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A SET-UP FOR MEASURING LOCAL OPTICAL SPECTRA

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Гичка Цуцуманова, Мария Биволарска, Цветан Велинов, Браян Прево, Орлин Велев, Стоян Русев. АПАРАТУРА ЗА ИЗМЕРВАНЕ НА ЛОКАЛНИ ОПТИЧНИ СПЕКТРИ

Описана е апаратура за измерване на локални оптични спектри. Изследваният образец се проектира върху екран с диафрагма. До детектора, поставен зад екрана, достига светлина само от малка област от образеца, преминала през диафрагмата. Тъй като изображението е увеличено, точното позициониране на дадена област се улеснява. Получената разделителна способност е 4 μm. Използвайки тази апаратура, е показано, че локалните оптични спектри на островни филми, състоящи се от златни наночастици, отложени върху стъклена подложка, са различни от спектрите, получени със стандартните спектрометри, и се променят в отделните точки на образеца. Тази разлика се приписва на влиянието на локалните микроструктури от агрегирали частици, които променят позицията на абсорбционния пик.

Gichka Tsutsumanova, Maria Bivolarska, Tsvetan Velinov, Brian Prevo, Orlin Velev, Stoyan Russev. A SET-UP FOR MEASURING LOCAL OPTICAL SPECTRA

A setup for measuring local optical spectra is described. The investigated sample is imaged onto a screen with a pinhole and only light that has passed through the small area of the sample which is imaged on the pinhole reaches to the detector. Because the image is magnified, positioning of the area of interest is facilitated. The obtained spatial resolution is 4 μm. Using this setup, it is shown that local optical spectra of island films, consisting of Au nanoparticles deposited on a glass substrate are different from spectra obtained with conventional spectrometers and vary with the scanning position. This difference is ascribed to the influence of the local microstructure of the aggregated nanoparticles, which influences the position of the absorption peak.

Keywords: local optical spectra, pinhole, inhomogeneous films, thin films
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1. INTRODUCTION

Optical spectrometers are the most widely used spectroscopic instruments due to their versatility, simplicity and straightforward data interpretation. Their importance in physics, chemistry and life science can not be overestimated. They have excellent spectral resolution but rather poor spatial resolution because the light spot that impinges on the samples is large. This might be a serious drawback when investigating optically inhomogeneous samples. Several techniques have been proposed to overcome this limitation of the standard spectrometers. One approach is similar to scanning microscopy techniques: the beam is focused on the sample and then the sample is scanned to obtain spectra from different points [1]. These optical methods can be very sensitive but focusing the light means that rays from different parts of the beam will fall on the sample at different angles and polarizations. When these angles exceed a few degrees sophisticated data interpretation is necessary, as, for example, in imaging ellipsometry [2, 3]. An alternative approach is to image the sample onto a pixelated detector, a CCD or CMOS camera, and to record spectra from every pixel [4]. This is analogous to wide field microscopy. Each of the two approaches: scanning and wide field has its advantages and disadvantages. As a general rule, scanning techniques are more sensitive while full field ones are faster.

In this paper we propose a simple spectroscopic technique for measuring local optical spectra that combines features of both wide-field and scanning techniques. In Section 2 the setup is described and its characteristics are specified. In Section 3 local and standard spectra from an island film consisting of Au nanoparticles are compared and the results are discussed. Finally, the advantages of the new system are outlined and discussed in Section 4.

2. EXPERIMENTAL SETUP

The principle of the system for measuring local optical reflectivity/transmittance is simple. The sample under investigation is imaged onto a screen with a pinhole. Only light coming from the small area of the sample which is imaged on the pinhole will reach the detector behind the screen, thus giving information for the local optical properties of the sample.

The experimental setup we used to demonstrate the workability of this idea is shown in Fig. 1. The monochromatic light coming out from a standard spectrometer (Spektromom 195D) fell normally on the sample mounted outside the spectrometer. The sample surface was imaged by an objective on a plane with a pinhole with a diameter of 50 μm fixed on mechanical stages. The pinhole diameter was chosen to be much larger than the wavelength in order to avoid excitation of evanescent waves and waves with high spatial frequencies during the interaction of the light with the aperture and to let sufficient amount of light through. The light beam was modulated by a mechanical chopper. The light that passed through the aperture was detected by a photomultiplier and the electric signal was measured by a lock in amplifier. By moving the stages spectra from different parts of the samples were recorded. Positioning is facilitated by the fact that the movement in the image plane is scaled by the magnification factor in the object plane.

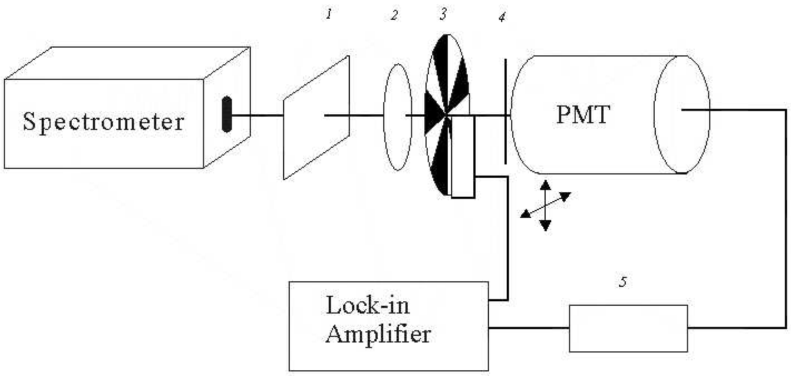

Fig. 1. A block diagram of the experimental setup: *1*—sample; *2*—objective; *3*—mechanical modulator; *4*—screen with a pinhole mounted on two dimensional stage; PMT—photomultiplier; *5*—current-voltage converter

The magnification of the system was measured by imaging of a grid consisting of alternating dark and bright stripes with a period of 100 μm and was found to be approximately 16X. Having in mind that the diameter of the aperture was 50 μm one could expect that the lateral resolution of the system would be about 3 μm. To verify this estimate, the image of a knife edge was scanned perpendicularly to the edge. The results are presented in Fig. 2. The x-axis is calibrated to correspond to the movement of the sample, i.e., the actual displacement of the pinhole was divided by the system magnification. A standard measure to assess the spatial resolution of an optical system is the change of the signal from 10% to 90% of their final values when light passes trough a step-like change in the reflectivity/transmittance of the sample. When applying this criterion to the results in Fig. 2 one obtains resolution of 4 μm. Theoretical results for coherent and incoherent light, based on Fresnel diffraction theory [5] applied to the specific optical system, are also shown in Fig. 2. The light that passes through the aperture comes from a region with linear dimensions of about 4 μm and has a certain degree of spatial coherence. This is probably the reason for the difference between the experiment and the two limiting cases of the theory. All the results presented in Fig. 3 are for a wavelength of 620 nm.

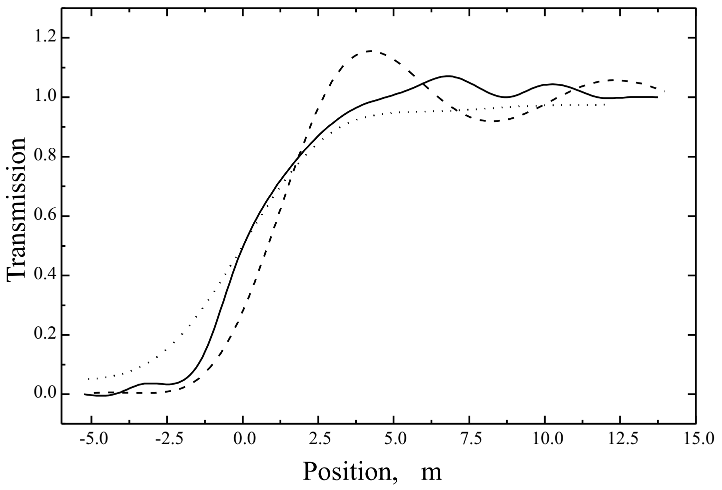

Fig. 2. An image of an edge: solid curve—experiment, dashed curve—theoretical calculations for coherent illumination; dotted curve—theoretical calculations for incoherent illumination

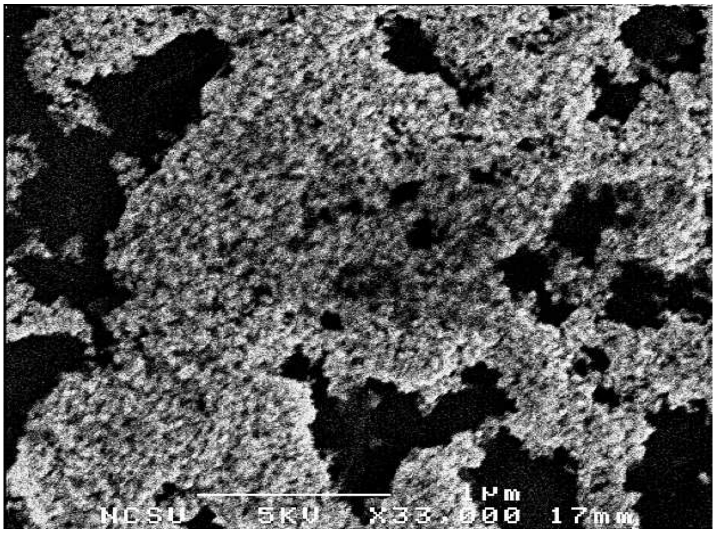

Fig. 3. An electron micrograph of the metal nanoparticle sample studied

3. LOCAL SPECTRA OF AN INHOMOGENEOUS FILM

The next step in demonstrating the potential of the microspectroscopy system was to investigate a sample consisting of gold nanoparticles with mean diameter of 17 nm deposited via convective assembly from aqueous suspension and stabilized with non-ionic surfactant (Tween 20) onto a glass substrate [6]. As seen from the electron micrograph, Fig. 3, the sample was highly inhomogeneous, consisting of irregular patches of aggregated particles with different shapes and sizes (much of them with linear size around and above 1 μm). This sample was chosen for two reasons: first, samples containing particles of noble metals reveal characteristic peaks of absorption, and second the position and shape of those peaks depend on the local arrangement of the particles [7]. Since this arrangement varies spatially on the microscale it was expected that the local spectra coming from different areas of the sample would be different.

The interaction of light with an isolated particle of noble metal (mainly Au and Ag) leads to resonance excitation of local electromagnetic modes at certain wavelengths (called local plasmons) confined within and near the particle. As a result of this excitation light absorption dramatically increases. These modes are well described by Mie theory [8]. On the other hand, optical spectra of sufficiently diluted solutions of such particles can be modelled by using effective medium theories [9, 10]. In this case the spectra depend on the dielectric constants of the particles and the surrounding medium, and the volume fraction of the diluted particles only. However, when the particles are situated close to each other they begin to interact strongly and their optical response changes. The main result is broadening of the resonance peaks. More elaborated theories are needed in this case to adequately describe the spectra [11,12,13].

In Fig. 4 the transmittance spectra obtained with a standard spectrometer is shown. The size of the illuminated area was about 1 cm^2. In the same Figure we have also plotted results from local spectrometric measurements at 3 different points with the nanoparticle island sample described in the previous section, together with a curve obtained by averaging the local spectra measured at ten different points. Finally, a curve obtained from Maxwell Garnet effective medium theory with realistic parameters is shown in the same figure. In order to take into account the interaction between the closest neighbors the following formula is used [9]:

$$\varepsilon_{\text{eff}} = \varepsilon_m \frac{1 + 2f\Lambda}{1 - f\Lambda}. \tag{1}$$

Here f is the volume fraction of the particles (also known as filling factor), ε_{eff} and ε_m are the effective dielectric constant and the dielectric constant of the medium where the particles are embedded; Λ is given by:

$$\Lambda = \frac{\eta}{2}\left[\frac{1}{1+\eta(r/d)^3} + \frac{1}{1-2\eta(r/d)^3}\right], \quad \eta = \frac{\varepsilon - \varepsilon_m}{(\varepsilon + 2\varepsilon_m)}, \tag{2}$$

where ε is the dielectric constant of the particles, r is their mean radius and d is the average distance between the particle centers. If $r/d = 0.5$ the particles are in contact with each other, in case of $r/d = 0$ the particles do not interact and (1) is reduced to the usual Maxwell Garnet formula. We used $f = 0.7$ and $r/d = 0.45$. These parameters were chosen in order for the calculated curve (1) to be as close fit to the results obtained with the standard spectrometer as possible. Specifically, the aim was to obtain a broad minimum and the positions of the two minima to coincide.

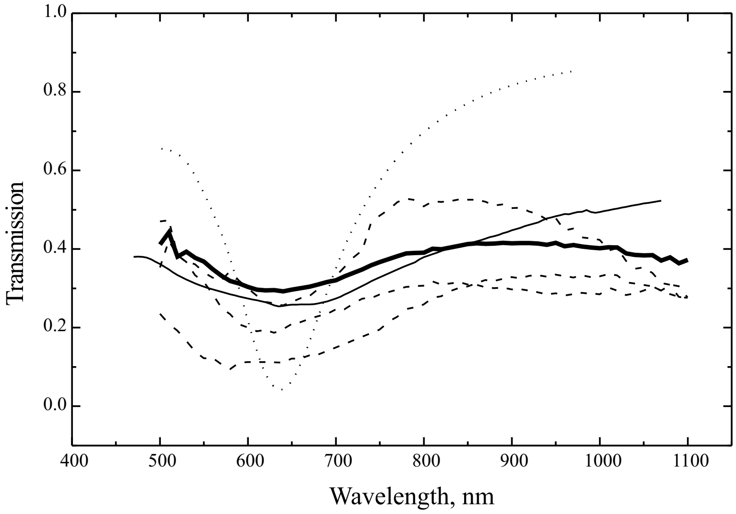

Fig. 4. Optical spectra of the sample obtained by different techniques: thin solid curve—spectra from conventional spectrometer; dashed curves—local measurements at three different points; thick solid curve—a curve obtained from averaging ten such local curves; dotted curve—calculations with Maxwell Garnet theory

It is very informative to compare the different curves in Fig. 4. First, as it was mentioned, the effective medium theory can not adequately describe the optical spectra of highly inhomogeneous films consisting of deposited nanoparticles. The broadening of the experimental curve is mainly due to the interactions between the particles. Second, the spectral curves obtained by local measurements are quite different from each another indicating different arrangement of the particles. Specifically, one can see that the position of the minimum, which corresponds to resonance absorption, varies from curve to curve. Third, it is seen that local curves are deeper and with more pronounced features than the one from a large area. This is not surprising since the later is an averaged sum of many local curves with minima at different wavelengths. Indeed, when comparing the results from the standard spectrometer with the curve obtained by averaging the local measurements one can see that they are very similar.

4. DISCUSSION AND CONCLUSIONS

We have presented a system for measuring local optical spectra of inhomogeneous samples and shown that local spectra of such samples may be different from those obtained from large areas. The system is simple and versatile. The source of light, the imaging lens and the detector can easily be changed in order to change the spectral range and optical resolution. Although scanning is necessary the system does not suffer from problems of confined geometry typical of some scanning systems and systems using microscopes.

Spectral resolution and spectral range, lateral resolution and sensitivity are the most important parameters of a setup for measuring local optical spectra. The spectral resolution and range of our setup are the same as those of the spectrometer we used as a monochromatic light. The resolution depends on how much the slit of the monochromator is open and is typically 1 nm.

The obtained spatial resolution of 4 μm in our case was limited by the amount of light that the pinhole let trough to the detector. However, this is not a theoretical limit; with an additional optical system the light intensity that falls on the sample can be increased by orders, thus allowing larger magnification and/or smaller apertures, so that optical diffraction limit can be reached. This should be compared with other scanning systems where, to avoid complex data manipulation, it is necessary to work with NA not exceeding 0.1 (that means that the beam can not be focused on an area with a diameter smaller than about 7μm). Otherwise, the angle of incidence of the outer parts of the focused beam becomes larger than 5°–6° and this will alter light reflection/transmission and will make data interpretation more complex.

The purpose of this paper is to demonstrate the applicability of the idea rather than to achieve ultimate sensitivity but it is clear that the use of a high sensitive light detector and narrow band technique to reduce the noise allows sensitivity superior to those of the existing CCD cameras to be achieved. Local spectrometry of the type developed could be used to resolve the optical characteristics of metallic nanostructures, which is of significant interest due to the potential of use of such nanostructures in plasmonic devices [14].

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