

Optically active luminescent perylene thin films deposited by plasma polymerization

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ABSTRACT

This work reports about the preparation of plasma polymerized thin films of perylene with thicknesses ~30-150 nm, their characterization by different methods and the analysis of their optical properties. Highly absorbent and fluorescent films have been obtained by this method that combines the sublimation of the perylene molecules and their controlled polymerization by the interaction with remote Ar plasma. The polymeric films are very flat with a RMS roughness in the range 0.3-0.4 nm. In

contrast with the sublimated layers of perylene that present a high scattering of light, the polymerized films depict the well defined absorption bands in the region 400-450 nm and fluorescence spectra of the perylene molecule at ~475 nm. The films are formed by a matrix formed by cross-linked fragments of perylene and intact molecules that confer the observed optical properties to this material. The optical and microstructural characteristics of this type of thin films and the possibility to perform their deposition by using lithographic procedures make them suitable for their integration into photonic components for various applications. A preliminary study of the use of these films as an optical sensor of NO₂ is also presented.

KEYWORDS: Perylene dye, optical sensors; filters; fluorescence; remote plasma polymerization; lithographic processing.

Introduction

Plasma polymerization is a well established synthetic procedure that permits the synthesis of organic thin films virtually from any volatile organic or organometallic molecule. When organic volatile molecules are introduced in a plasma discharge they are extensively fragmented producing the deposition of a macromolecular cross-linked and branched solid network in the surfaces exposed to the discharge.¹⁻⁴ In general, the plasma polymers do not retain the structure of the starting monomers. Therefore, to incorporate well defined chemical functionalities of a precursor molecule the deposition is usually carried out under mild conditions that reduce the fragmentation processes. The most important synthetic methodologies to obtain such functional plasma polymers at present are based on radio frequency (RF) parallel plate plasma reactors using very low powers and pulsed RF discharges.^{4,5} By these methodologies it has been possible to fabricate functional plasma polymer thin films for biological, electrical, low k dielectrics, optical and many other applications.^{6,7} In addition, there are several examples in the bibliography about the use of phthalocyanine, merocyanine, rhodamine and

perylene derivative dyes by means of plasma-based processes in RF parallel plate reactors at low power⁸⁻¹¹ and about the sublimation of dye molecules using magnetron discharges.¹²

Very recently we have proposed a novel procedure for the deposition of dye containing thin films by using a remote microwave discharge.^{13,14} The procedure is based in the control of the interaction of the precursor molecules with the boundary of a remote microwave plasma.¹³ Up to now, the procedure has been applied to the tailored synthesis of optically active thin films from Ethyl red and Rhodamine 6G dyes.^{13,14} The methodology presents interesting characteristics like the possibility to prepare highly absorbent and/or luminescent ultrathin films in one-step at room temperature with optimal properties in terms of planarity and uniformity. Other advantages of the method deserving a specific mention are its reproducibility and its compatibility with the procedures of synthesis used in the electronic and optoelectronic technologies.

Perylene and perylene derivatives are polycyclic aromatic hydrocarbon dyes that have been widely utilized in optoelectronics, waveguides, in semiconductor devices and OLEDs.¹⁵ Perylene has been also used as optical NO₂ gas sensor.¹⁶ For all these applications is critical a strict control of the material properties and their compatibility with the other components of the systems. This imposes very strict conditions for the preparation of the perylene containing materials. Classical methods of synthesis are based in sol-gel and other chemical procedures, consisting generally of several step processes which are not always compatible with sensitive substrates. Therefore, the main scope of the present work is to investigate for the first time the feasibility of preparing optically active perylene thin films by remote plasma polymerization. Besides the characterization of the films and the study of their optical and luminescent properties, the synthesized materials are tested as optical gas sensors. Some additional data corresponding to a perylene derivative dye will be also included to demonstrate the general character of the synthetic procedure.

Experimental methods

Two perylene dyes have been studied in this work: perylene from Aldrich and 2,9-Dimethyl-anthra[2,1-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetrone (Me-PTCDI) from Sensient Imaging Technologies.

Plasma procedure. A general scheme of the experimental set-up used for deposition was presented elsewhere.¹³ It consists of a vacuum chamber with two zones for the plasma and for the remote deposition. A set of magnets surrounding the chamber sustain a discharge in the plasma region under microwave electron cyclotron resonance (ECR) conditions. The microwave is applied to the plasma chamber through a flat Pyrex window. The system is fitted with a set of Knudsen cells to sublime the dye in the deposition zone. The pressure of the system was controlled by an automatically regulated pressure controller connected to a capacitance pressure gauge (Baratron). Argon plasma gas is dosed to the plasma chamber using a calibrated mass flow controller (MKS). The microwave power was varied in the range 30-300 W and the argon pressure in the range 1×10^{-1} and 1×10^{-3} mbar. The system was pumped before and after deposition with a turbomolecular pump to achieve a base pressure of $\sim 10^{-7}$ mbar. One side polished Si(100) wafers, quartz and glass slides used as substrates were placed in the deposition chamber.

The polymerized perylene and Me-PTCDI thin films were prepared by sublimation of the dye molecules in the downstream region of an Ar microwave ECR plasma. Film thickness and evaporation rate are controlled by using a quartz crystal monitor placed besides the sample holder in the deposition region. Typical growing rates between 2-4 nm/min were achieved by controlling the heating of the Knudsen cells. By depositing the films using relatively low growth rates was possible to control efficiently the deposition of ultrathin films of in the range 30-150 nm. The substrate and the evaporators were moved together to keep constant the amount of the evaporated molecules arriving to the substrate. The degree of polymerization control was obtained by changing the distance z between the substrate and the plasma region, the power of the plasma and/or the pressure during the discharge. The objective of such experiments was to keep a given number of chromophore centers in the films avoiding complete fragmentation of all molecules arriving to the substrate. Thus, for shorter distances z , higher plasma

power and/or higher values of pressure, more important was the interaction of the evaporated dye molecules with the plasma species. This yielded to a higher fragmentation of the dye molecules and to a higher polymerization degree of the dye precursor in the films.^{13,14,17} Among all these parameters, the most sensitive one was the distance z between the sample holder and the plasma.¹³

Thin film characterization. The mass spectra of the samples were recorded on a TOF-SIMS IV instrument from Ion-ToF GmbH Germany. The sample was bombarded with a pulsed Bismuth ion beam. The generated secondary ions were extracted with a 10 kV voltage and their time of flight, from the sample to the detector, was measured in a reflectron mass spectrometer. Typical analysis conditions in this work were: 25 keV pulsed Bi^+ beam at 45° incidence, rastered over $500 \times 500 \mu\text{m}^2$. An electron flood gun for charge compensation was used during the measurements.

UV-Vis transmission spectra were recorded in a Varian Cary 300 spectrophotometer for samples deposited in quartz slides.

Fluorescence spectra were measured in a Jobin-Yvon Fluorolog3 spectrofluorometer using grids of 2 and 3 nm for the excitation and emission, respectively. For this analysis the samples were deposited in quartz slides. The fluorescence spectrums were excited with radiation of 390 nm for the evaporated layers and 420 nm for polymerized thin films. Fluorescence microscopy images were obtained with a Leyca TCS SP2 confocal fluorescence microscope.

The optical properties of the thin films deposited on Si(100) have been measured with a variable angle spectroscopic ellipsometer (VASE) from J.A. Woollam Co., Inc. The analyzed spectral range was 200-2000 nm and the measurements were performed at 60° , 65° and 70° angles of incidence. Depolarization and transmission measurements were additionally carried out.

The thickness of the films has been measured with a Mahr Surf XR-20 profilometer and by VASE for samples deposited on Si(100).

The XPS spectra were recorded on an ESCALAB 210 spectrometer that was operated at constant pass energy of 20 eV. Non-monochromatized $\text{MgK}\alpha$ radiation was used as excitation source. Atomic ratios and surface concentrations were quantitatively determined from the area of C1s, O1s and Si2p peaks. A

Shirley-type background was subtracted and the peak areas were corrected by the electron escape depth, spectrometer transmissions and photoelectron cross-sections.¹⁸

Fourier transform infrared (FT-IR) spectra were collected in transmission mode in a Nicolet 510 spectrometer for samples deposited on Si(100) wafers.

Non-contact AFM measurements were carried out with a Cervantes AFM system from NANOTEC using commercial non-contact AFM tips from MikroMasch.

Field Emission Scanning Electron Microscopy (FESEM) micrographs were obtained with a Hitachi Field Emission S-5200 Microscope for samples deposited on Si(100).

The evolution of the UV-Vis and fluorescence spectra of samples exposed to NO₂ were measured in a steel chamber connected to the UV-Vis spectrometer and to the spectrofluorometer by a set of optical fibers. A flow of 500 ppm of NO₂ (500 ppm/air) was mixed with a regulated industrial air flow to achieve the desired NO₂ concentrations at atmospheric pressure. For these measurements the samples were deposited in quartz slides .

Results and discussion

Optical characterization of the thin films. The UV-Vis spectra of a selected set of perylene plasma polymer thin films of 150 nm thickness are shown in Figure 1a). The corresponding experimental conditions are reported in Table 1. Sample a) in Table 1 is deposited at the shortest **z** distance and with the higher power. Sample b) is deposited at a higher distance and with a lower power and sample c) was deposited in the same position than in this latter case but cycling the plasma power from the value corresponding to Sample b to a lower value. The experimental protocol of sample c) was chosen to enable a very low interaction of the sublimated molecules with the plasma for short periods of time during the synthesis. Thus, the interaction of the sublimated dye molecules with the plasma species during the preparation of the perylene plasma thin films follows the sequence Sample a) > Sample b) > Sample c). The plasma polymer thin films in Figure 1a) present absorption features characteristic of the perylene molecule¹⁹⁻²¹ as it has been observed in solution and in solid state in matrix,^{22,23} respectively.

Thus, the films a) and b) show well defined features at 447, 422 and 398 nm characteristic of the perylene molecule and a broad light absorption for wavelengths below 350 nm in the UV region of the spectra. These films are transparent for wavelengths higher than 470 nm. The three well defined molecular absorption features are also present in the spectrum of the thin film produced by variable plasma power (Sample c in Figure 1). In this sample it is also possible to observe some light dispersion for wavelengths higher than 470 nm. The spectrum of the sublimated perylene layer in Figure 1 is characterized by a strong light dispersion in all the analyzed range of wavelengths and by the absence of well defined absorption features corresponding to the perylene molecule as it appears for the polymerized thin films a)-c).

The evolution of the UV-Vis spectra of a series of samples prepared according to the conditions of sample a) in Table 1 as a function of their thickness is shown in Figure 2. It is worth to mention that the perylene plasma polymer thin films present an intense yellow color even for thicknesses as low as ~35 nm (see Figure 2) and are transparent for wavelengths higher than ~470 nm independently of the thickness (see dotted line in Figure 2). In addition, it is possible to observe in Figure 2 a nearly complete light absorption below ~470 nm when the film thickness is higher than 300 nm.

A similar trend is obtained for perylene derivative (Me-PTCDI) plasma polymer thin films. Figure 1b) shows the evolution in UV-Vis spectra of Me-PTCDI thin films (90 nm thickness) deposited under different experimental conditions. All samples were prepared with the substrates at the same distance of deposition set at $z = 7$ cm. For samples a' and b' the microwave power was $P = 200$ W and for sample c' was $P = 100$ W. Additionally, there were changes in deposition pressure; for sample a' it was $P = 1 \times 10^{-1}$ mbar and for the rest of samples $P = 1 \times 10^{-2}$ mbar. The absorption spectral features of the plasma thin films are similar to those reported for the dye molecule in solution and in solid matrices.²⁴⁻²⁷ Thus, the bands at 472, 503 and 540 nm are observed in the three spectra. Their different intensities must be related with a distinct degree of polymerization in each case. Their shape is also quite different than the broad absorption bands of the sublimated film also reported in Figure 1b). Similarly to the perylene plasma thin films an intense light absorption is observed for wavelengths lower than 350 nm. It is also

worthy of mention that plasma films prepared at shorter z values do not present the reddish color typical of the Me-PTCDI dye molecule (spectra not shown). All these results show that different derivatives of the perylene thin films can be used for the preparation of polymerized thin films, although the experimental conditions must be adjusted to each specific case. In particular, for the Me-PTCDI plasma thin films it has been found that this molecule is more sensitive to the plasma conditions than perylene and that, therefore, it requires a more precise adjustment of the polymerization conditions.

The fluorescence emissions of the plasma thin films and a sublimated layer of perylene are shown in Figure 3. The fluorescence emission of the polymerized thin films is similar to that described in the bibliography for the perylene molecule in various systems, like dissolved in cyclohexane or toluene,¹⁹⁻²¹ adsorbed onto alumina and silica gel,²² sublimated in strata together with water²⁸ or forming a Langmuir-Blodgett films²⁹. These spectra are characterized by a fluorescence maximum at $\lambda_{\text{max}} = 475$ nm, typical of isolated molecules of perylene. The sublimated layer yields a fluorescence originated from the aggregation of perylene molecules. Under this situation, the interaction of neighboring perylene molecules results in an excimer fluorescence similar to that previously observed in a crystalline phase of a cyclohexane solution.^{19,22} According to previous publications, the fluorescence maximum of microcrystals of perylene appears at $\lambda_{\text{max}} = 575$ nm.^{19,22,29} Meanwhile, Vitukhnovsky et al.²⁹, studying this type of spectra, suggested that in the region comprised between 500 and 650 nm they can be distinguished two separated emissions, a first one attributed to dimmer species (500 to 600 nm) and a second one due to excimer species (550 to 650 nm). In our series of polymerized samples, decreasing degree of polymerization (from sample a to c, see Table 1) permits a clear distinction between the aggregate and molecular contributions to fluorescence. Thus, film c in Figure 3, deposited using variable plasma power, presents a fluorescence spectrum that can be ascribed to the emission from the monomer species in the region 450-500 nm plus the emission from dimmer and excimer species at higher wavelengths. Figure 3b) shows a picture of samples a, b and c excited with UV light of 365 nm. The light emitted by the films varies from sample a), characterized by a blue bright emission typical of isolated perylene molecules, to the orange emission observed in the more aggregated sample c). Note

that fluorescence emissions have been measured and observed in air although the fluorescence of perylene is efficiently quenched by oxygen.³⁰

Refractive index (**n**) and extinction coefficient (**k**) curves of selected plasma polymeric thin films have been obtained by spectroscopic ellipsometry. The **n** and **k** curves are plotted in Figure 4. The thin films used for this characterization are prepared under different experimental conditions avoiding the formation of light dispersing dyes aggregates. The obtained **n** values are very similar in all the cases with slight variations from **n**=1.71 to **n**=1.75 at 635 nm (Figure 4a)) as the microwave power decreases from 300W to 40W and the distance *z* increases from 5 cm to 10 cm. The extinction coefficients were relatively low (**k** < 2x10⁻³ at 635 nm) in comparison with previously reported optical plasma polymeric thin films.³¹ In combination with the previous analysis these results show that high quality optical thin films presenting a high luminescent intensity can be deposited by the presented methodology.

Composition and structure of the plasma polymerized thin films. Determination of surface composition of perylene thin films has been carried out by XPS for samples deposited in Si(100). The results are summarized in Table 1 where atomic percentages are presented for the evaporated and polymerized films with different degree of polymerization. All the samples contain oxygen even if this element is not present in the perylene monomer and no oxygen flow is added to the discharge. A higher amount of oxygen is noticed for films with lower degree of polymerization (b : 25.5 % and c : 24.0 %) in comparison with the film with higher degree of polymerization (a : 13.7 %). Oxygen enrichment is a well know phenomenon in plasma polymerized organic materials. Its origin can be post-deposition reactions of the samples exposed to the air or/and direct incorporation of residual oxygen from the reactor during the deposition process.¹⁻³ The observation of some content of silicon in the evaporated sample can be explained by the formation of perylene microcrystals which do not cover completely the substrate surface.

Sample	C1s	O1s	Si2p	z (cm)	Pressure (mbar)	Microwave power (W)
<i>a</i>	86.3	13.7	0	5	1x10 ⁻¹	300
<i>b</i>	74.5	25.5	0	10	1x10 ⁻¹	40
<i>c</i>	76.0	24.0	0	10	1x10 ⁻¹	(10-40)*
Sublimated layer	75.5	13.3	11.2	-	1x10 ⁻³	-

* The power was set at 10 W for 30 seconds two times during the deposition

Table 1. Surface composition in atomic percentages determined by X-ray Photoelectron Spectroscopy (XPS) for perylene thin films corresponding to a sublimated layer and to polymerized films deposited by using different process parameters as indicated.

The FT-IR spectroscopic examination of the perylene thin films provides important information about the chemical bonds and functional groups constituting the film structure. Figure 5 shows the FT-IR spectra of an evaporated perylene and a plasma polymerized layer (Sample b). To record this latter spectrum, it was necessary to deposit films with a thickness in the range 500-600 nm to have enough sensitivity. Assignment of the bands in the FT-IR spectra has been done according to the bibliography.^{11,32} The FT-IR spectrum of sublimated perylene layer is dominated by two bands at 764 and 810 cm⁻¹ attributed to C-H in out-of-plane bending. Less intense bands have been observed and assigned in the following way: 1185 cm⁻¹ to C-H in plane bending; 1415 cm⁻¹ associated to ring stretching; 1515, 1604 cm⁻¹ attributed to aromatic C=C stretching; 1673-1756 cm⁻¹ assigned to C=O stretching vibration in the carbonyl phenyl group. The polymerized perylene film shows the following bands: low intense features at 630-675 cm⁻¹ assigned to C-C-C in plane bending; 770-815 cm⁻¹ to C-H in out-of-plane bending; 1047, 1270 cm⁻¹ to C-H in plane bending; 1380, 1442 cm⁻¹ associated to ring

stretching; 1510, 1584, 1628 cm^{-1} assigned to aromatic C=C stretching; 1672-1740 cm^{-1} attributed to C=O stretching vibration in the carbonyl phenyl group; 2926 cm^{-1} that can be assigned to C-H stretching vibrations. The plasma polymer spectrum shows an additional wide and intense band at $\sim 3450 \text{ cm}^{-1}$ due to O-H vibrations, what is congruent with the XPS results showing the incorporation of oxygen within its structure (see Table 1). Broadening of the IR bands is a typical effect in plasma polymers.¹⁻³ Thus, the wide experimental shape of the FT-IR spectrum of the polymerized films of perylene can be interpreted as resulting from the cross-linking of perylene molecules during the plasma deposition (i.e., extensive fragmentation of the dye molecule in the layer) and the partial hindering of vibration modes of intact dye molecule confined within the cross-linked polymeric matrix. In addition, the very intense C-H bands observed in the plasma polymer films can be also ascribed to the formation of a polymeric cross-linked hydrocarbon matrix formed by the recombination of dye molecule fragments originated by interaction of the molecules with the glow discharge. It is important to stress that the presence in the FT-IR spectra of the polymerized films of bands due to aromatic stretching modes typical of benzene rings supports that in these materials there are active perylene molecules embedded in a polymeric matrix.

Figure 6 shows the ToF-SIMS spectra of a sublimated perylene layer and a perylene plasma polymerized thin film. The perylene from the sublimated film are easily ionized without extensive fragmentation, being possible to clearly observe the pattern due to the dye molecule. Thus, the most important features in the spectra of the sublimated perylene layer are a series of lines centered at the position of the perylene molecular ions M^+ and MH^+ at $m/z = 252$ and 253 (equivalent to $\text{C}_{20}\text{H}_{12}$, the molecular formula of perylene) and a series of low intensity peaks appearing around $m/z: 503$, a position roughly corresponding to $m/z = 2\text{MH}^+$. The spectrum of the polymeric thin film is different from the previous one. It is characterized by a set of low intensity peaks appearing in all the scanned range. The most intense peaks appears for $m/z < 100$, surely due to small C-H(O) fragments of the film matrix. In addition other peaks in the spectrum appears at $m/z: 165$ (C_{13}H_9), $m/z: 221$ ($\text{C}_{16}\text{H}_{13}\text{O}$), $m/z: 226$ ($\text{C}_{18}\text{H}_{10}$), $m/z: 239$ ($\text{C}_{19}\text{H}_{11}$), $m/z: 281$ ($\text{C}_{20}\text{H}_9\text{O}_2$) and $m/z: 325$ ($\text{C}_{24}\text{H}_{21}\text{O}$). These ion fragments are

related with the molecular formula of perylene and many of them contain oxygen in their structure, what is congruent with the previous XPS and FT-IR analysis showing that some oxygen is incorporated in the films. Very likely, these fragments are the result of the partial fragmentation of the perylene molecule during the formation of the films. Another important difference with respect to the sublimated layer is the absence of peaks around m/z : 503 due to the aggregation of two perylene molecules. However, the most important feature in the spectrum of the polymerized thin film with respect to their optical properties is the appearance of peaks at the m/z values corresponding to the perylene molecular ion (M^+ and MH^+). Although its intensity is smaller than in the sublimated films, its appearance in the spectrum confirms that a percentage of integer perylene molecules are present in these materials.

The XPS, FT-IR and ToF-SIMS analyses of the polymeric thin film are congruent with a cross linked structure resulting from the fragmentation of the perylene molecules during the film growth. SIMS analyses also indicate that some perylene molecules are incorporated intact inside of the film. These molecules are responsible for the light absorption and fluorescence emission shown in Figs. 1-3. On the other hand, the polymeric matrix has a high unsaturation degree. The unsaturated network forming the thin film matrix is the responsible of the important light absorption in the UV region shown in Figs. 1 and 2 and also for the high extinction coefficients for wavelengths lower than 400 nm shown in Fig 4.

Microstructure and surface morphology. The surface morphology of the samples has been studied by SEM and AFM microscopies. Figure 7 a) show the normal and cross-sectional SEM micrographs of an evaporated perylene layer on Si(100) and Figure 7 b) the cross-sectional SEM micrograph of a plasma polymer thin film. The sublimated layer is formed by dye crystallites which are formed on the substrate surface during the evaporation process. These dye microcrystallites are weakly adhered to the substrate and are the responsible for the light dispersion at wavelengths higher than 470 nm shown in Figure 1. The SEM micrographs of perylene polymeric thin film do not show any contrast observable by this technique (figures not shown). The absence of observable features is independent of the different plasma conditions used for the deposition of the layers leading to different polymerization degrees. The

plasma polymer thin films can be only observed in cross sectional micrographs (see Figure 7b)) showing a homogeneous and regular structure.

The surface topography of the polymeric films can be studied by AFM. Figure 8a) shows the AFM images of the surface of a perylene thin film with a high degree of polymerization (Sample a) in Table 1). Figure 8b) shows a similar image for a sample with lower degree of polymerization (Sample b in Table 1). The first image (i.e., Figure 8a)) presents a quite homogeneous and featureless surface. In contrast, nanometric globular aggregates can be distinguished in the surface of the second film (Figure 8b). This difference in the topography is clearly seen in the cross-sectional surface profiles shown in Figure 8c). In this figure the Z value of sample a does not exceed 0.3 nm while for sample b $Z \leq 5$ nm. Nevertheless, it is interesting to stress that both type of plasma polymers are very flat being their RMS roughness 0.29 nm (Sample a) and 0.41 nm (Sample b), respectively. Similar results have been obtained from the analysis of a set of ten samples with thicknesses in the range ~90-150 nm that were deposited under different plasma conditions (results not shown). Thus, the deposition of very flat thin films seems to be a characteristic of the method as it has been observed previously for Rhodamine 6G and Ethyl Red plasma polymerized thin films.^{13,17} The observation of globular nanoaggregates at the surface of materials deposited under relatively mild polymerization conditions can be directly related with the light dispersion and fluorescence features due to aggregates found in the UV-vis absorption and fluorescence emission spectra of this type of samples (cf. Figures 1-3).

Lithographic processing of the plasma polymerized thin films. Perylene polymerized thin films are being developed as processable active layers for the fabrication of photonic structures and devices. For this reason, a preliminary study has been carried out to demonstrate the possibility of processing the perylene plasma polymeric thin films using masks. Figure 9 shows two confocal microscopy fluorescent images of patterned films. The first micrograph (Figure 9 a)) corresponds to an array of fluorescent ~20 μm diameter discs obtained by covering the Si(100) substrate with a Ta shadow mask before the deposition. The corresponding negative pattern using the same shadow mask is presented in Figure 9 b).

This fluorescent pattern is obtained by the selective etching of a previously deposited plasma polymer thin film. For this purpose, the films were covered by the shadow mask and introduced again in the plasma reactor where they were etched during 15 minutes with oxygen plasma excited with 300 W at 10^{-2} mbar. The layer composition and properties are not affected by the presence of a metallic mask covering the substrate. Additional studies will be carried out to determine the size limit of the structures that can be generated by the combination of such processes.

Sensor response. Perylene containing thin films have been proposed for optical nitrogen dioxide sensing due to the changes in color and fluorescence emission observed when they are exposed to NO_2 .¹⁶ The fluorescence quenching phenomena and the simultaneous color change are attributed to the formation of non-fluorescent nitroperylene by a very selective reaction of perylene with NO_2 . The concentration of NO_2 can be calculated from the rate response of the sensor material.¹⁶ The color change is due to the development of an absorbing band in the range 470- 520 nm that increases in intensity with the exposure time. Similar color changes and fluorescence quenching have been observed in plasma polymer thin films exposed to NO_2 . Figure 10 shows the evolution of the absorption intensity at 520 nm as a function of the exposure time for the following NO_2 concentrations: 50, 125 and 500 ppm. As the nitroperylene band increases the color of the films changes from intense yellow to dark brown-reddish (see Figure 10b) and Figure 11). In Figure 11 the **n** and **k** values of a perylene plasma polymer after and before the exposition to NO_2 is depicted. The figure shows that, apart from the change in color previously described, the NO_2 exposition also produces a gradual increase in the refractive index for wavelengths higher than 450 nm. This variation in **n** in the analyzed range can be also exploited for the optical sensing of NO_2 additionally to the color change and fluorescence quenching. A complete study of the use of perylene plasma polymerized thin films as NO_2 gas sensing is out of the scope of this paper and will be the subject of a forthcoming piece of work. Our preliminary results here that these materials can be used for the fabrication of inexpensive optical sensors and optical dosimeters.

Resume and Conclusions

The reported results have shown that luminescent polymeric thin films can be prepared by remote microwave enhanced CVD using perylene dye as the sole organic precursor. The method permits tailoring the dispersion degree of the dye in the thin film matrix from a molecularly dispersed state to another consisting of nanoaggregates of the perylene molecule. Both type of films present different properties. The thin films containing dispersed perylene molecules do not disperse the light and show blue light luminescent emission. The luminescent emission shifts to higher wavelengths as the percentage of nanoagreggates increases (i.e., orange luminescent emission of light).

Another immediate application of these materials is as decorative coatings due to the high light absorption detected even for films of some tens of nanometer. In turn, the nearly complete light absorption at wavelengths lower than 470 nm shown in Figure 2 indicates that these films can be used as nanometric long pass optical filters.

A very low surface roughness and absence of light dispersion in plasma polymerized perylene thin films are important requisites for the use of such dye containing layer as active optical thin films. Their synthesis based on a one-step solventless method is compatible with the present silicon technology. In addition the films can be easily processed using shadow masks in combination with standard etching processes. All these features, together with the stability of the films, make that they are ideal candidates for their integration together with other optical components for the fabrication of a large variety of phonic devices like filters, photonic sensors, etc.

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FIGURE CAPTIONS

Figure 1. a) UV-Vis spectra of a set of plasma polymerized perylene thin films (thickness ~ 150 nm) deposited under different plasma conditions. b) UV-Vis spectra of a set of Me-PTCDI polymeric thin films (thickness ~ 90 nm) prepared under different experimental conditions. Spectra of the corresponding sublimated dye layers are included for comparison. The corresponding dye formulas are also included in the figures.

Figure 2. UV-vis spectra of a set of plasma polymerized perylene thin films as a function of thickness. The thin films are deposited under identical experimental conditions but for different deposition times.

Figure 3. a) Fluorescence emission spectra of three perylene plasma polymerized thin films deposited under different experimental conditions (see Table 1) and a sublimated film. b) Images of the three perylene polymerized thin films illuminated with UV light ($\lambda = 365$ nm) in air.

Figure 4. a) Refractive index (n) and b) extinction coefficient (k) values determined by VASE for two perylene thin films deposited under different experimental conditions as indicated in the figure.

Figure 5. FT-IR spectra of a plasma polymerized thin film and a sublimated layer of perylene

Figure 6. ToF-SIMS spectra of a plasma polymerized thin film and a sublimated layer of perylene

Figure 7. a) Cross-sectional SEM views of a) an perylene sublimated layer and b) a perylene plasma polymerized thin film deposited on Si(100). The inserted image in the top panel shows a normal view of the sublimated layer.

Figure 8. AFM images of two polymerized thin films of perylene prepared under plasma conditions yielding a) a high and b) a low cross linking of thin film structure. The plots in c) correspond to linear scans across each image.

Figure 9. Fluorescence microscopy images of patterns generated using a shadow mask. a) perylene plasma polymerized thin film (~ 100 nm thickness) deposited through the mask (positive pattern, diameter of the disk ~ 20 μm). b) Perylene plasma polymerized thin film etched using the previous mask (negative pattern, diameter of the holes ~ 20 μm).

Figure 10. Top) Evolution of absorption intensity at $\lambda = 520$ nm of a perylene plasma polymerized thin film as a function of the exposure time to different concentrations of NO₂ in air. Bottom) Color change when a perylene plasma polymer thin film is exposed to NO₂.

Figure 11. a) Refractive index (n) and b) extinction coefficient (k) values determined by VASE for two perylene plasma polymerized thin film after and before exposition to 125 ppm of NO₂ during 30 h.

TABLES

Table 1. Surface composition in atomic percentages determined by X-ray Photoelectron Spectroscopy (XPS) for perylene thin films corresponding to a sublimated layer and to polymerized films deposited by using different process parameters as indicated.

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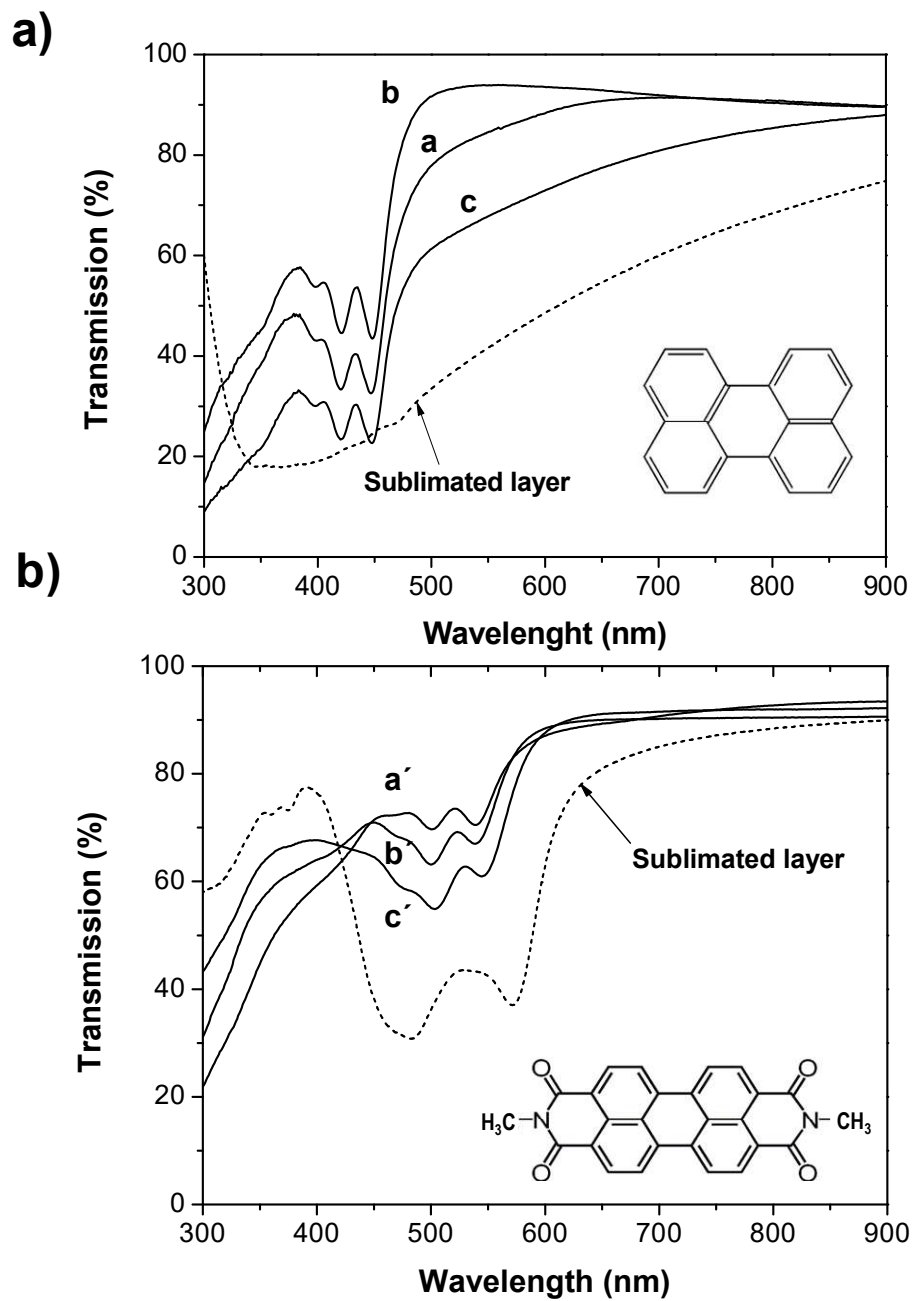


Fig. 1

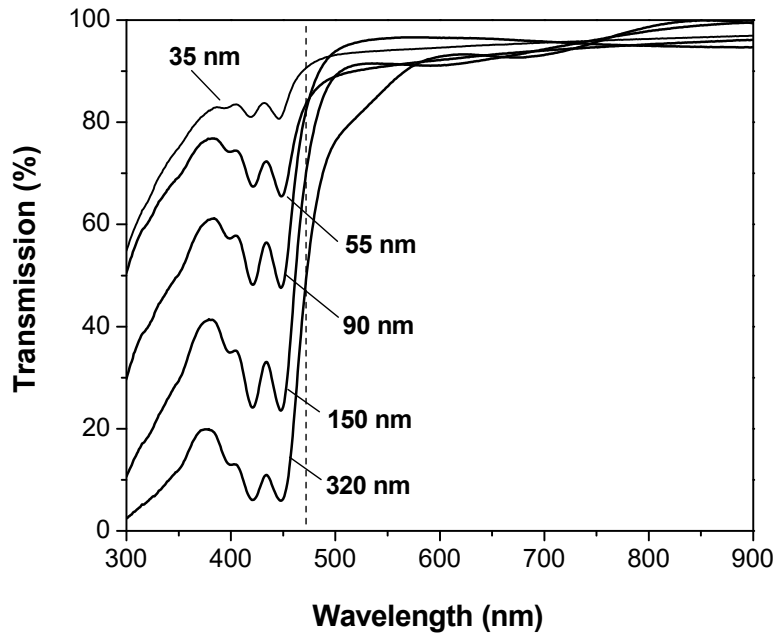


Fig. 2

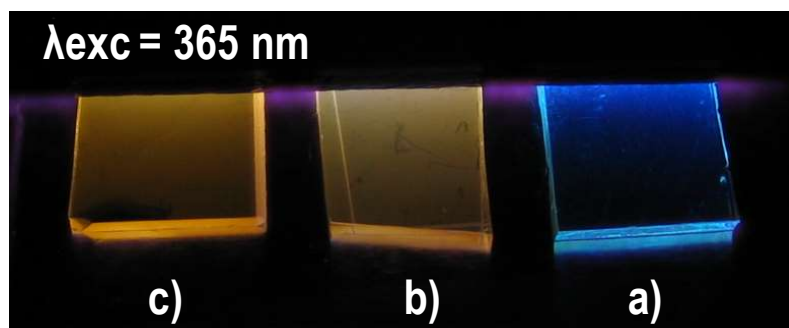
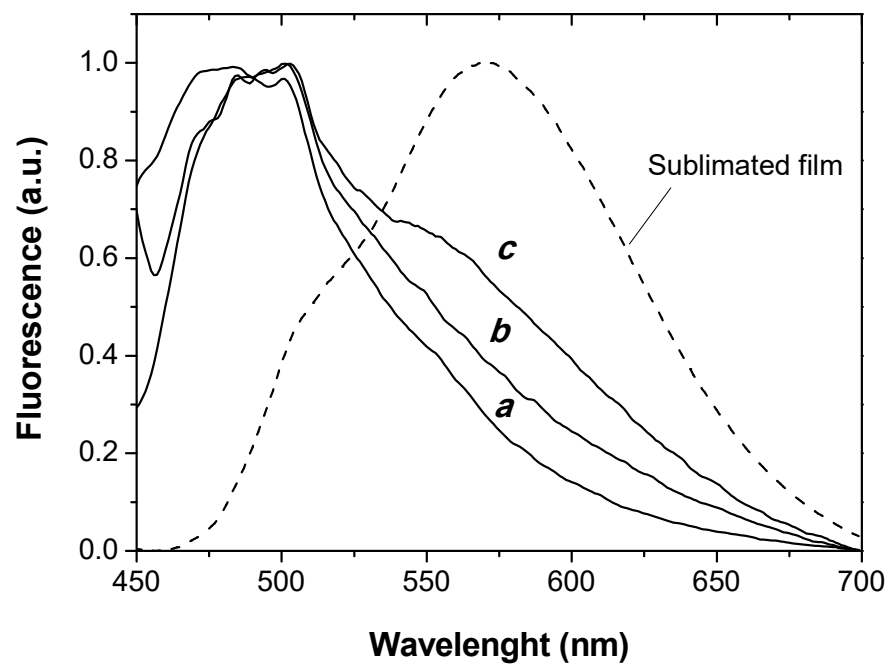


Fig. 3

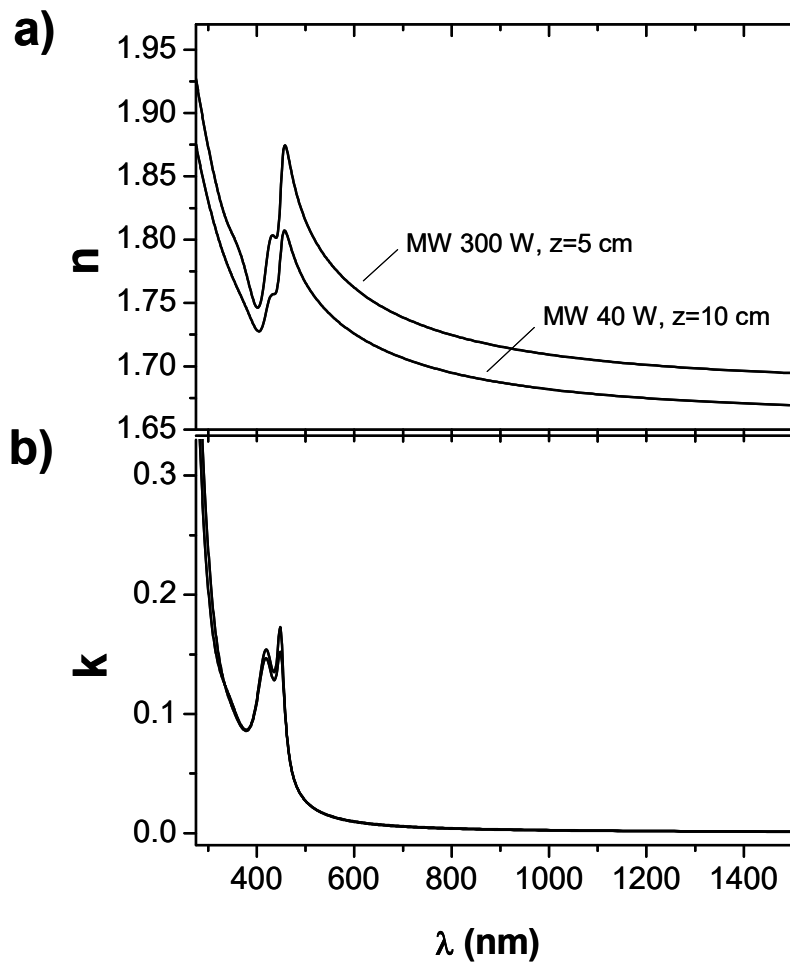


Fig. 4

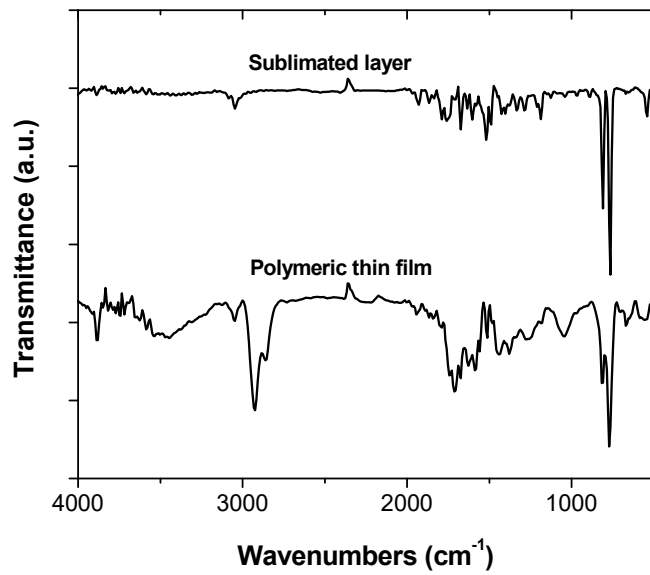


Fig. 5

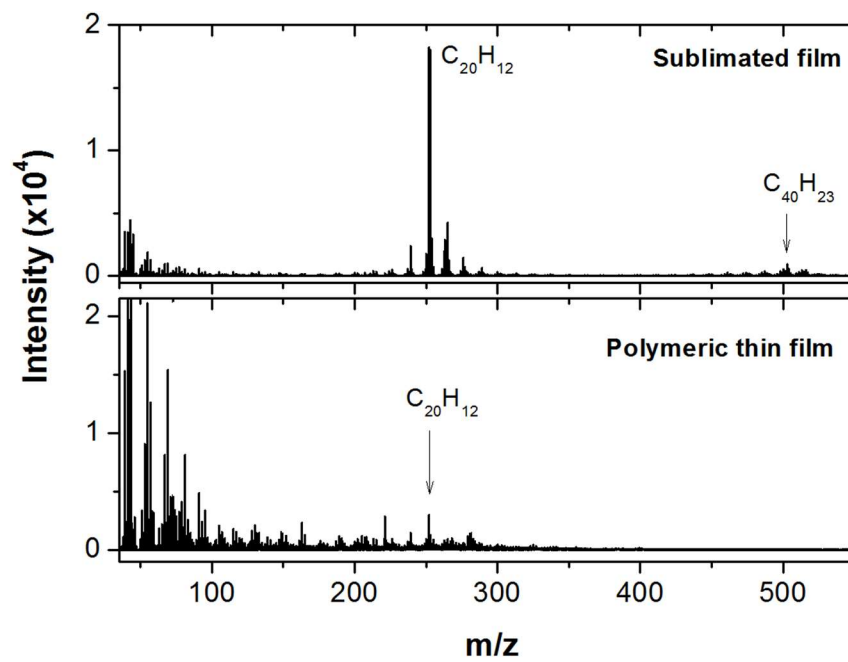


Fig. 6

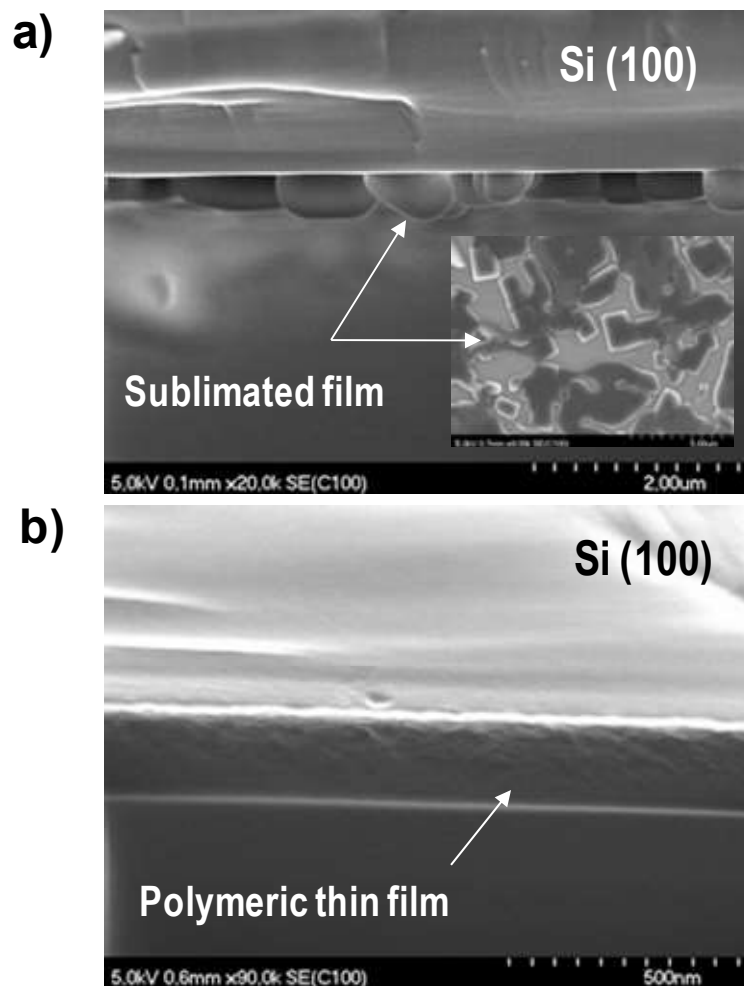


Fig. 7

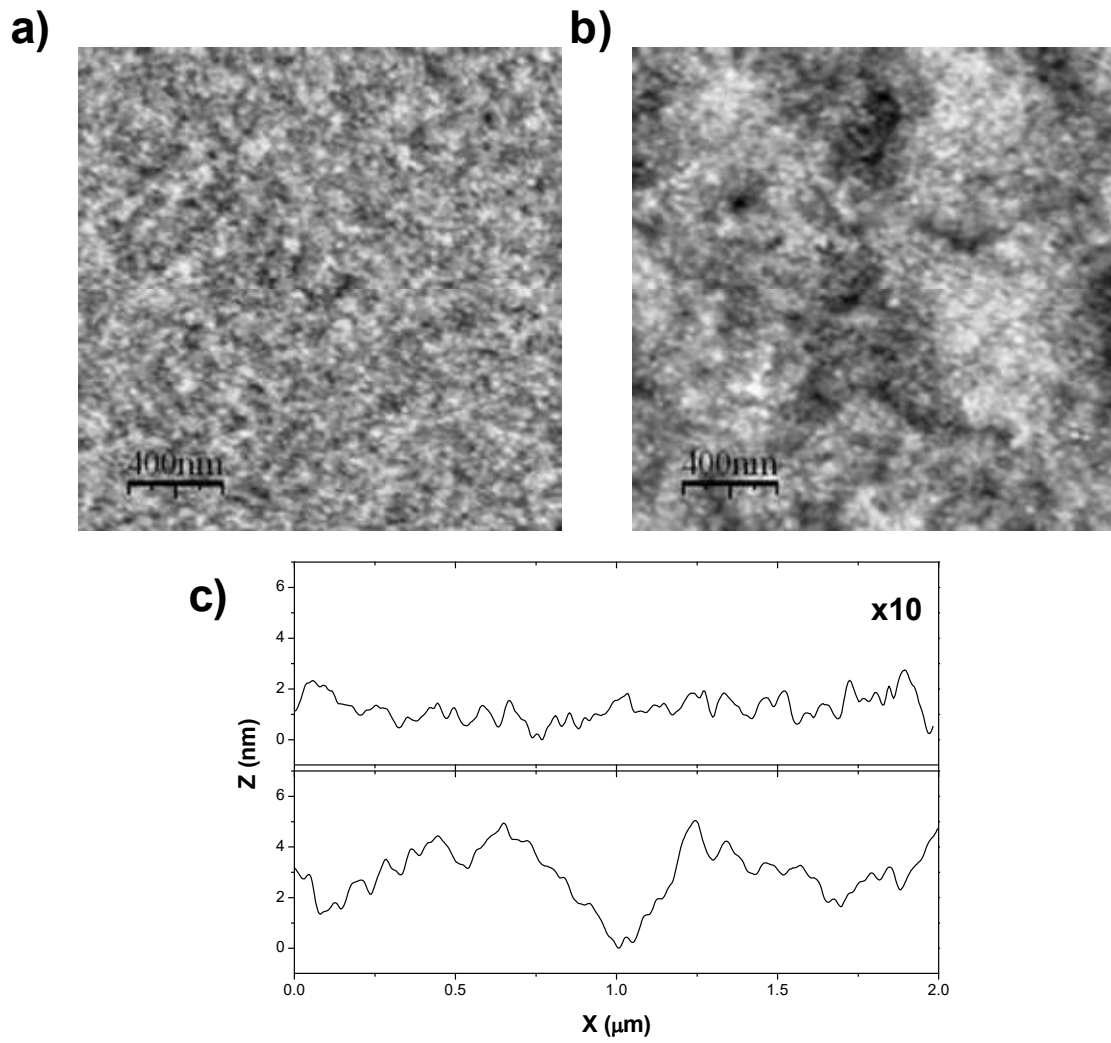


Fig. 8

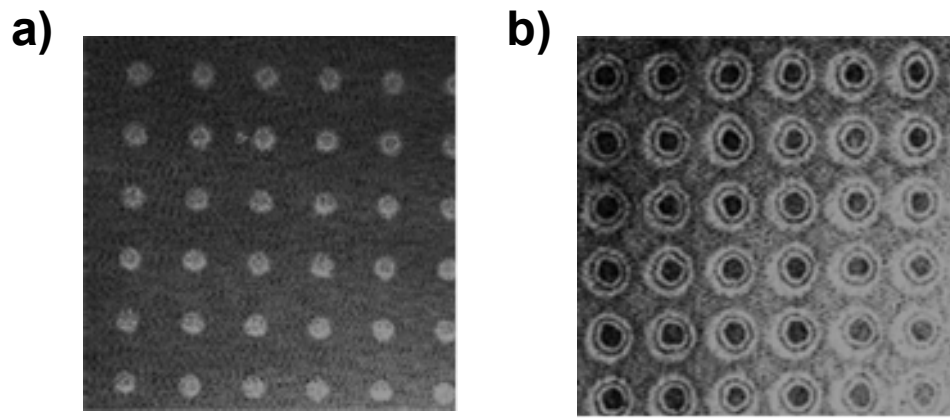


Fig. 9

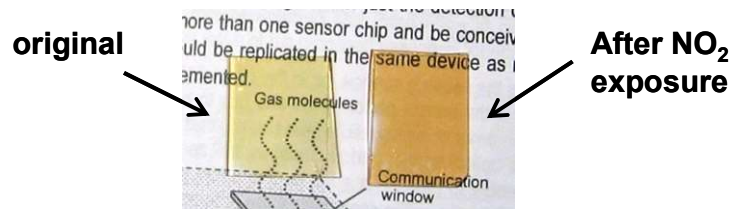
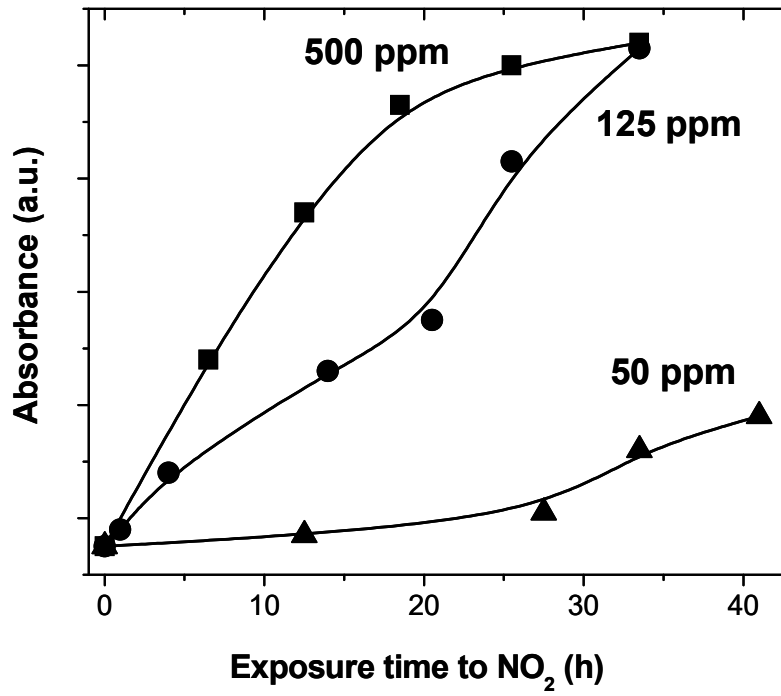


Fig. 10

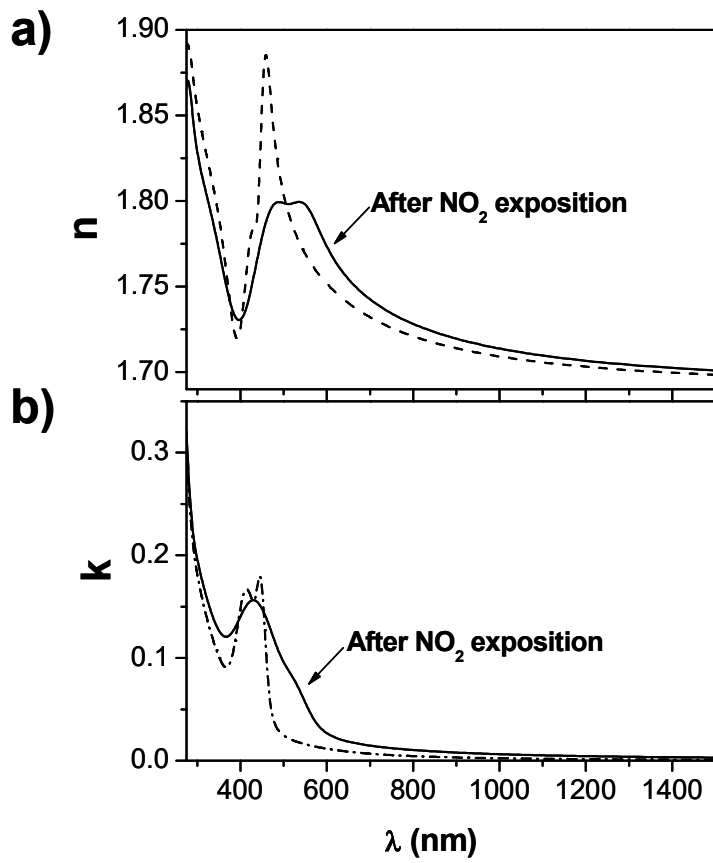


Fig. 11

