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Near-field optical microscopy of strongly scattering microporous metal/polymer membranes

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Abstract

Optical properties of microporous polymer membranes coated with metal have been studied using scanning near-field optical microscopy. The electromagnetic field distribution close to pores of various sizes ranging from 35 to 750 nm has been investigated in the different illumination configurations. Individual pores as small as 35 nm were seen in the near field. For directly illuminated membranes the field distribution is related mainly to the pores themselves. However, when surface plasmon polaritons were excited, the field distribution exhibited much more complex structure related to the interaction of surface polaritons with the ensemble of randomly distributed pores and metal surface roughness as well as localized surface plasmon effects. The results will be of importance for the understanding of optical properties of subwavelength apertures in strongly scattering films as well as optics of randomly structured metal films.

Keywords: Near-field optical microscopy; Optics of microstructured thin films

1. Introduction

Optical properties of nanostructured thin films attract currently much attention due to their possible technological applications in photonics, optoelectronics, and optical communications in addition to the rich physics involved. Both periodically nanostructured metal films and random (especially self-affine) structures have revealed distinctively different optical properties than smooth films [1–3]. This can, to a large extent, be explained by the electromagnetic interactions on a structured metal surface. At the same time, the optical properties of individual subwavelength apertures in metal films continue to attract attention despite numerous previous studies in this field [4–7]. Subwavelength apertures are needed in scanning near-field optical microscopy (SNOM), photonics, and optoelectronics. Unusual electrodynamics in small pinholes in metal films promises important technological applications for single-photon sources and for all-optical switching [8,9].

Metal-coated microporous polymer membranes present the opportunity to study optical properties of individual subwavelength pores as well as their

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agglomerations in strongly scattering (turbid) media. The optical behavior of such systems can be different from that of a metal film on transparent (nonscattering) film. Microporous polymer membranes (also known as nuclear filters) are not expensive, easy to handle, and survive harsh conditions of low (liquid helium) temperature and solvent exposure. The size distribution of the pores is relatively narrow, and surface of the films could be readily modified to suit a specific application. Such membranes are widely used for mechanical filtering of different particles by their size as well as to test the spatial resolution in electron and X-ray microscopy [10]. The applications of such membranes in optics include spectral filtering in the UV, extreme UV and soft X-ray ranges [11] as well as attempts to employ them as subwavelength-sized diaphragms to improve the resolution of confocal microscopy.

In this paper we present the results of near-field optical studies of subwavelength holes in metal-coated strongly scattering polymer films. The electromagnetic field distribution close to the pores of various sizes from 35 to 750 nm has been investigated in different illumination configurations. Individual pores as small as 35 nm were observed in the near field. While for directly illuminated membranes the field distribution is related mainly to the pores themselves, when illuminated to excite surface plasmon polaritons (SPPs), the field distribution exhibits much more complex structure related to the interaction of surface polaritons with the ensemble of randomly distributed pores and metal surface roughness. The localized surface plasmons (LSPs) at pore agglomerations provide additional field enhancement for certain orientations of light polarization with respect to geometrical structure of agglomerations. The presented results will be of importance for the understanding of the optical properties of subwavelength apertures in strongly scattering films as well as optics of randomly structured metal films.

2. Experiment

The microporous membranes used in our experiments were produced using polyethylene terephtalate films of 5–20 μm thickness. Pores of various sizes (ranging from tens of nanometers to tens of microns) and surface densities were produced by irradiating the film with a beam of high-energy heavy ions and subsequent chemical treatment (see, e.g. [12]). To assess the uniformity of the obtained pore sizes, the samples having the mean pore diameter of 750, 350, and 35 nm were imaged with an atomic-force microscope (AFM). The AFM images are presented in Fig. 1. The histograms obtained by processing several images of each type of the samples reveal a narrow distribution of the pore diameters in each type of the membranes. Thus, although not exactly the same, the pore size produced by ion-irradiation is relatively uniform while the spatial distribution of the pores cannot be controlled and is completely random.

Samples of the microporous membranes obtained in this way were coated with a metal layer to enhance optical contrast related to the pores. The coating of the membranes having 350 and 750 nm pores proved to be straightforward procedure after cleaning the surface. However, attempts to uniformly coat the 35 nm pore membranes with aluminum and platinum failed. The metal, instead of keeping the pores clear, tended to form bumps covering the holes. Nevertheless, a gold coating preserved the original pore structure up to a metal thickness of a few tens of nanometers. Thicker coatings tended to form cracks in the metal surrounding the pores.

Near-field optical imaging of the metal-coated membranes was performed in two configurations, namely, the normal incidence transmission mode and the total internal reflection geometry under illumination through a prism. For transmission measurements a home-made SNOM with shear-force feedback based on dynamic force monitoring using heterodyne phase controlled oscillator was used [13,14]. Near-field images were measured in both illumination and collection modes. In the former case, a membrane was illuminated through the SNOM tip and transmitted light was detected in the far-field. In the collection mode, the samples were illuminated from the far field and transmitted light was collected with the SNOM tip. For the measurements under the surface polariton excitation conditions the conventional amplitude feed-

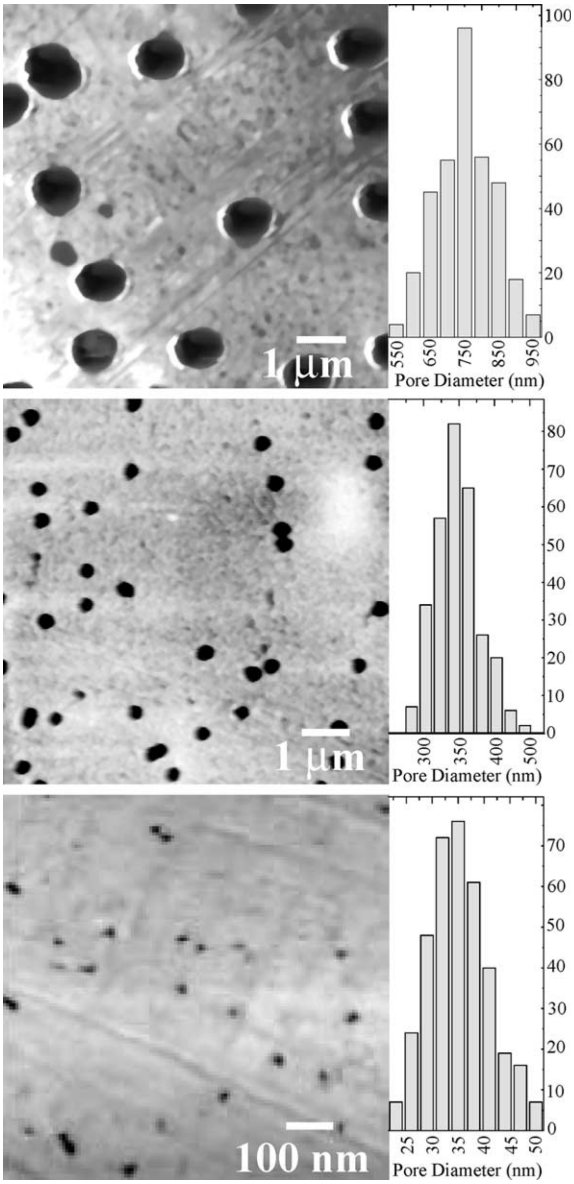

Fig. 1. Tapping-mode AFM images of the membranes having the mean pore diameters of (a) 750 nm, (b) 350 nm, and (c) 35 nm. Black-to-white contrast variations correspond to low-to-high topographic variations. Histograms of the pore size distribution for each type of the membrane obtained from multiple images are also shown.

back of the tuning-fork-based shear-force distance regulation was used. To achieve SPP excitation, the membranes were mounted onto a glass prism and illuminated at the angle of resonant SPP excitation with the 633 nm light of a He–Ne laser. By rotating a half-wavelength plate placed in the path of the incident laser beam, the polarization of the illuminating light with respect to the membrane plane was controlled. Uncoated adiabatically tapered fiber tips were used to ensure small electromagnetic interaction between the tip and the sample.

3. Results and discussion

3.1. Near-field transmission of microporous membranes

Near-field optical images of a membrane with the largest pores coated with a 30 nm-thick gold film are presented in Figs. 2(a) and (b). These images were obtained in the collection and illumination modes, respectively. To avoid problems with topographical artifacts resulting from the SNOM tip following topography and thus penetrating into the pores beneath the metal film, the images were taken in the constant-height feedback mode. The shear-force feedback signal has been adjusted in such a manner that the SNOM tip only follows the global inclination of the sample surface during scanning (“quasi open feedback loop” mode) and is not influenced by local topography related to the microporous structure. The mean tip-sample distance was of the order of a few tens of nanometers. In this manner the optical intensity at the same distance from the membrane was recorded even when the tip was scanning above the pores.

The SNOM images reveal individual as well as closely spaced pores overlaid onto a pronounced stripe structure which is not related to the position of the pores (Fig. 2). This stripe structure is probably related to the topography and optical contrast variations of the polymer membrane itself. In addition to the fact that the polymer membrane is a strongly scattering (turbid) medium at the microscopic scale, a pronounced regular stripe-structure can be identified in optical images of the membranes with a conventional optical microscope. The far-field scattering (through the membrane) on this stripe structure is a most probable cause of the stripe-like structure observed

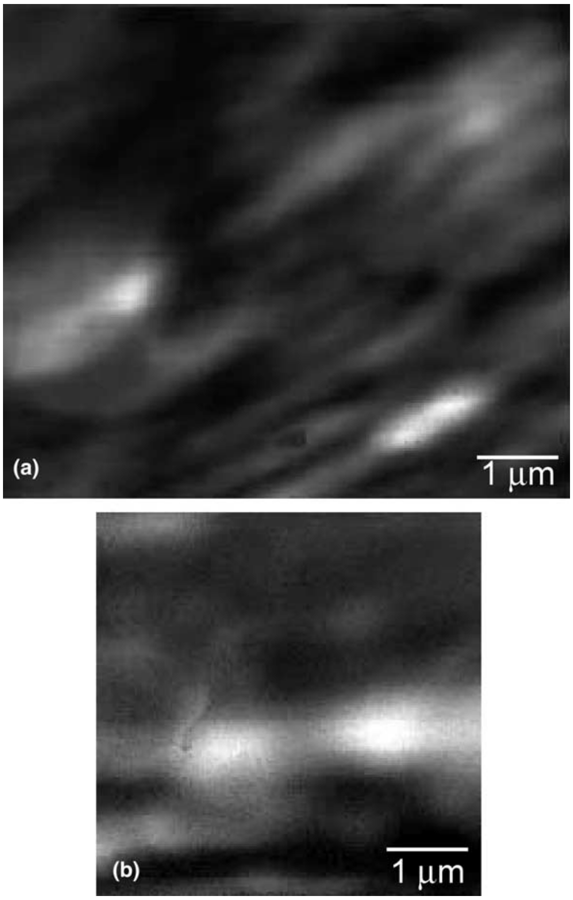

Fig. 2. SNOM images of the membranes with the pores of 750 nm diameter obtained in (a) collection and (b) illumination configurations. The SNOM was operating in a constant height mode without following membrane topography. The membranes are coated with a 30 nm-thick gold film. Black-to-white contrast variations correspond to low-to-high intensity variations of the transmitted light.

in the near-field optical images. Analogous stripe structures have also been discussed in the context of light transmission through a subwavelength aperture in a metal film with scratches [15]. It was shown that the structures, which are almost undetectable in the far-field images, become pronounced in the near field leading to the stripe-like structure in the direction of the topographical scratches regardless of the light polarization. In our case this is observed with the membrane having, in addition to the macroscopic stripe structure, strong microscopic scattering. The stripe structure of the image is less pronounced in the illumination mode (Fig. 2(b)) since, in this case, the sample is illuminated locally through the probe aperture and the far-field scattering from the membrane film takes place only within the illuminated spot. In contrast, in the collection mode many stripes contribute to the far-field scattering and related interference effects (due to the membrane thickness, the near-field of the metal surface corresponds to the far-field of the membrane where scattering takes place).

The difference in the origin of the optical signal above the pores and above the intact flat region of the membrane is confirmed in the measurements of the transmitted light intensity dependencies on the tip-surface distance (Fig. 3). If the fiber probe is positioned above the pore, the intensity of the transmitted light decreases with distance from the surface in accordance with the theoretical depen-

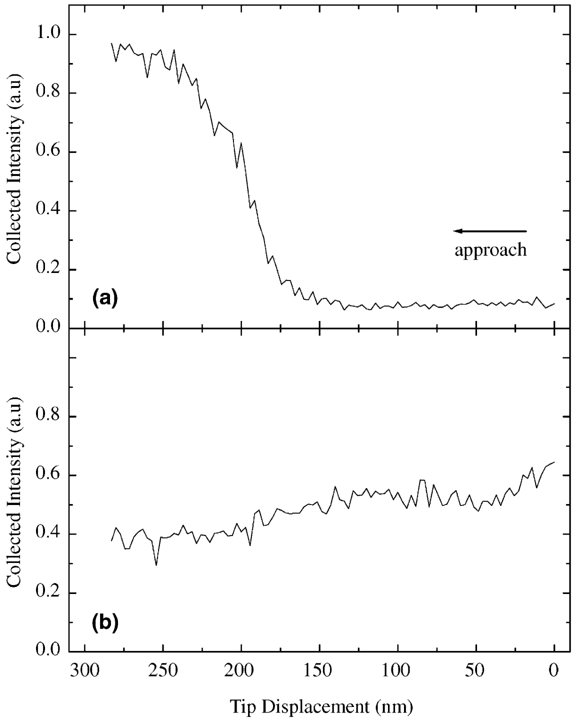

Fig. 3. Dependencies of the transmitted light intensity on the tip-sample distance: (a) the fiber tip is positioned over the 750 nm pore and (b) the fiber tip is positioned over the intact membrane surface. The membrane is coated with a 30 nm-thick gold film.

dence for the diffraction on an aperture in a metal film of finite thickness if no resonant localized plasmons are excited [5]. The latter condition is probably satisfied at the wavelength and pore-size used in the experiments. In contrast, the approach curves recorded when the fiber tip is positioned above the intact region of the membrane, reveal negligible variations of the transmitted light intensity with distance from the surface (Fig. 3(b)). This suggests that the optical signal in this region is mainly related to the far-field scattering in the bulk of the polymer membrane.

The images of the membranes with smaller pores are presented in Fig. 4. These images were recorded with the samples illuminated in total internal reflection using a prism but under conditions when surface plasmon polaritons are not resonantly excited. Again, individual pores can be resolved in the images even for pores of 35 nm size. Since the scanned area is smaller in these experiments, the stripe-like far-field structures are less visible in the images. The contrast of the pore images decreases with pore size. The contrast of the 350 nm pores ($M \sim 3$) is more than 10 times smaller than that of the 750 nm pores ($M \sim 30$). This behavior is consistent with what should be expected for sub-wavelength-sized apertures illuminated at a wavelength far from the resonances of the localized plasmon excitation. Under such conditions the transmission decreases as the fourth power of the pore size [4–6]. The optical contrast

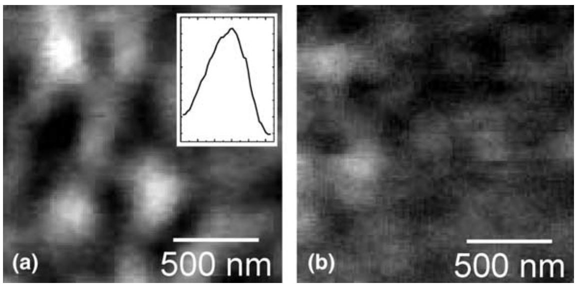

Fig. 4. SNOM images of the membranes with the pore diameters of (a) 350 nm and (b) 35 nm. The SNOM was operating in a constant height mode. The membranes are coated with a 30 nm-thick gold film. Black-to-white contrast variations correspond to low-to-high intensity variations of the transmitted light. Light intensity distribution across one of the pores of 350 nm diameter is shown in the insert.

of the 35 nm pores was even smaller. The apparent size of about 100 nm observed for the smallest pores is about three times larger than their geometrical diameter (Fig. 4(b)). This corresponds well to the size of the aperture of the SNOM fiber tip used in the experiments. Nanoscale apertures in metal-coated membranes can be regarded as an ideal object for testing SNOM resolution.

The distribution of the measured optical signal across the pore is a smooth Lorentzian-type curve as shown in the insert in Fig. 4 (cf. the results of the numerical calculations given in [5,6]). Due to strong scattering in the membrane, it was not possible to observe the polarization dependencies of the transmitted light distribution close to the pores. The individual pores have rather symmetrical images, while the elongated images correspond to closely spaced pores (Figs. 2 and 3). No electromagnetic field enhancement related to the electrostatic effects due to the direction of the incident light polarization was observed in the vicinity of the edges of the pores in the metal-coated films under these illumination conditions. This is consistent with the calculations which show that such an enhancement exists only at very small distances from the aperture [5,16]. In addition, a turbid substrate might influence this effect as well due to depolarization of light.

It should be noted the different contrast mechanisms of SNOM imaging of dielectric and metal films. In the case of dielectric films, the contrast can arise from the impedance mismatch between optical fibre and structure that can result in the stronger transmission observed through a dielectric film in a presence of a SNOM tip than through holes in the film [17].

3.2. Surface plasmon effects in optical properties of microporous membranes

Surface plasmon polaritons and localized surface plasmons play an important role in the determining the optical properties of metal films. Under certain conditions, complex electromagnetic field distributions over a metal surface can occur due to scattering and (multiple) interference of surface polaritons [18]. Surface polaritons are also responsible for the so-called enhanced optical transmission of periodically structured metal films at certain wavelengths [3,16]. To elucidate the surface polaritons influence on the optical properties of a microporous membrane we have studied the near-field optical distributions over the metal surface illuminated through a prism in the total internal reflection geometry at the angle of incidence close to the angle of the resonant SPP excitation. The near-field images under illumination with s-polarized light (no resonant SPP excitation) and p-polarized light (resonant SPP excitation) reveal distinctively different field distributions over the surface (Figs. 5 and 6). It should be noted that the nonresonant SPP excitation is possible due to diffraction on the pores and surface roughness [19]. Nevertheless, the observed near-field images reveal low efficiency of such nonresonant process probably due to the influence of the scattering substrate.

Comparison of the topographical and optical images shows that the transmission of s-polarized light, in addition to the transmission related to the pores themselves as in the case of direct transmission (Figs. 2 and 4), exhibits strong maxima located between the closely spaced pores. In Figs. 5 and 6 the optical images are taken in a constant-distance mode, thus, the optical probe follows the topography of the pores. In such conditions the topographical artifacts related to the penetration of the tip in the pore could occur. However, since in the present case we are interested in the comparison of the field distribution between the pores over the metal film, these artifacts are not relevant in the discussion of the images. Under these illumination conditions, the excitation of localized surface plasmons on surface roughness and between the closely spaced pores is important mechanism of the field enhancement determining

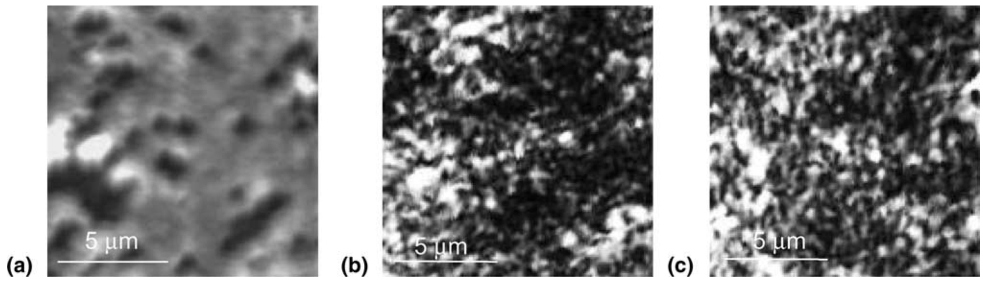

Fig. 5. Shear-force topography (a) and near-field intensity distributions over the membrane with pores of 500 nm diameter coated with 30 nm gold film illuminated in the total internal reflection geometry with (b) s-polarized and (c) p-polarized (resonant SPP excitation conditions) incident light. The density of pores is lower than in Fig. 6. Black-to-white contrast variations correspond to low-to-high intensity variations of the transmitted light. Illuminating light is incident in horizontal direction from left to right.

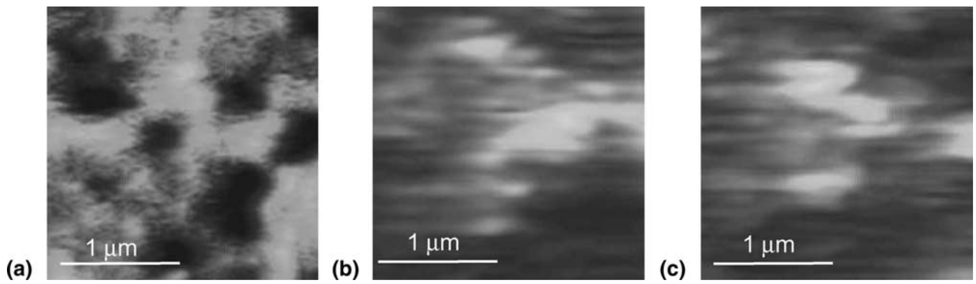

Fig. 6. Shear-force topography (a) and near-field intensity distributions over the membrane with pores of 500 nm diameter coated with 80 nm gold film illuminated in the total internal reflection geometry with (b) s-polarized and (c) p-polarized (resonant SPP excitation conditions) incident light. The density of pores is higher than in Fig. 5. Black-to-white contrast variations correspond to low-to-high intensity variations of the transmitted light. Illuminating light is incident in horizontal direction from left to right.

the electromagnetic field distribution over the surface (Figs. 5(b) and 6(b)). Such enhancement depends on the orientation of the electric field of the incident light with respect to the geometrical orientation of pore pairs, triplets etc., as well as the separation between the pores. The LSP excitation is a probable reason of the observed field distributions.

In the case of p-polarized excitation, the electric field of the incident light is perpendicular to a film surface, thus different localized plasmon resonances than those excited in the case of s-polarized excitation are observed (cf. Figs. 5(a) and (b) and 6(a) and (b)). In addition, under such excitation conditions, resonant SPP excitation can take place. However, for strongly scattering metal films with roughness and porous structure, the efficiency of the resonant SPP coupling is low as was in the experiments on SPP localization [2,18]. Both the excitation of localized surface plasmons as well as localization of SPP due to multiple scattering may contribute to the resulting field distribution. This results in even more complex electromagnetic field variations over the surface than for s-polarized incident light. Light transmission in these conditions is determined not only by the pores themselves but the resonant tunneling of light directly through the metal film with the excitation of surface plasmons of one or another kind [20].

4. Conclusions

The optical properties of strongly scattering microporous metal/polymer membranes with different pore sizes have been studied. It was shown that the dependencies of the light intensity passing through individual pores in a metal-coated membrane on the distance from the pore, its distribution across the pore and the total efficiency of the light transmission follow well the theoretical description of the near-field behavior of the subwavelength-sized apertures in a thin metal film in conditions when localized surface plasmons are not excited at pores. At the same time, the polarization dependencies of the transmission distribution are completely lost. For directly illuminated membranes, the electromagnetic field distribution is related mainly to the pores themselves. Under the illumination in the total internal reflection geometry, the field distribution exhibits much more complex structures related to the interaction of surface polaritons with the ensemble of randomly distributed pores and metal film roughness as well as to localized surface plasmons at agglomerations of the pores.

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