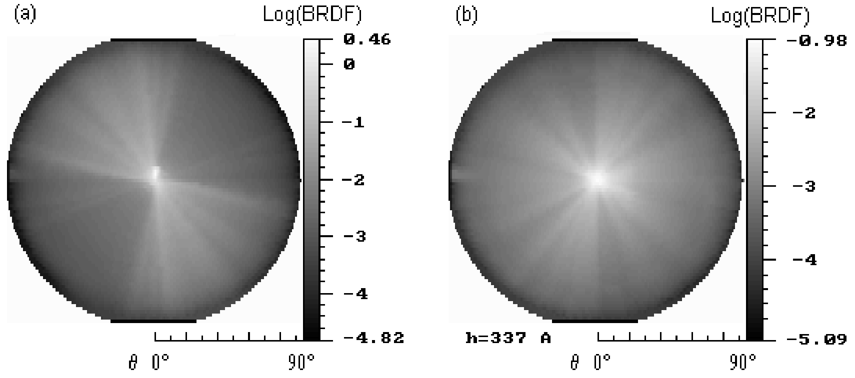

Fig. 3. (a) log (BRDF) without NP; (b) log (BRDF) with NP.

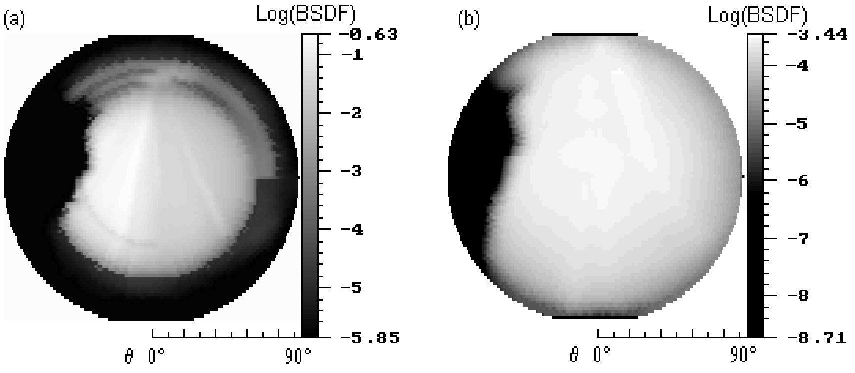

Fig. 4. (a) log (BSDF) measured in conditions of SPR without NP; (b) log (BSDF) measured in conditions of SPR with NP.

lar distribution BRDF (θ,φ) does not exhibit a cylindrical symmetry, as would be expected from a perfect sample without NP; some deviation from the cylindrical symmetry comes from optical polish defects of the prism. In Fig. 3b, the presence of NP superimposes its proper scattered light to what comes from the prism surface itself. Recall that NP are in the liquid state, randomly distributed on the substrate, and do not induce any crystallography-related anisotropy. This superposition of two different kinds of scattered light tends to smooth anisotropy of the BRDF (θ,φ). However, some fine structure remains in the scattered light; this is beyond the scope of this paper.

BRDF (θ,φ) resembles scattered light arising from surface roughness. No characteristic features can be attributed to the presence of NP, the main reason being that they are much smaller than an intrinsic roughness of the prism. More quantitatively, using the total integrated scattering [4], one deduces an equivalent roughness $h = 33.7\,\mathrm{nm}$, which represents the effect of the prism added to the effect of the NP.

From Fig. 4, a comparison of the values of the BSDF shows significant difference in intensity: The scattered intensity coming from the NP's sample (see Fig. 4b) is approximately three orders of magnitude lower than that coming from the sample without NP. This corresponds to the increase of $R_{p\,\mathrm{min}}$ as seen in Fig. 1; the NP' s sample absorbs energy more efficiently and in a different way than those without NP.

We also notice that scattering extends to higher angles as compared to Fig. 3. Recall that the experimental procedure uses an SEW which propagates along the interface, supporting the NP and the polish defects instead of a laser beam normal to this interface. It is known that the roughness of a surface has a strong influence on the intensity: The higher the roughness, the higher the intensity [7]. Furthermore, one can ask if the presence of the NP could create also some angular dependence by itself. As a matter of fact, the presence of a single defect with the same symmetry as our NP creates a strong angular dependence in the scattered light [8]; in our case, the size distribution of NP spreads the angular dependence over a wider range of scattering angles. So, the angular dependence of the scattered intensity BRDF (θ,φ) seems to be less important than in Fig. 3. In contrast, at least qualitatively, the presence of NP causes a strong scattering down to grazing incidence. This puts clearly in evidence that each method, ARS and ATRSPR, brings different physical information about the scattering centers and the way they are excited.

In conclusion, the combination of both the techniques of ATR and ARS has enabled us to conduct a study showing the influence of metallic NP on electromagnetic processes involved in surface plasmon resonance (SPR) and angle resolved scattering (ARS) of light. We have shown that NP influence the reflectance seen with SPR conditions. Then, when the sample is illuminated in such conditions, one gets BSDF (θ,φ) results. A strong difference between both techniques appears: Scattered intensity varies on a much larger scale in the case of BSDF (θ,φ) than of BRDF (θ,φ). An important point is that the scattered intensity be much stronger influenced by the presence of NP in ATRSPR than in ARS conditions. This gives valuable information for the study of the interactions of SEW with NP.

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