

Optically Active Thin Films Deposited by Plasma Polymerization of Dye Molecules

Angel Barranco^{1,2}, Francisco Aparicio¹, Angel Yanguas-Gil¹, Pierangelo Groening⁴, José Cotrino^{1,3}, Agustín R. González-Elipe¹*

1. Instituto de Ciencia de Materiales de Sevilla (CSIC-Universidad de Sevilla). Avda. Américo Vespucio 49. 41092 Sevilla, Spain.

2. Dept. Química Inorgánica. Universidad de Sevilla.

3. Dept. Física Atómica. Molecular y Nuclear. Universidad de Sevilla.

4. EMPA Materials Science and Technology Feuerwerkerstrasse 39 CH-3602 Thun, Switzerland.

*Corresponding author e-mail: angelbar@icmse.csic.es

Key words: dyes, plasma polymerization, coloured thin films, Rhodamine 6G, Ethyl red

Abstract

Coloured and fluorescent thin films are prepared by polymerization of dye molecules by interaction with a remote plasma of Ar while they are sublimated on a substrate. The films are formed by a cross-linked matrix of fragments of the original dye and some unreacted molecules. Films made of Ethyl red or Rhodamine 6G dyes have been characterized and studied with regard to their optical properties. Plasma characterization by Optical Emission Spectroscopy (OES) has evidenced the fragmentation of the evaporated dye molecules by interaction of the dye molecules with the electrons of the plasma. The electron energy seems to be the main parameter controlling the polymerization degree of the films.

Introduction

Plasma polymerization is a very well established technique widely used for the synthesis of a large variety of polymeric materials in the form of thin films. ^[1-3] In many cases, plasma polymerization is carried out under very mild conditions that only produce a controlled and partial breaking of the monomer molecules in the plasma. In this way the chemical functionalities of the original molecules can be preserved when they become incorporated in the films during the film growth. This approach is illustrated by numerous examples of polymers intended for many applications as conductive coatings, biological surfaces and others. ^[2-6]

Dye molecules embedded in different matrices in the form of thin films are the basis of specific materials used for laser cavities, optical filters, optical gas sensors, etc. ^[7-10] Usually, the synthesis of this type of thin films is intended by sol/gel and similar wet methods and the films use to have a thickness of several microns. These procedures present some inconvenients as, for example, the need of different steps for drying, annealing, etc. Other limitations come from the microstructure of the films (e.g., surface roughness), that may impose some restrictions when these materials have to be integrated in optical and photonic devices. Trying to circumvent these problems there have been some essays of preparation of dye thin films by sublimation techniques. However, the resulting films are formed by small crystalline aggregates whose size increases with time and that are easily removable from the substrates during they manipulation. ^[11] Another limitation of evaporation or sublimation procedures is that the actual concentration of dye molecules and their aggregation at an atomic scale cannot be controlled. This feature is critical if the absorption/fluorescence activity is the envisaged property for the final application of the films. ^[12-15]

In the present paper we discuss a new methodology based on the plasma polymerization of dye molecules that circumvent the above mentioned problems. It permits a tailored synthesis of optically active thin films containing dye molecules which are active as absorbent or fluorescence emitters (i.e., coloured and fluorescent films). The principle of this new procedure is the partial polymerization of dye molecules that are evaporated over a substrate while exposed to an Ar plasma. As a result of this process a polymeric thin film is produced where some dye molecules keep intact their optical activity (although eventually, their optical response can be slightly modified by matrix effects. ^[15-17] By comparison with conventional thin films containing dyes prepared by

sol/gel and similar procedures, this new type of dye thin films are much thinner (for example some tenths of nms are enough to get similar extinction coefficients that several micron films prepared by wet routes), are very flat and permit a very easy control of the matrix effects that influence the optical response of the dye molecules. To our knowledge, this is the first time that such a type of polymerization process rendering optically active films has been successfully achieved.

To illustrate the possibilities of the technique we present here results for two different dye molecules, the Ethyl red, a neutral azoic dye used as pH sensor, and the Rhodamine 6G, a xanthene derivative cationic dye which is typically used as gain media in tuneable laser dyes.^[18,19] In this communication we focus on the description of the method and on the analysis of the polymerization process by comparing the thin films characteristics with the plasma properties analyzed by Optical Emission Spectroscopy (OES) under the deposition conditions. A more complete analysis of the optical properties of the Rhodamine 6G films can be found in previous publications.^[15, 16]

Results

OES investigation of the plasma during thin film deposition

When no dye is being evaporated, the OES spectra of the plasma of Ar are quite similar to those of this type of plasma discharges produced in similar experimental set-ups.^[20,21] Basically, they consist of a series of emission lines involving the 4s-4p and 4s-5p excited states of Ar. The spectrum is significantly modified when the dye molecules are being evaporated over the substrate. Figs. 1 and 2 show typical spectra recorded under deposition conditions for the two dyes studied in this work. In these spectra a series of new bands appear superimposed on the lines involving Ar de-excitation processes (indicated in the top panel of Fig. 1) that have significantly decreased in intensity if compared with the plasma of pure Ar. These new bands include the C₂ swan bands and the C₂ Deslanders-d'Azambuja bands, lines due to other radicals such as CH (the 3900 Å band and the 4300 Å band), CO (the third positive and 5B bands) and CN (Violet system). Strong emission lines of H_α and H_β are also recorded in this case.^[22] The observation of these species was a common feature for the two dye molecules investigated here although, as illustrated in Fig. 1, their intensity was relatively higher for the Rhodamine 6G. This difference may either indicate an easier fragmentation of this molecule and/or the fact that the films of Rhodamine 6G are prepared by placing

the substrate and evaporation sources closer to the plasma zone (see experimental section).

The appearance of these new lines and the partial quenching of the peaks due to Ar* species clearly indicates that, in both cases, the Ar plasma is effectively interacting with the evaporated dye molecules and that the observed carbon and hydrogen species are formed by fragmentation of the evaporated molecules. Other interesting observations by this OES characterization of the plasma are that the intensity of the carbon species was not significantly affected by the microwave power within a range comprised between 100 and 200 W, although it was very sensitive to the pressure of the plasma gas. Fig. 2 illustrates this behaviour for the Rhodamine 6G and shows how the intensity of the different bands due to the C₂, CO, CH and CN decreases by approximately one half when the pressure increases from 10⁻³ to 10⁻² Torr. According to the known behaviour of the plasma discharges in a similar chamber (Nowak JVSTA-1992, see experimental section), these results seem to indicate that changes in electron temperature and/or in ion flux are the main plasma parameters affecting the formation of these excited species in the utilized ECR plasma set-up.

Optical properties of the thin films

As a result of the interaction of the plasma species with the evaporated dye molecules, different types of thin films, characterized by a different capacity of light absorption, can be deposited. An efficient control of the extinction coefficient can be achieved by adjusting the distance between the substrate and the plasma zone. At this point it must be mentioned that another parameter that provides a certain control over the degree of polymerization of the films was the power of the plasma. However, we preferred to change the distance as a working parameter because it rendered more reproducible results. Fig. 3 shows as an example a series of photographs and UV-vis spectra of polymerized thin films of Ethyl red, all of them with ~100 nm thickness. The different samples were obtained by changing systematically the distance *z* between the substrate and the plasma region. For shorter distances most of the evaporated dye molecules are affected by the plasma species. The result is a yellowish polymeric layer where no absorption bands associated to the dye molecules can be distinguished in the spectrum (spectrum e in Fig. 3). On the contrary, separating the substrate from the plasma region leads to coloured thin films where the intensity of the absorption band increases with separation (spectra b-d) Finally, for very long distances, conventional evaporated films

are obtained (spectrum a). Contrary to the polymerized films, these evaporated films, formed by discrete crystallites of the Ethyl red molecules, were not mechanically stable and could be easily removed by a gentle brushing with the hand or dissolved by immersion in water. Fig 3 also shows a similar set of results for the plasma polymerization of Rhodamine 6G where, similarly, a transition from a non-coloured and cross-linked plasma polymer to non-modified sublimated films can be observed in the UV-Vis spectra as a result of the change in the distance z between the substrate and the plasma zone (spectra from B to E in Fig. 3).

The polymerized Rhodamine 6G films were fluorescent and yielded a very interesting fluorescent pattern as previously reported for this type of thin films.^[16] On the other hand, the polymerized films of Ethyl red presented, among other properties, an increase in the red colour intensity when exposed to vapours of a hydrogen chloride solution. This is the typical behaviour of this dye commonly used as a pH sensor. Keeping the absorption, fluorescent and sensor properties of the dyes when they are in the polymerized films confirms that a certain number of integer dye molecules are preserved in the films during their deposition by polymerization.

Compositional and structural characterization of the films

The polymeric character of the films could be proved by FT-IR analysis. Assignments of the bands in the FT-IR spectra have been taken from the bibliography.^[23-26] Fig. 4 shows as an example, the FT-IR spectrum of a polymerized film of Rhodamine 6G prepared under conditions similar to those used in Fig. 3 to prepare sample C. In this case the films were much thicker to have enough sensitivity to detect their FT-IR spectrum. For comparison the spectrum of an evaporated layer of this dye is also included in the figure. The evaporated film shows bands in the following regions/positions: 400-570 cm^{-1} assigned to torsional ring bending, low intense features at 615-670 cm^{-1} assigned to C-C-C in plane bending, 1215 cm^{-1} to C-O-C stretching, 1115 cm^{-1} to C-H aromatic in plane bending, 1140, 1165, 1208 cm^{-1} to C-H in plane bending and C-C stretching, 1315, 1365, 1444 cm^{-1} associated to aromatic C-C and C-N stretching, 1490, 1550 and 1630 cm^{-1} assigned to aromatic C-C stretching, 1730 cm^{-1} attributed to C=O stretching vibration in the carbonyl phenyl group, a low intense band at $\sim 2950 \text{ cm}^{-1}$ that can be attributed to C-H stretching vibrations and two weak bands at 3200 and 3390 to N-H vibrations. The spectrum of the plasma polymerized film in Fig. 4 shows several wide bands at 1170-1350 cm^{-1} , 1360-1505 cm^{-1} and 1520-1820 cm^{-1} .

The latter is the more intense and includes the vibration bands of aromatic C-C and C=O stretching modes. The broadening of the IR bands is a typical effect in plasma polymers.^[1,3] In this case, the FT-IR spectrum features can be interpreted as the result of the cross-linking of the Rh6G molecules during the plasma deposition (i.e., extensive fragmentation of the dye molecule in the layer) and the complete or partial hindering of vibrational modes of the dye molecules confined in a cross-linked polymeric matrix. A similar effect has been observed in dye-doped silica xerogels.^[24] The plasma polymer spectrum shows an additional wide and intense band at $\sim 3350\text{ cm}^{-1}$ due to O-H vibrations, what is congruent with the XPS results discussed in the next paragraph.

Information about the composition of the dye thin films can be obtained by XPS. Determination of surface composition by this method renders the results summarized in Table 1 where atomic percentages for the evaporated and optically active polymerized films are compared with the nominal composition deduced from the formulas of the two dyes. In a first approximation, the atomic percentages are close to those derived from the composition of the molecules, thus indicating that by either the sublimation or the polymerization procedures the original atomic percentages are relatively well reproduced in the films. However, a finer analysis of the data reveals that the Ethyl red films are slightly depleted in N, particularly for the evaporated films. This probably indicates that some Ethyl red molecules decompose during evaporation and loss nitrogen as N_2 (see the azo $-\text{N}=\text{N}-$ bond structure in the formula of this molecule in Fig. 1). Less nitrogen is lost during polymerization, probably because under these conditions plasma species of nitrogen are able to become incorporated in the film. Most significant difference between the two types of films refers to their oxygen content. Thus, while for the Ethyl red the percentage of this element is close in all cases to the formula value, for the Rhodamine 6G films it is significantly higher than that predicted by the nominal composition. In addition, for the polymerized Rhodamine 6G the concentration of oxygen reaches a maximum. The oxygen enrichment is a well-known phenomenon in plasma polymerized organic materials. The origin of this oxygen can be post-deposition reactions of the samples exposed to the air and/or direct incorporation of oxygen from the reactor during the deposition process.^[1,3] Since the two types of thin films have been prepared according similar polymerization protocols, we believe that the extra incorporation of oxygen in the polymerized Rhodamine 6G occurs during its deposition and is likely related with the fact that these films are prepared with the substrate in a position z close to the plasma zone. Formation of C(O) species in the polymerized

Rhodamine 6G is confirmed by its C1s spectrum reported in Fig. 5. This spectrum is characterized by an intense peak at around 285 eV due to C-C and C-H bonds. It also presented a marked asymmetry at ~ 286.6 eV that extends up to ~ 288.8 eV where a defined shoulder appears. This shape of spectra is typical of the presence of -C-OH (in agreement with the FT-IR spectrum of this sample in Fig. 4), -C=O and -COO⁻ bond structures in the film.^[27] As expected from the atomic percentages in Table 1, the relative intensity of that shoulder is significantly smaller for the evaporated film. Meanwhile, the C1s spectra of the polymerized Ethyl red is more symmetric and its shoulder at around 288.8 eV is also small, thus confirming the relatively small oxygen content in this sample. The relative high intensity of the shoulder at ~ 288.8 eV in the evaporated film of Ethyl red indicates that the concentration of -COO⁻ groups is rather abundant in this case (note that in the structure of this molecule there is a -COOH group, see Fig. 1).

Table 1.- *Atomic percentages of evaporated and polymerized films of the two dyes molecules studied in this work compared with the percentages derived from their formula.*

	%C	%O	%N
Ethyl red (poly.)	77.2	11	11.8
Ethyl red (evap.)	77	14.9	7.7
Ethyl red (formula)	75	10	15
Rhodamine 6G (poly.)	68	26	6
Rhodamine 6G (evap.)	79	15	6
Rhodamine 6G (formula)	85	9	6

From the point of view of the use of these thin films for photonic applications, a critical issue is that they present a very low roughness, an important feature to avoid the scattering of light. AFM analysis of the surface roughness of these films showed that they were very flat with a root mean square (RMS) surface roughness of ~ 0.4 nm for 90 nm thick layers (see a more complete set of results in ref 15). RMS values within this range are much smaller than those typically obtained for dye thin films prepared by wet

chemical routes where the thickness has to be much higher to get similar high extinction coefficients.^[23]

Etching behaviour of the polymerized dye thin films

Due to the polymeric character of our films, they can be easily etched by plasma attack, either directly or through masks. In this latter case the formation of lithographic patterns, of great importance for certain photonic applications, would be possible. Fig. 6 shows an image of the fluorescence emission obtained with a confocal fluorescence microscope for a polymer film of Rhodamine 6G that has been exposed through a mask to an oxygen plasma. The image clearly shows a well defined pattern resulting from the etching of the film in the zones directly exposed to the plasma. It is important to note that although degradation of the colour may also occur by exposure of the films to the UV light emitted by the plasma, in this case the fluorescence pattern corresponds to a selective etching of the films as proved by its posterior analysis with a profilometer.

Discussion

The dye thin films prepared here can be considered as formed by a polymeric structure of dye molecules fragments. This means that the dye molecules are equivalent to the monomer entities used by conventional plasma polymerization processes.^[1] The main singularity of these thin films is that a given number of chromophore centres formed by the dye molecules remain intact after polymerization. This confers the colour and the optical activity (i.e., fluorescence) to the films.

From the point of the manufacturing process, control of the optical activity of the films requires a very precise balance between the density of plasma species arriving to the surface of the growing films and the flux of evaporated molecules. For given plasma conditions (i.e., power, pressure of gas, etc.) a very simple way of achieving a precise control of this ratio is by moving the position of the substrate with respect to the plasma. It has been proved that this is the most efficient way of controlling experimentally the optical properties of the films. In this regard, it has been also observed that the sensitivity to the plasma of the different evaporated dye molecules is different. For the two molecules investigated here, it resulted that the Ethyl red was very sensitive to the plasma and that, therefore, it has to be deposited at longer distances z than for the Rhodamine 6G. This fact produces slight differences in the characteristics of the

polymer matrix as evidenced by the increase in the oxygen content in the polymerized films of this latter molecule.

During plasma deposition with Ar as plasma gas, C₂, CN and CH_x species have been detected in the plasma. C₂ species can be considered as an intermediate species of the formation and/or etching of carbon materials with plasmas of Ar*.^[28] Their detection, together with bands due to CN and CH_x species, indicates that the dye molecules coming from the Knudsen cell are effectively activated and part of them even fragmented by interaction with the plasma. In general, an increase of the pressure of the plasma gas produces a decrease in the kinetic energy of the plasma electrons. This was effectively proved by Nomak et al.^[20] in a previous characterization study of the plasma discharge in a reactor with a similar architecture than the one used here. These authors showed that while the concentration of electrons in the plasma was little affected by the pressure within the range considered here, their average energy (comprised between 1 and 3 eV for an Ar plasma) decreased with this parameter. Therefore, the observation that the intensity of the emission lines of these carbon species decreases with the operating pressure (cf. Fig. 2) suggests that the kinetic energy of the plasma electrons is critical for the activation/fragmentation degree of the dye molecules during deposition.

The key point of our procedure is that, even if the majority of the dye molecules become polymerized, some of them remain embedded within the polymeric structure without undergoing any significant modification of their structure and, therefore, optical properties. The UV-vis absorption spectra reported for both the Ethyl red and the Rhodamine 6G molecules clearly show that it is possible to prepare thin films with a gradation of the extinction coefficient by just separating the substrate from the plasma zone. Besides the possibility of controlling such a gradation in colour, another important characteristic of our method is the fact that ultrathin thin films (around 100 nm for the thin films whose spectra are reported in Fig. 3) yield very high extinction coefficients. The high planarity of our films and the fact that they can be very thin are ideal properties for their integration together with photonic structures to develop new families of photonic devices (e.g., sensors, wavelength couplers, photonic structures, etc.). In this regard, the possibility of fabricating lithographic patterns with our films (cf. Fig. 6) is another advantage for their practical integration into photonic components.^[7, 12, 15]

A final remark concerning the fabrication procedure is that it would permit the integration of the dye thin film within a stacking structure formed by different layers of other materials (e.g. dielectric layers of silicon or other oxides, silicone-like films,

conducting polymers, etc.) and/or dye thin films of other compositions. We believe that this new fabrication method based on plasmas may open quite interesting possibilities for the use of plasma techniques for the manufacturing of photonic materials and devices.

Experimental

A scheme of the experimental set-up used for deposition is shown in Fig. 7. It consists of a chamber with two zones, a plasma and a deposition zone. In the plasma zone a discharge is sustained under ECR conditions thanks to a set of magnets surrounding the chamber. The microwave was applied to the plasma chamber through a flat Pyrex window. In the deposition zone there is a substrate in a remote configuration with respect to the plasma zone and two dye evaporators (home-made Knudsen cells) to sublimate the Rhodamine 6G and Ethyl Red (Aldrich). The distance between the sample-holder and the plasma zone, a critical parameter for the control of the process, have been measured as indicated in the figure (z value). The pressure of the system was controlled by an automatically regulated pressure controller connected to a capacitance pressure gauge (Baratron). Ar was dosed to the plasma chamber using a calibrated mass flow controller (MKS). All the experiments have been carried out by using Ar as plasma gas. The microwave power was 200 W and the (Ar) pressure during the discharge 10^{-2} and 10^{-3} mbar. The reflected power measured was less than 10 W. It was minimized by achieving a good coupling between the rectangular and the circular waveguides.

This ECR system was characterized previously by two diagnostics methods: A Langmuir probe and an electrostatic energy analyzer.^[20] Measurements of the electron density as a function of pressure showed a maximum of the electron density at approximately 7×10^{-3} Torr. The ion flux, measured as a function of the working pressure in the centre of the chamber, was higher at low pressures, decreasing rapidly as the pressure or the distance z between plasma zone and substrate increases. These measurements also evidenced that the Ion Energy Distribution Function (IEDF) shifts to lower energies for higher pressures.^[20]

Plasma polymerization occurs while the dye is being sublimated. The deposition process was controlled by a quartz crystal monitor placed besides the substrate in the deposition zone. Typical growing rates between ~ 2 -5 nm/min were achieved by controlling the heating of the Knudsen cells. These relatively low growth rates were selected to efficiently control the deposition of ultrathin films of ~ 50 -100 nm. The

substrate and the evaporators move together to keep constant the amount of the evaporated molecules arriving to the substrate.

OES spectra were collected under deposition and non deposition conditions by using an optical fibre to collect the spectra from the plasma zone of the chamber with a CVI Digikrön monochromator (DK480, 1/2 meter computer-controlled) and a Hamamatsu photomultiplier in the range 200-900 nm.

One side polished Si (100) wafers, quartz and glass slides were used as substrates in the deposition chamber depending on the characterization method to be applied.

The XPS spectra were recorded on an ESCALAB 210 spectrometer that was operated at a constant pass energy of 20 eV. Non-monochromatized MgK α radiation was used as excitation source. Atomic ratios and surface concentrations were quantitatively determined from the area of the C1s, N1s and O1s peaks. A Shirley-type background was subtracted and the peak areas were corrected by the electron escape depth, spectrometer transmissions and photoelectron cross-sections.^[29]

Fourier transform infrared (FT-IR) spectra were collected in transmission at normal geometry in a Bonem MB Series spectrometer for samples deposited on Si(100) wafers.

UV-vis spectra were recorded in a Perkin-Elmer λ 12 spectrophotometer for samples deposited in glass slides.

Florescence microscopy images of the etched thin films have been obtained with a Leyca TCS SP2 confocal fluorescence microscope.

The thickness of the films has been measured with a KLA-Tencor HRP 75 profilometer.

Acknowledgments

We thank EMPA and MECD (Nanolambda project Ref. NAN2004-09317-C04-01 and Ramon y Cajal program, Ref. 2004/00001198) for financial support.

References

- [1] H. Yasuda, *Plasma Polymerization*, Academic Press, **1985**.
- [2] A. Grill, *Cold Plasma in Materials Fabrication*, IEE PRESS, **1994**.
- [3] R. d'Agostino, P. Favia, F. Fracassi, Eds. *Plasma Processing of Polymers*, Kluwer Academic, **1996**.
- [4] P. Gröning, *Cold Plasma Processes in Surface Science and Technology*, in Nalwa, H.S., Ed. *Handbook of Thin Film Materials*, Academic Press **2001**, *1*, 219.
- [5] F.S. Denes, S. Manolache, *Prog. Polym. Sci.* **2004**, *29*, 815.
- [6] L.M.H. Groenewoud, G.H.M. Engbers, J. Feijen, *Langmuir* **2003**, *19*, 1368.
- [7] P. Yang, G. Wirnsberger, H.C. Huannng, S.R. Cordero, M.D. McGehee, B. Scott, T. Deng, G.M. Whitesides, G.F. Cmelka, S.K. Buratto, G.D. Stucky, *Science* **2000**, *287*, 465.
- [8] J. Loerke, F. Marlow, *Adv. Mater.* **2004**, *14*, 1745.
- [9] G. Wirnsberger, P. Yang, B.J. Scott, B.F. Chmelka, G.D. Stucky, *Spectrochimica Acta A* **2001**, *57*, 2049.
- [10] M.C. Burt, B.C. Dave, *Sensors and Actuators B* **2005**, *107*, 552.
- [11] O. Hertz, H. Böttcher, U. Fischer, H. Fichtner, *Thin Solid Films* **1991**, *199*, 153.
- [12] R. Vogel, P. Meredith, M.D. Harvey, H. Rubinsztein-Dunlop, *Spectrochimica Acta Part A* **2004**, *60*, 245.
- [13] R. Vogel, P. Meredith, I. Kartini, M. Harvey, J.D. Riches, A. Bishop, N. Heckenberg, M. Trau, H. Ruinsztein-Dunlop, *ChemPhysChem* **2003**, *4*, 595.
- [14] F. Del Monte, J.D. Mackenzie, D. Levy, *Langmuir* **2000**, *16*, 7377.
- [15] A. Barranco, P. Groening, *Langmuir* **2006**, *22*, 6719.
- [16] A. Barranco, M. Biemann, R. Widmer, P. Groening, *Adv. Eng. Mater* **2005**, *7*, 396.
- [17] I.M. Kalogeras, E.R. Neagu, A. Vassilikou-Dova, *Macromolecules* **2004**, *37*, 1042.
- [18] B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley, **2001**.
- [19] F.P. Schäfer, Ed. *Topics in Applied Physics, vol. 1, Dye Lasers*, Springer-Verlag, New York **1973**.
- [20] S. Nowak, P. Gröning, O.M. Kuttel, M. Collaud, G. Dietler, *J. Vac. Sci. Technol. A* **1992**, *10*, 3419.

- [21] A. Yanguas-Gil, A. Barranco, J. Cotrino, P. Groening, A.R. González-Elipe, *Chem. Vap. Depos.* Submitted.
- [22] R.W.B. Pearse, A.G. Gaydon, *The Identification of Molecular Spectra*, 4 th ed., Wiley, New York **1976**.
- [23] T. Oishi, *J. Non-Cryst. Solids* **2003**, 332, 80.
- [24] A. Parvathy Rao, A. Venkateswara Rao, *Science and Technology of Advanced Materials* **2003**, 4, 121.
- [25] H. Günzler, H.U. Gremlich, *IR Spectroscopy*, Wiley-VCH, **2002**.
- [26] L. Wang, A. Roitberg, C. Meuse, A.K. Gaigalas, *Spectrochimica Acta A* **2001**, 57, 1781.
- [27] G. Beamson, D. Briggs, *High Resolution XPS of Organic Polymers*, John Wiley&Sons, **1992**.
- [28] J. L. Hueso, A.R. González-Elipe, J. Cotrino, A. Caballero, *J. Phys. Chem. A* **2005**, 109, 4930.
- [29] J. Yeh, I. Lindau. *At. Data Nucl. Data Tables* **1985**, 32, 1.

Figure captions

Fig.1.- Broad scan OES spectra recorded during plasma polymerization of the Rhodamine 6G (top) and the Ethyl red (bottom) thin films. The formula of the two dye molecules is included in the figure. The region where the lines due to the Ar plasma appear are indicated in the top panel of the figure.

Fig. 2.- OES spectra recorded during the plasma polymerization of the Rhodamine 6G films recorded at two different total pressures. The spectra are presented in an enlarged scale to clearly show the formation of different excited species coming from the partial fragmentation of the dye molecules.

Fig. 3.-UV-vis. absorption spectra of polymerized thin films (~100 nm thickness) of ethyl red (top) and Rhodamine 6G (bottom) as a function of the running parameter z (distance from the substrate to the discharge zone). The spectra of evaporated thin films are included for comparison. Photographs of the films deposited on glass are included for illustration.

Fig. 4.-FT-IR spectra of the Rhodamine thin films prepared by evaporation and by plasma polymerization. This latter is prepared under conditions similar to those of sample C) in Fig. 3.

Fig. 5.- C1s photoemission spectra of evaporated and polymerized thin films of Ethyl red (top) and Rhodamine 6G (bottom).

Fig. 6.- Fluorescence image recorded with a confocal fluorescence microscope for a Rhodamine thin film subjected to etching through a mask with a plasma of oxygen. The width of the patterns is 50 μm .

Fig. 7.- Scheme of the experimental set-up used for the deposition of dye thin films by plasma polymerization

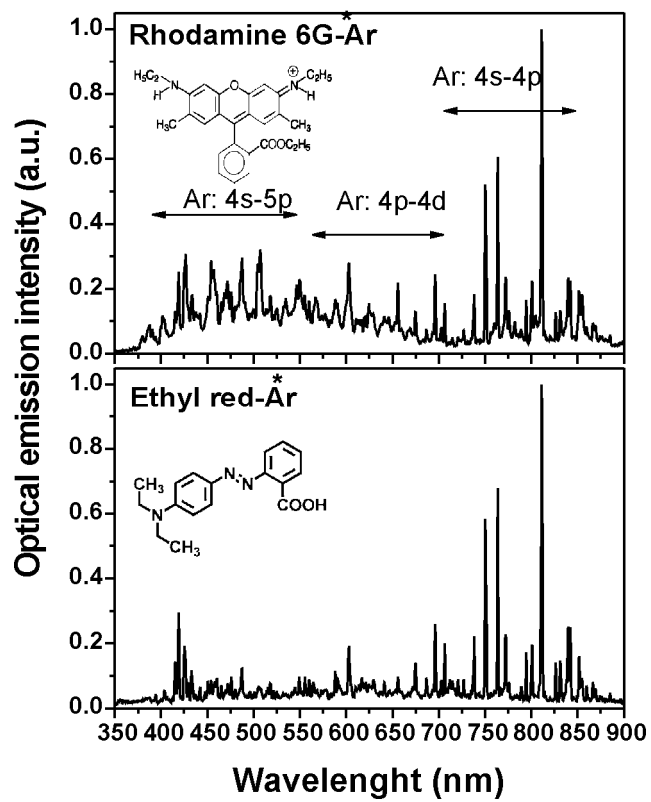


Fig. 1

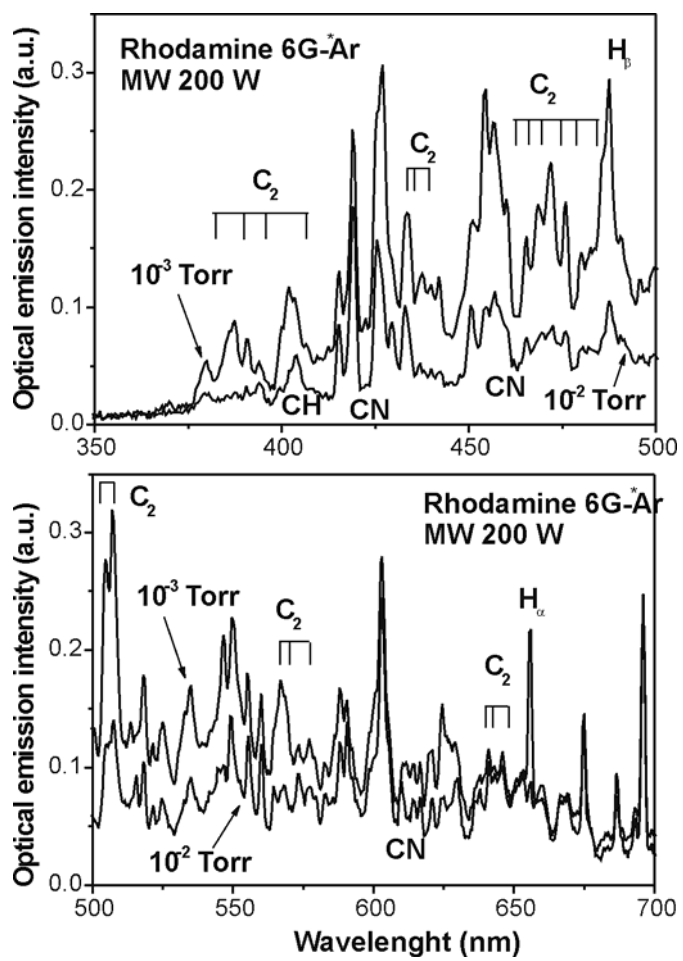


Fig. 2

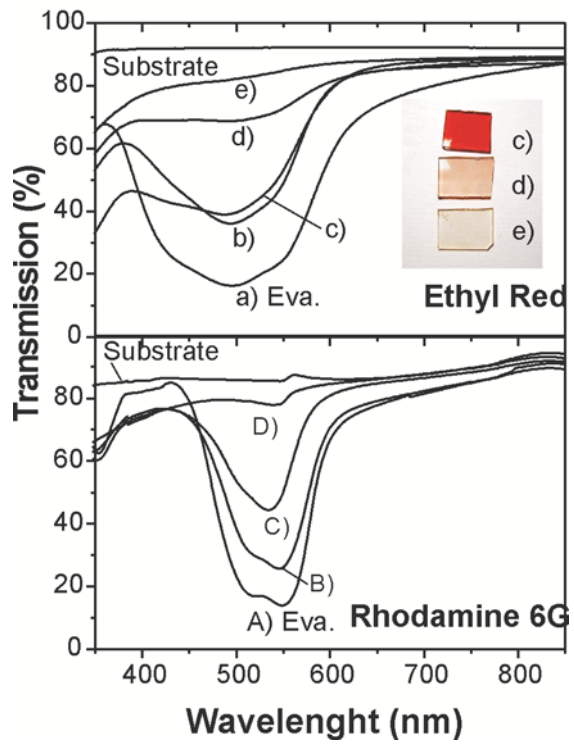


Fig. 3

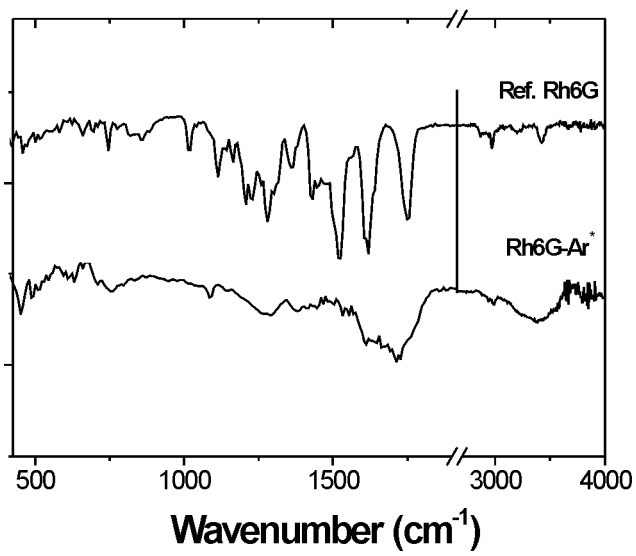


Fig. 4

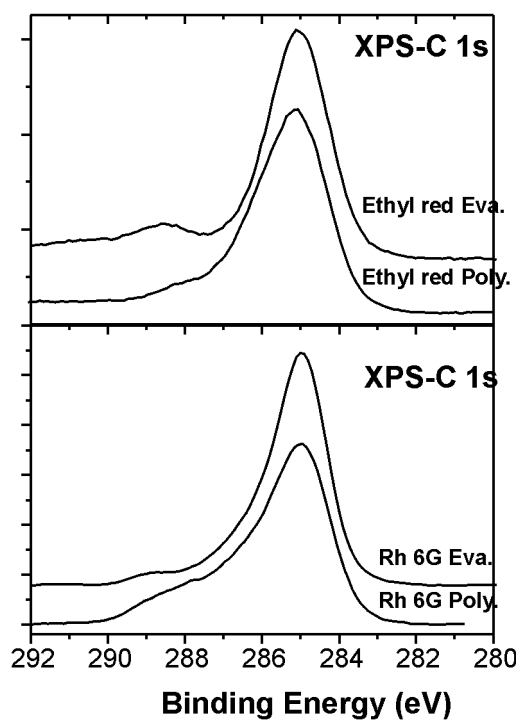


Fig. 5

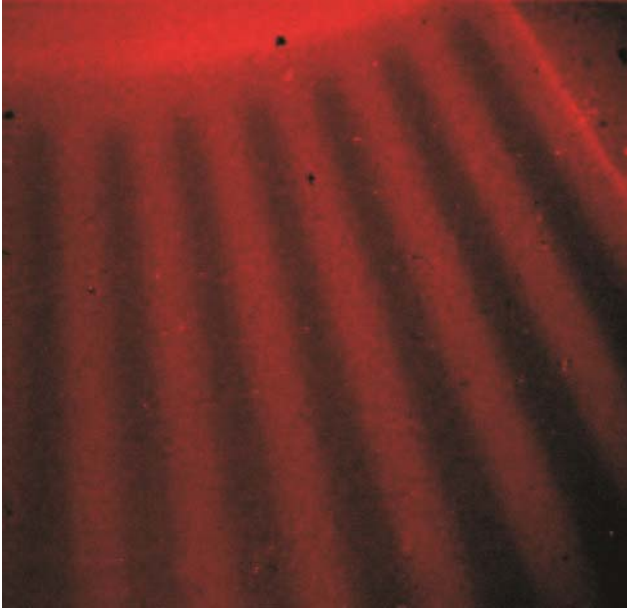


Fig. 6

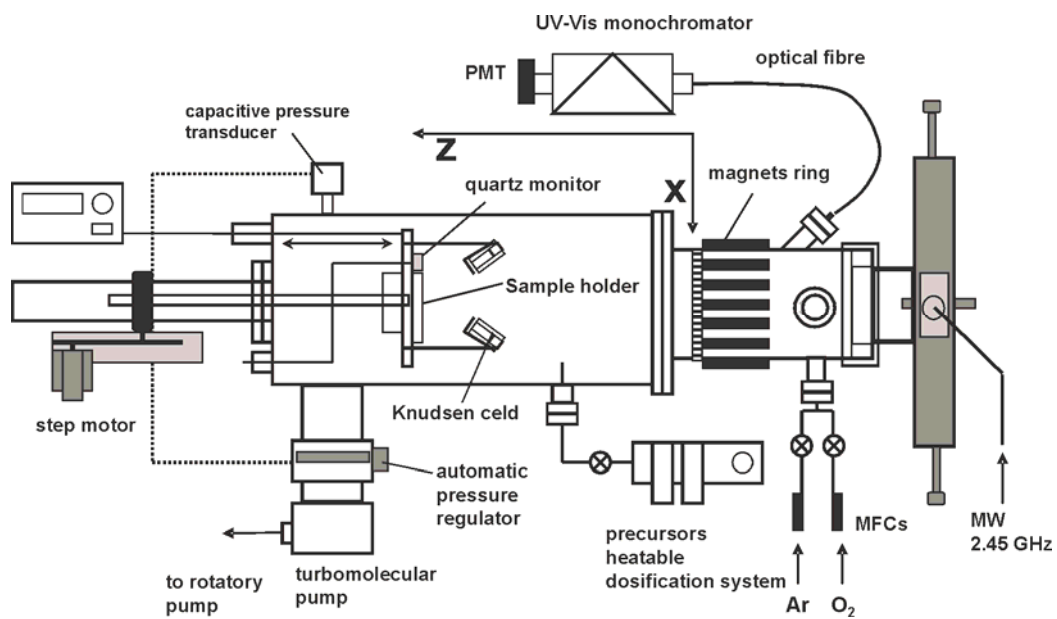


Fig. 7