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Morphology of polyethylene nanolayers: a study by evanescent light microscopy

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Abstract Thin films morphology investigation of polyethylene by the differential evanescent light intensity (DELI) imaging method has been performed. The films of nanometer thickness were obtained by the matrix-assisted pulsed laser evaporation (MAPLE) technique. MAPLE was demonstrated to be suitable for the synthesis of organic materials in form of nanostructures. To prepare targets, 3% polyethylene powder was dissolved in toluene and frozen at liquid nitrogen temperature. In MAPLE, the organic material is protected by the frozen solvent against the direct laser and plasma action. Polyethylene thin films of various thicknesses, below 200 nm, were thus fabricated by varying the deposition conditions. We applied the DELI microscopy technique for fast and low cost morphology investigation of large polyethylene nanolayer zones. A phenomenological model for the interaction between the evanescent waves and the deposited material is presented.

Introduction

Since the near field microscopy became a powerful technique for nanometer thick samples characterization, many studies, both experimental and theoretical, have appeared [1–9]. The evanescent wave (EW) light illumination is used for the excitation and detection of scattering and fluorescent particles in the vicinity of optical waveguide surfaces. Techniques based on focused EWs, i.e., using a total internal reflection (TIR) microscope objective or patterned substrates, have been also developed to observe nanoparticles layers [2].

Evanescent waves which occur in TIR play a key role in many fields such as guided optics, optical fiber couplers, integrated optical elements, and inner reflection spectroscopy [2]. When TIR is produced inside a waveguide, deposited material on top of the waveguide transforms the EWs into outward propagating waves. The transformation of EWs into propagative ones is the basis of a recently developed technique—the photon tunneling microscopy (PTM) [2]. This technique is sensitive to very small height variations based on TIR, and measurements are performed by reflection, rather than by transmission [6, 7, 10].

Despite the growing number of microscopy EWs based systems used for imaging nanostructures, no detailed models are yet available [1–9].

The evanescent light illumination technique has the advantage that the electromagnetic field propagating in the waveguide does not interfere with the field extracted perpendicular to the substrate surface. It gives, therefore, an excellent dark background, providing good spatial contrast for very small objects near the surface structures as compared to other optical transmission or reflective microscopy techniques [11, 12].

Polyethylene (PE) nano films are extensively studied currently for various applications. In particular, new composite materials containing PE are studied since they have gas-sensing potential [13, 14]. It was demonstrated also that nanoparticle filled polymers have enhanced electrical and mechanical properties. For instance, it has been proved that the electrical breakdown properties of polymer composites

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can be substantially improved when the filler particles are of nanometer size. These benefits are likely related to the attenuation and redistribution of inner charges [13, 14].

For simultaneous imaging of large areas (hundreds of mm^2) of polyethylene nanostructures, we used the differential evanescent light intensity (DELI) imaging method [11, 12]. The method is an optical microscopy technique based on the capture of the propagating optical field redirected by the nano layer from the evanescent fields in optical waveguides [11, 12].

It is certainly easier and less expensive to use the DELI technique rather than atomic force microscopy (AFM) or scanning electron microscopy (SEM) for the evaluation of large areas of nanometer profiles.

The PE nanostructures were obtained by the matrix-assisted pulsed laser evaporation (MAPLE), a technique [15] derived from pulsed laser deposition (PLD) [16].

Spin coating, drop-casting, and ink-jet methods have been used to deposit organic materials as thin films. The results were not satisfactory due to limitations of the methods in resolution, deposition speed and films quality (lack of homogeneity, presence of aggregates) [17]. The PLD [15, 16] and plasma spraying were also applied for synthesis of organic films, but the polymers to be deposited were decomposed by high temperature achieved under laser irradiation.

In our experiments, the PE nanostructures were thus obtained by MAPLE [15]. When optimizing the procedure, homogenous thin films of polymers can be grown avoiding the risks of degradation or other modification of the organic material [18]. Under selective conditions (low laser fluence, moderate laser repetition rate, diluted concentration of solute in the matrix), it is possible to produce by MAPLE very smooth, uniform, and adherent coatings of nanometric thickness. It is presumed that the roughness of the surface depends not only on the deposition conditions, but also on the arrangement of the molecular chains in the film.

Fabrication of PE nanofilms

MAPLE differs from PLD in both target preparation and the deposition process. In MAPLE, the molecules of the organic material are gently transferred from the target and deposited onto the substrate in an undamaged form. MAPLE was developed to produce thin films consisting of large *organic* molecules and is especially suitable for obtaining films of nanometer thicknesses.

In MAPLE, a frozen solution of a polymeric compound dissolved in a volatile solvent (matrix) is used as target. The solvent quantity is chosen so that the polymer can dissolve to form a particulate-free solution. The target usually contains <5% polymer. In fact, each solute molecule is surrounded (shielded) by a large amount of solvent. The laser energy is absorbed by the frozen solvent molecules and not by the solute. Consequently, both thermal and photonic damages of the polymer are avoided during the laser-induced volatilization. The polymer molecules are entrained in the plume of matrix molecules leaving the frozen target due to collisions. A film of polymer is growing on the substrate, while the solvent molecules with low sticking coefficients are evacuated by the pumping system [18].

We obtained MAPLE targets by using a suspension of 0.75 g PE powder in 25 mL toluene (concentration 3 wt%) and freezing the mixture in liquid nitrogen. In all experiments, the target–substrate distance was set at 4 cm, in order to get the best possible compromise between a large enough deposition rate and a high uniformity degree of the final structures. The deposition was performed at the residual gas pressure in the deposition chamber.

We used for MAPLE deposition, an excimer KrF* UV laser source (wavelength $\lambda = 248$ nm, pulse length $\tau_{FWHM} = 25$ ns, and pulse repetition frequency $\nu = 10$ Hz) [15].

Our deposition experimental set-up is schematically presented in Fig. 1, and the deposition conditions are given in Table 1.

We deposited the PE nanostructures directly on glass substrates. Rough or smooth layers could be fabricated depending on the deposition conditions [15].

Morphology studies of PE nanofilms

The phenomenon of photon extraction from traveling waves in waveguides by nanosize material deposited on their top surface has not yet a rigorous model [1, 2, 8–12]. To observe by DELI [12], the morphology of the PE

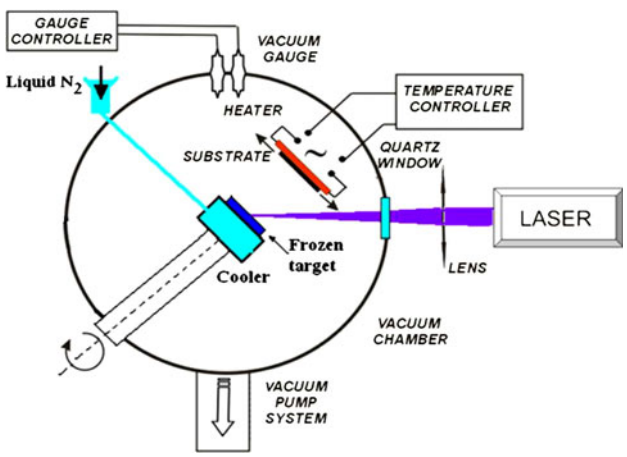

Fig. 1 The MAPLE set-up used in the experiments

Table 1 Deposition conditions of PE nanofilms on glass waveguides substrates

Sample	M4A	M4B	M4C	M5A	M5B	M5C
Laser fluence, F, mJ/cm^2	400	500	600	400	400	400
Pulse energy, E, mJ	40	50	60	40	40	40
N (number of pulses)	5,000	5,000	5,000	7,000	5,000	3,000
Sample		M1A		M1B		M1C
Laser fluence, F, mJ/cm^2		500		500		500
Pulse energy E, mJ		90		90		90
N (number of pulses)		5,000		3,000		1,000

nanolayers deposited on the glass substrates, we captured 2D images at several zooming powers (down to the range of micrometer resolved x–y areas) using an optical microscope equipped with a CCD camera. The DELI investigation method used in this work is a far field technique developed to achieve a high resolution of nanometer profiles in the z-direction, i.e., into the samples depth. The technique uses basically the phenomenon of TIR [1, 2] where EWs occur. This technique has the advantage that the far field image does not include direct transmitted or reflected light. In fact we rely on the "evanescent light extraction power" of the nanoparticles and nanolayers on the substrate which also serves as an optical waveguide.

Experimental results

The DELI technique captures the light intensity pattern extracted by the deposited particles at the waveguide surface from a light beam propagating through the glass substrate. This technique has the advantage over reflective or transmission microscopy that the propagating electromagnetic field in the waveguide does not interfere with the field extracted perpendicular to the substrate surface thus giving an excellent dark background. The method is also easier to use than AFM and SEM and suitable for evaluating large areas for its nanometer profile. The light source used was a visible light source GE-Thorn, Quartz Halogen lamp, model DDL. This device consists of a fiber illuminator, type Volpi AG, supplying a light intensity of $I_0 = 3.75$ W/cm^2 within the visible region of 400–800 nm at the fiber tip. The optical image of the evanescent light emanating from the waveguide was captured by a zooming microscope, model Leica Wild M3Z with magnification of 65–400 and equipped with a CCD camera, with a peak wavelength response at 555 nm.

In case of PE nanolayers obtained by MAPLE with different laser fluences (F) and number of pulses (N), the gray level images of the deposited zones obtained by DELI have the typical form shown in Fig. 2a.

We used a CCD camera mounted on the microscope to capture the nanolayer images and extracted from them the normalized integrated optical density (IOD), using the DELI method described in detail in [12]. IOD was defined as the mean image light intensity of the measured zone:

$$\mathrm{IOD} = \frac{\iint_S D(x,y)\mathrm{d}s}{S}, \quad (1)$$

where $D(x, y)$ is the gray level value of each pixel (0–255) and S is the area of the 2D zones as shown in Fig. 2b. As seen from Fig. 2b, the image of sample M4A (see Table 1) exhibits a detailed nano-thickness profile variation across the areas measured.

We observed also the films profiles at the deposited borders by analyzing the IOD profiles. In Fig. 3a, a typical film border area of deposited PE nanolayer is shown with a magnification of ×65. In Fig. 3b, images of three samples with areas 530 × 530 μm^2 from the deposited area in Fig. 3a show the images to the left of the border (1), at the border (2), and to the right of the border (3). The black area (4) is the image of the undeposited area, and Fig. 3c shows the 3D plots of the three areas from Fig. 3b.

DELI photon extraction model

As shown in [11, 12], DELI derives from the evanescent fields generated by TIR in the waveguide which are transformed by the nanolayer into outward propagating waves, the later reaching the CCD camera and captured as 2D images. The phenomenon used is very similar to the principle of scanning tunneling optical microscope (STOM), where EWs are generated by illuminating the sample with a light beam with an angle of incidence larger than the critical angle for TIR. However, the experimental accomplishment of STOM is much easier than the interpretation of the results [2]. The same problem arises in photon tunneling microscope (PTM) when the images are obtained at TIR conditions by measuring the reflectance and introducing the so-called effective thickness [2, 10] for evaluating the changes in the reflectance measured.

The light power extracted from the waveguide depends on the number of deposited nanoparticles on the surface and their size. Due to varying wetting properties, the nanolayers are nonuniformly covering the glass substrate, and some areas remain only partially covered. In the nondeposited areas, absolute TIR occurs for the trapped light beams propagating in the waveguide and the image captured is black.

In our DELI phenomenological analysis, we assume that the evanescent field in the air close to the waveguide is perturbed by the deposited material molecules. The

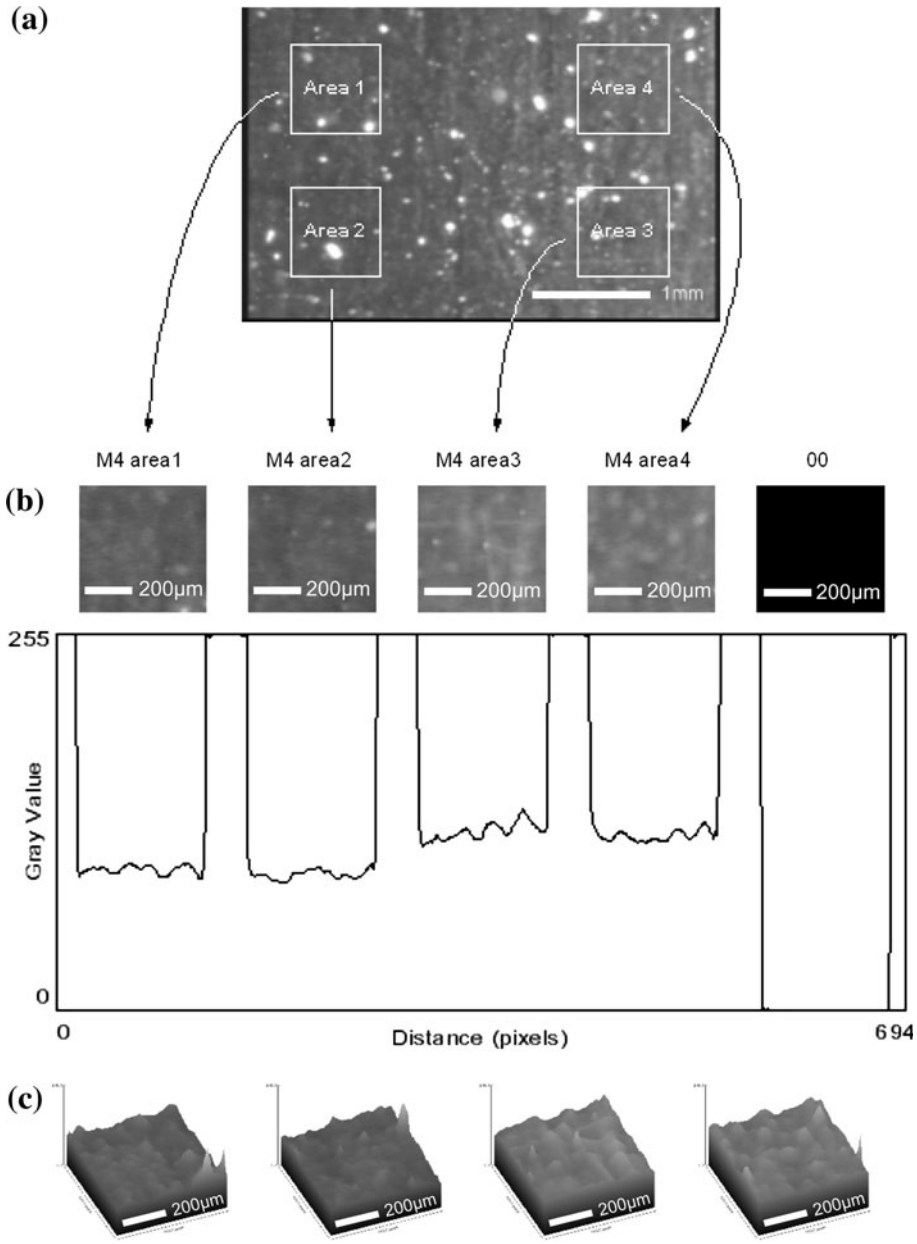

Fig. 2 **a** 2D intensity image of the deposited area of sample M4A (65× magnification and sampling four areas of 530 × 530 μm^2). The area of the image captured for 65× magnification was 3.8 × 2.5 mm^2; **b** 2D profiles of the four areas shown in (**a**); the fifth black zone is for calibrating purposes; **c** 3D plots of the areas shown in (**a**)

molecules are polarized in the presence of the electric component of the evanescent field and the dipole emission model can be applied [2].

The extracted light intensity $I_z(x, y)_{\text{det}}$ normally incident onto the detector is given by:

$$I_z(x,y)_{\text{det}} = \eta(x,y) I_0, \tag{2}$$

where I_0 denotes the evanescent field intensity at the waveguide/material interface. $\eta(x, y)$ is the photon extraction efficiency function from the propagating field in the waveguide at the point (x, y) of the film deposited onto the waveguide surface and given by integrating a generation function $g(z)$:

$$\eta(x,y) = \int_0^{z=h(x,y)} g(z)\mathrm{d}z, \tag{3}$$

where $h(x, y)$ is the film thickness at point (x, y) and the function $\eta(x, y)$ can be determined from the light intensity distribution measured by the detector.

The function $g(z)$, is derived from an appropriate physical hypothesis regarding the photons extraction process from the waveguide. Since the extracted light intensity $dI_z(x, y)$ is proportional to the extracted number of photons from the nanolayer, we assume the following differential equation for the extracted light intensity:

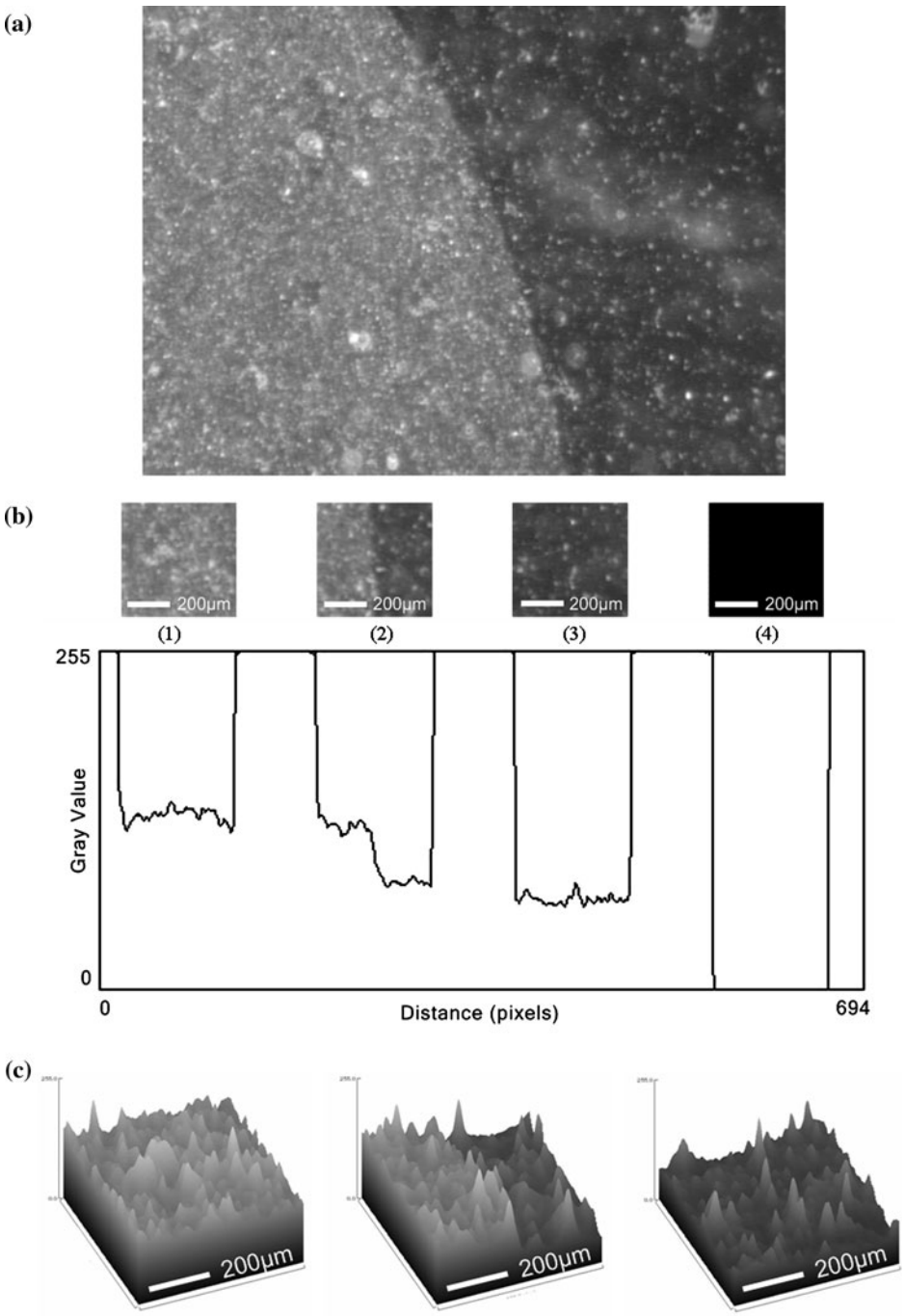

Fig. 3 **a** 2D intensity image of a typical nanolayer-substrate border on sample M1A with 65× magnification; (**b**) images of three sampled areas from the deposited zone shown in (**a**) of 530 × 530 μm^2 across the border and their 2D profiles; the black area from the undeposited zone is for calibration purposes; **c** 3D profile plots of the areas shown in (**b**)

$$\frac{dI_z(x,y)}{dz} = \gamma\,[I_0 - I_z(x,y)] \tag{4}$$

Here, γ is a parameter describing phenomenologically the ability of the nano-structured material deposited on the substrate to extract the evanescent photons from the waveguide.

By integrating Eq. 4 in the z-direction, through the nanolayer thickness from 0 to $h(x, y)$ we obtain:

$$I_z(x,y) = \left(1 - e^{-\gamma\,h(x,y)}\right) \cdot I_0 \tag{5}$$

This gives for η:

$$\eta(h(x,y)) = \left(1 - e^{-\gamma\,h(x,y)}\right) \tag{6}$$

η has the physical significance of a material–photon extraction efficiency depending on the interaction between the photons and the deposited particles on the waveguide. Correspondingly, the generating function $g(z)$ in Eq. 3 has the form:

$$g(z) = \gamma \cdot e^{-\gamma \cdot z} \tag{7}$$

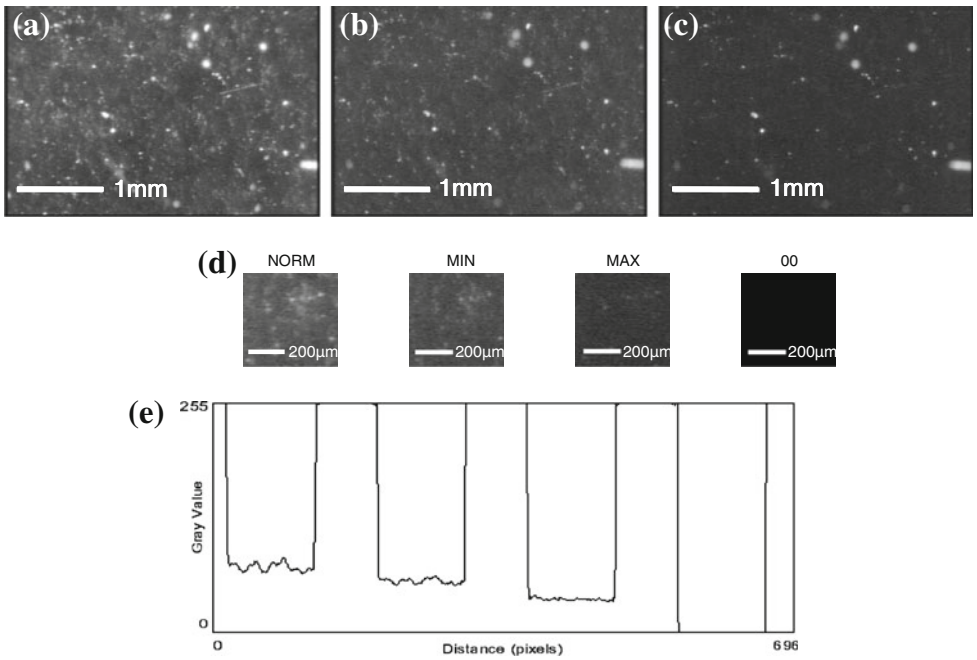

Fig. 4 Results of polarization measurements for a typical PE sample **a** without polarizer, **b** maximum transmittance with analyzer, **c** minimum transmittance with analyzer, **d** 2D average profiles of the three areas shown in (**a**–**c**) obtained at the same location; and **e** 2D profiles of the four areas shown in (**d**)

In the more general case, when we consider also absorption of light in the nanolayer, characterized by an optical absorption constant, α, $g(z)$ is given by:

$$g(z) = ((\alpha + \gamma)e^{-\gamma z} - \alpha) \cdot e^{-\alpha z} \tag{8}$$

and $\eta(h(x, y))$ becomes:

$$\eta(h(x,y)) = \left(1 - e^{-\gamma h(x,y)}\right) \cdot e^{-\alpha h(x,y)} \tag{9}$$

Since our PE films were <200 nm thick, we neglected the optical absorption in the thin films and used the simpler Eq. 6 in this investigation.

Polarization effects

According to the dipole model of field excitation in air [1, 2, 6], the field penetrating through the nanolayer and captured by the detector prevalently contains the TM modes.

We used a linear analyzing polarizer and determined from the maximum and minimum transmission, the polarization state of the light emanating from the polyethylene nanolayer. As seen from Fig. 4, there is a difference in the intensity of the evanescent light in the two orientations of the analyzer filter, confirming that the emanating light is partially polarized. As mentioned in "Experimental results" section, we take IOD as a measure of the intensity reaching the camera. We obtained from Fig. 4 a maximum IOD (with the analyzer) of $I_{\max} = 57.4$ a.u. and a minimum IOD (with polarizer) of $I_{\min} = 37.4$ a.u. Defining the degree of polarization by,

$$P = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}} \tag{10}$$

we obtain a value of $P = 0.21$ from our measurements.

Discussion

As mentioned in "DELI photon extraction model" section, in our phenomenological analysis of photon extraction by thin PE nanolayers (of <200 nm) the optical absorption can be neglected. Thus, according to Eqs. 2 and 6 we can use for two PE nanolayers of thickness h_1 and h_2, the following ratio for the extracted integrated optical densities:

$$\frac{\mathrm{IOD}_2(h_2)}{\mathrm{IOD}_1(h_1)} \approx \frac{\eta_2}{\eta_1} = \frac{(1 - e^{-\gamma h_2})}{(1 - e^{-\gamma h_1})} \tag{11}$$

For the simplest case $\gamma h < 1$, a linear proportionality between the nanolayer thickness and the normalized intensity is then inferred:

$$\frac{\mathrm{IOD}_2(h_2)}{\mathrm{IOD}_1(h_1)} \approx \frac{h_2}{h_1} \tag{12}$$

Accordingly, the measured ratio of the Integrated Optical Densities provides an estimation of the ratio between the two nanolayers thicknesses.

Then, by calibrating h_1, we can estimate from Eq. 11 the absolute thickness h_2 of any other layer. h_1 can be measured by other independent techniques such as spectrometry, SEM, AFM, or mechanical profilometry. The results of IOD measurements and PE thickness estimation for samples M5 are given in Table 2.

The thickness variation seen in Table 2 allowed us to obtain an evaluation of the photon extraction efficiency, γ, of the PE MAPLE deposited nanofilms. Thus, if we define for two different thicknesses a ratio K as $K = \eta_2/\eta_1$, for $h_2 > h_1$ and $K > 1$ we have from Eq. 11: $K/(K-1) \approx e^{\gamma h_1}$. Hence, γ is given by:

Table 2 Absolute thickness values estimated by DELI for three zones on sample M5

Zones	A	B	C
IOD	68.3	39.4	32.7
h, nm	173.2	100	82.9

$$\gamma \approx h_1^{-1} \ln\left(K(K-1)^{-1}\right) \quad (13)$$

From the data corresponding to samples M5A and M5C, we obtained $K = 2.1$ which gives:

$$\gamma \approx \frac{1}{82.9} \ln \frac{2.1}{1.1} \approx 0.0077(\mathrm{nm}^{-1}). \quad (14)$$

Thus, the effective thickness of the evanescent photons/material interaction defined as $d_{\mathrm{eff}} \approx \gamma^{-1}$ for PE is about $d_{\mathrm{eff}} \approx 130$ (nm).

Conclusions

We investigated by DELI the profiles of PE nanofilms deposited by MAPLE on glass waveguides. The goal of this work was to analyze the MAPLE process suitability for obtaining PE films with nanometer thickness by the simple and convenient DELI technique.

For MAPLE deposition, we used a KrF* excimer laser source ($\lambda = 248$ nm, $\tau_{\mathrm{FWHM}} = 25$ ns) and the UV laser beam was focused to obtain an incident laser fluence of 0.4–0.6 J/cm^2. The deposition parameters determined the roughness and homogeneity of the deposited structures.

From polarized light measurements, we observed that the light extracted by the nanolayer was polarized. We measured by DELI the nanoprofiles and thickness at different locations on the surface of the PE films. The film thicknesses grew monotonously with both laser fluence and number of pulses, in the range of 70–200 nm.

We determined the evanescent extraction constant $\gamma \approx 0.0077$ (nm^{-1}) which characterizes the ability of the PE nanofilms to extract photons from the waveguide. The corresponding effective thickness of the evanescent photons–PE material interaction found was $d_{\mathrm{eff}} \approx 130$ (nm).

Thus, DELI allowed a simple nondestructive evaluation of the profiles and thickness of PE nanofilms of large areas deposited by MAPLE.

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