Deposition of Thin Dye Coatings by Glow Discharge Induced Sublimation

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A novel method for the vacuum deposition of thin fluorescent dye coatings by means of glow discharge induced sublimation (GDS) is disclosed. Powdered organic compound is put on a radio frequency plasma sputtering source and bombarded by low energy (<1 keV) noble gas ions and electrons. Ion bombardment gives rise to a local heating which induces sublimation of the dye molecules. The method has been successfully used for deposition of 3-hydroxyflavone (3-HF) coatings on silicon substrates. Plasma diagnostics, as performed by means of mass spectrometry and in situ optical emission spectroscopy, point out both the sublimation of integer 3-HF molecules and the presence of 3-HF molecular fragments in the glow discharge. The integer 3-HF molecules are positively ionized or protonated before reaching the substrate. Rutherford backscattering spectrometry and elastic recoil detection analysis confirm that the deposited film is stoichiometric within the experimental errors. FT-IR analysis points out all the main characteristic peaks reported in the literature for pure 3-HF. Fluorescence analysis shows that the spectroscopic properties of 3-HF are preserved after the deposition process, despite the gas-phase ionization and protonation of the molecules. In particular, the emission features are typical of molecules embedded in an apolar and aprotic environment.

1. Introduction

Fluorescent dye molecules containing thin films are widely used in the production of waveguide laser cavities,[1] optical gas sensors,[2] radiation detectors,[3] electroluminescent devices,[4] and optical memory storage systems.[5] One of the most interesting fluorescent organic compounds is 3-hydroxyflavone (3-HF) which has been widely used as a wavelength shifter in many application fields because of its large Stokes shift ($\Delta\lambda \sim$180 nm).[6−9] In plastic scintillators 3-HF has been encapsulated in a polymer-based matrix in order to achieve a better match with the optimum response wavelength of most photomultiplier tubes.[10−12] The large Stokes shift of the 3-HF molecule enhances light yield by decreasing reabsorption by the chromophore and by radiation-induced color centers, which mainly absorb in the near UV range. In biological applications 3-hydroxyflavone has been used for probing its microenvironments in model membrane systems.[13]

The large Stokes shift of the 3-HF molecule is due to the formation of the excited-state tautomeric form (T* in Figure 1) by means of an intramolecular excited-state proton transfer (ESIPT).[14] The emission band of the 3-HF tautomer has been reported to be in the range 500 to 575 nm, whereas the normal emission band of excited 3-HF (N* in Figure 1) is found between 375 and 475 nm.[15]

The ESIPT process in the 3-HF molecule in liquid media has been extensively studied.[11,16] The tautomeric

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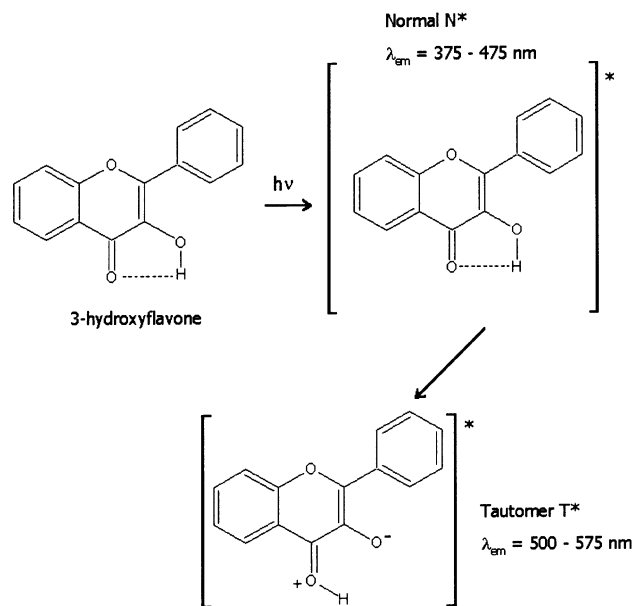(11) Brucker, G. A.; Swinney, T. C.; Kelley, D. F. *J. Phys. Chem.* **1991,** *95,* 3190.
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Figure 1. ESIPT mechanism in the 3-HF molecule.

equilibrium between 3-HF excited structures N* and T* is strongly affected by the protic nature and polarity of the surrounding medium, with structure N* being most favored in protic/polar environments. [9] In particular, the peak intensity ratio (I_T/I_N) between the T* and N* fluorescence bands depends on solvent effects and related environmental parameters: I_T/I_N is about 5 in highly polar solvents such as methanol, whereas only the T* band appears in nonpolar solvents such as *n*-heptane.[9] In protic/polar environments the intramolecular proton transfer, which enables the formation of the tautomeric form, can be inhibited owing to the formation of intermolecular hydrogen bonding.

In the synthesis of wavelength-shifting systems 3-HF is embedded in solid matrixes. During this process the use of highly polar/protic materials and/or solvents is often mandatory, thus possibly compromising the formation of the excited tautomer.

Recently a solvent-free deposition technique, based on plasma-discharge-induced sublimation, has been developed for the realization of thin organic coatings.[13] This method is based on the use of a weakly ionized glow discharge produced in standard radio frequency magnetron sputtering equipment. Low energy ($E < 1$ keV) noble gas (He, Ar, etc.) ions impinge on the solid organic precursors (e.g., pyromellitic dianhydride, PMDA, and 4,4′-oxydianiline, ODA, for the Kapton polyimide deposition), leading to the sublimation of the organic molecules and to their condensation onto the substrate. In the case of polyimide coating deposition, the as-deposited films mainly consist of a mixture of polyamic acid and nonreacted monomers, as revealed by Fourier transform infrared spectroscopy (FT-IR). Polymerization of the deposited coatings is completed only after a thermal treatment (typically 250 °C, 1 h, in air or argon). As compared to the well-known chemical syn-

thesis methods, the main advantage of this physical technique is the absence of any solvent.

In this work is investigated the deposition of 3-hydroxyflavone (3-HF) fluorescent thin coatings by this novel technique, named glow-discharge-induced sublimation (GDS). Sublimation of 3-HF molecules and their interactions with the plasma ions and electrons is studied by mass spectrometry and optical emission spectroscopy. As a matter of fact, the gas phase interaction of sublimated species with plasma ions and electrons plays a role as important for the final coating features as the ion−solid interaction on the target surface. Because the glow discharge is a very chemically reactive environment, both ionic and radical species can be easily produced. The gas-phase interactions can also interfere in the ionization/excitation processes characteristic of the glow discharge and in the related optical radiation emission.

The chemical structure of the deposited coatings is studied by FT-IR analysis. Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA) are used to determine the coating stoichiometry and to evaluate the 3-HF deposition rate. The luminescence properties of the deposited films are investigated by UV−Visible spectrofluorimetric measurements, to verify the presence of integer, neutral 3-HF molecules in the deposited coatings and to test the perturbation of the ESIPT mechanism as induced by the chemical surroundings of the dye molecule. As a matter of fact, the 3-HF peculiar spectroscopic properties make this dye particularly suitable for testing the presence of polar and protic environments into the coatings produced by means of the GDS.

2. Experimental Section

The experimental equipment used for the coatings deposition consisted of a stainless steel vacuum chamber evacuated by a turbomolecular pump to a base pressure of 10^{-5} Pa. The glow discharge sustaining device was a 1-in. cylindrical magnetron sputtering source connected to a rf power generator (600 W, 13.56 MHz) through a matching box. The 3-HF dye powder (99% purity, Sigma-Aldrich) was placed on the surface of an aluminum target positioned on the sputtering source. The amount of 3-HF powder was 0.5 g. The glow discharge feed gas was an argon 95% − O₂ 5% mixture. The oxygen gas was added to argon in order to promote removal of the carbon-rich surface layer of the organic compound powder due to the ion bombardment. As a matter of fact, oxygen-containing plasmas are widely used to strip hydrogenated carbon film by converting the C_xH_y-based species to volatile products which are pumped away.[14] As previously reported for pyromellitic dianhydride monomer, the carbon-rich surface layer can negatively affect the sublimation process.[15]

The pressure in the chamber was measured by means of a capacitive gauge. Working pressure was 5 Pa and target−substrate distance was 6 cm. The powder was ion-bombarded keeping the rf power as low as possible to minimize damage of the dye molecules. Typical values of rf power and target DC self-bias were in the ranges 10 to 30 W and −50 to −400 V, respectively.

A quadrupole mass spectrometer (Hiden Analytical, model PSM 001) was connected to the deposition chamber through an electrically grounded sampling orifice (100 μm diameter) and evacuated by a turbomolecular pump to a base pressure of 10^{-6} Pa. The sampled neutral and radical species (1−300 m/z range) from the plasma chamber were ionized by electrons emitted from a hot filament (70 eV electron energy) and detected by a secondary electron multiplier (SEM). When the

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hot filament was off, only the charged species could be collected. Two repeller electrodes could be biased in order to prevent plasma ions and electrons collection.

Light emission of plasma was collected by a quartz optical fiber connected to an optical emission spectrometer (Ocean Optics, S2000 series, 250−850 nm range, 1.3 nm resolution). The head of the optical fiber was put inside the chamber through a vacuum feedthrough and positioned parallel to the target surface at 2-cm height and at 4-cm distance from the target axis. To prevent contamination of the fiber head by the sputtered and sublimated species, a quartz window was put between the head and the plasma.

Infrared spectroscopy analysis was performed using a FT-IR Nicolet 5DCX spectrometer (4000 to 400 cm^{-1} range, 2 cm^{-1} resolution) on coatings deposited on double- sided polished 500-μm thick silicon wafers. A stylus profilometer (Tencor Instruments, model Alpha-Step 200) was used for measurement of the film thickness.

The film composition was determined by ion beam analysis (IBA) using a Van de Graaf accelerator at the Laboratori Nazionali di Legnaro. Carbon and oxygen concentration was determined by Rutherford backscattering spectrometry (RBS) using a 2.2 MeV ^{4}He$^+$ beam, at normal incidence and at the scattering angle of 160°. Hydrogen concentration was measured by elastic recoil detection analysis (ERDA) using a 2.2 MeV ^{4}He$^+$ beam at a recoil angle of 30° and at grazing incidence of 15°. Because the organic materials can be heavily damaged during the ion beam analysis and the desorption of volatile species from the sample surface leads to the invalidation of the experimental results, the integral area of C, O, and H peaks was measured as a function of the ion fluence. A low ion current density on the sample (about 1 μA/cm^2) was used in order to more accurately measure the ion fluence at the beginning of the spectrum collection. Ion beam analyses were performed on a 3-HF coating deposited on a graphite substrate. The graphite was chosen in order to obtain a well isolated oxygen peak. To separate the film carbon peak from the substrate carbon, a 120-nm-thick silicon interlayer was deposited on the graphite before the 3-HF coating deposition.

UV−Visible fluorescence analysis was performed with a Jasco FP-770 spectrofluorimeter, equipped with a 150-W Xe lamp. The samples were front face excited and the emission spectra were collected with a spectral bandwidth of 5 nm for both excitation and emission monochromators. The emission spectra were corrected by calculating the wavelength-dependent response function of the emission equipment (monochromator plus photomultiplier tube) from the spectrum of two calibrated deuterium and halogen lamps (Ocean Optics DHL-2000).

3. Results and Discussion

3.1 Characterization of the Deposition Process.
3.1.1. Mass Spectra. Mass spectra collected during GD-sublimation of 3-HF organic compound are reported in Figure 2. In (a) the repeller electrodes were kept at ground potential ($\Delta V_R = 0$ V) in order to collect all the neutral and ionized species; in (b) the repellers were biased ($\Delta V_R = 50$ V) so that the collection of positive ions was prevented; in (c) the repellers were at ground potential and the hot filament was kept off so that only charged species were detected.

All the characteristic fragmentation peaks of 3-HF molecule can be identified in Figure 2a: besides the molecular ion peak (m/z 238), the other features, due to fragmentation of the 3-HF molecule, appear at m/z 210, 181, 152, 105, 77, and 51. As compared to 3-HF mass spectra reported in the literature[16] the relative intensity of the molecular fragments peaks, with respect to the molecular ion one, is much higher (up to thirty times for the peak at m/z 51), pointing out that the
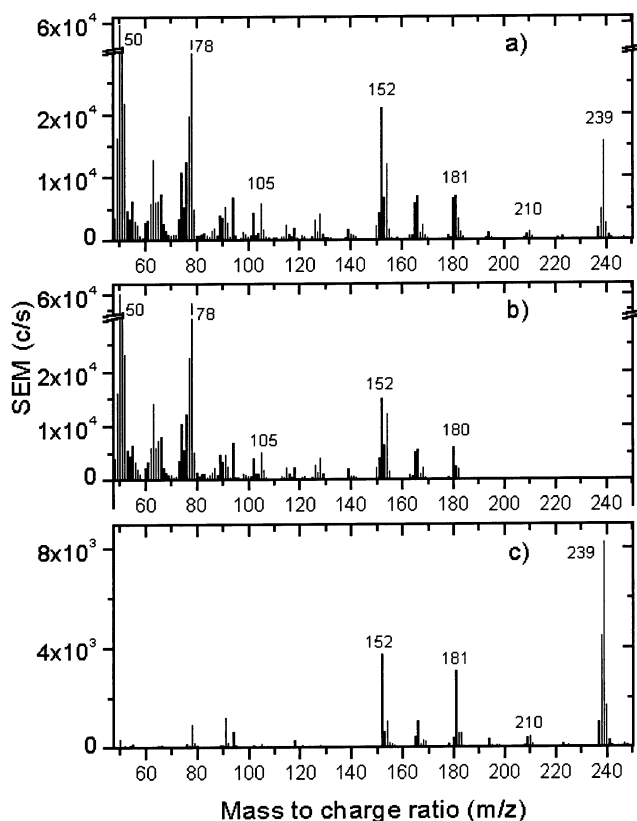
Figure 2. Mass spectra collected during GDS of 3-HF: (a) neutral and ionized species; (b) all the species except the positive ions; (c) only the ionized species (rf power = 20 W; target DC bias = −200 to −400 V; total pressure = 5.0 Pa). For each peak group the most intense one is labeled.

fragmentation of part of the 3-HF molecules occurs in the deposition chamber before entering the mass spectrometer. The molecular fragmentation is due to both the ion bombardment of the target and the gas-phase interactions of the sublimated 3-HF molecules with the plasma species.

In the low mass range (below m/z 50, not displayed) the intense peak at m/z 28 and the peak at m/z 44 (corresponding to CO and CO$_2$ species), which are absent in the 3-HF mass spectra reported in the literature, confirm the 3-HF molecular fragmentation occurring inside the deposition chamber. On the other hand, it has to be taken into account that the emission of CO$_x$ species from the target surface is also due to the reactive oxygen stripping of C$_x$H$_y$-based molecular species as produced by the ion-bombardment-induced damage of the dye molecules.

A comparison between the three spectra reported in Figure 2 points out the contribution of the positively charged species to the spectrum of Figure 2a: as a matter of fact the molecular ion peak is completely absent in Figure 2b, while it can be clearly identified in Figure 2c together with some high mass fragment peaks (at m/z 210, 181, and 152). Because most molecular species emitted from the target surface either by sublimation or by sputtering are neutral, this evidence shows that all the integer 3-HF molecules, which are emitted from the target and do not undergo gas-phase fragmentation, are ionized in the glow discharge either by electron impact or by charge exchange, according to

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the rules of organic mass spectrometry.[17] Both reactions are likely to occur in the Ar discharge, as 3-HF ionization potential is lower than the Ar^+ recombination energy. On the other hand, the presence of the (M + 1) peak (m/z 239), which is much more pronounced than the molecular ion one, suggests another reaction occurring in the deposition chamber and involving proton transfer to the 3-HF molecule. Proton-transfer reagents such as H_3O^+, arising from the protonation of residual H_2O, can be in fact present in the glow discharge and they give rise to abundant $(M + H)^+$ ions that undergo little fragmentation as previously shown for argon−water discharges.[18] The protonation of the molecular species emitted from the target was already observed in the GD-induced sublimation of PMDA monomer.[13]

The very pronounced peaks at m/z 78, 52, and 50 (Figure 2a and b) suggest the presence of benzene molecules. These molecules do not appear to arise from the electron-induced fragmentation of 3-HF molecules inside the mass spectrometer, as shown by the very low intensity of these peaks in the 3-HF mass spectra reported in the literature,[16] but they are expected to come from the fragmentation of 3-HF molecules in the deposition chamber. Moreover, the benzene molecules are not ionized by the plasma components as shown by the absence of these peaks in the spectrum of Figure 2c and by their comparable intensity in the spectra of Figure 2a and b.

3.1.2. Glow Discharge Optical Emission Spectra. Figure 3 shows the glow discharge optical emission spectra collected with 3-HF (upper curve) and without 3-HF (lower curve). In Figure 3a the main characteristic spectral lines of Ar I can be clearly identified in both spectra, while no other features can be observed because of the ion bombardment of 3-HF molecules on the sputtering source. In Figure 3b besides the Ar I lines some other peaks can be recognized, in particular the main CO emission lines at 520, 484, and 451 nm corresponding to the Ångstrom system,[19] whereas the other main CO line at 561 nm cannot be solved by the Ar I lines around 560 nm. The presence of these lines confirms the emission of CO/CO_2 species produced by the fragmentation of the 3-HF molecules and by oxygen stripping of damaged dye molecules, as observed by mass spectrometry. Further CO emission lines are visible in the 260 to 360 nm range (Figure 3c): the main features of the third positive bands are found at 283, 298, 313, 331, and 349 nm, and the small peak at 266 nm is expected to be the main feature of the 5B Bands.[19] As compared to the GDS of PMDA compound in He discharge,[15] where the gas-phase CO/CO_2 species produced by the PMDA molecular fragmentation strongly modify the glow discharge emission spectra, the presence of these species during GDS of 3-HF compound does not appear to have any considerable effect on the radiative processes of the excited Ar atoms as shown by the persistence of Ar I emission lines in both spectra of Figure 3. This different behavior is thought to be mainly due to the absence of O−C=O groups in the
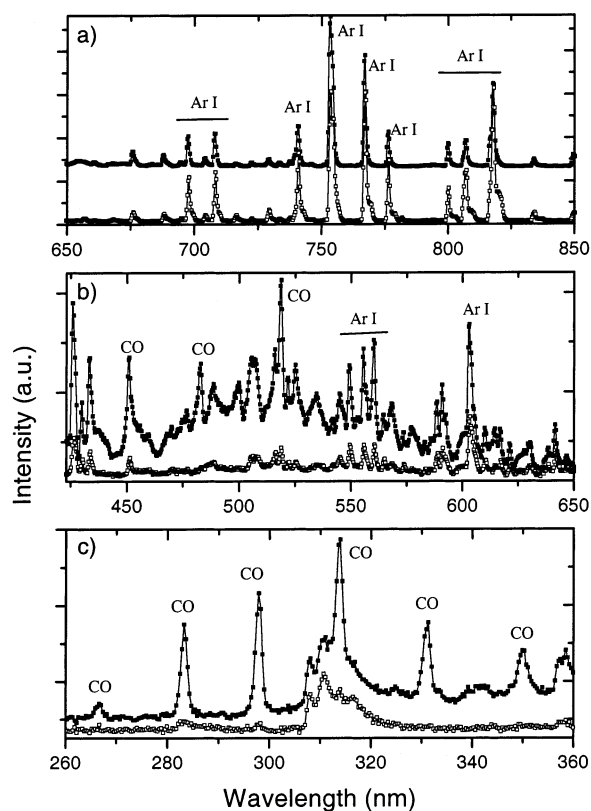
Figure 3. Glow discharge optical emission spectra in different wavelength ranges. In each figure the lower curve (-□-) is the spectrum collected without 3-HF compound (aluminum target) and the upper curve (-■-) is the spectrum collected with 3-HF compound.

3-HF molecule and to the lower amount of >C=O groups as compared to the PMDA molecule.

As a concluding remark on the characterization of the deposition process, the fragmentation of part of the 3-HF molecules takes place both during the target ion bombardment and by interactions with plasma ions and electrons. Nevertheless, a remarkable amount of integer molecules are sublimated and undergo either gas-phase ionization or protonation.

3.2 Coating Characterization. *3.2.1 Film Thickness.* The film thickness was measured by means of a stylus profilometer. By using 0.5 g of 3-HF powder, up to 1-μm thick coatings can be deposited for the experimental conditions of 10 W RF power and 6 cm target−substrate distance. The corresponding deposition rate is 6 nm s^{-1}.

3.2.2 FT-IR Spectra. An FT-IR spectrum of 3-HF coating deposited on silicon substrate by glow discharge induced sublimation (GDS) is reported in Figure 4 and compared to the spectrum of 3-HF powder in KBr pellet. The reported spectra are very similar and all the main features of the 3-HF molecule appear in the spectrum of the GDS coating. The most pronounced peak, assigned to C=O stretching and C=C aromatic in-plane skeletal vibrations, is found at 1614 cm^{-1}, and further peaks assigned to the same C=C vibrations are at 1568, 1548, 1486, and 1468 cm^{-1}. The IR spectrum of the 3-HF molecule is completed by the peak at 1418 cm^{-1} (O−H in-plane deformation), by the peaks at 1132, 1208, and between 1304 and 1288 cm^{-1} (C−O−C pyrone oxide vibration), and by the peaks at 760 cm^{-1} (−C−H out of

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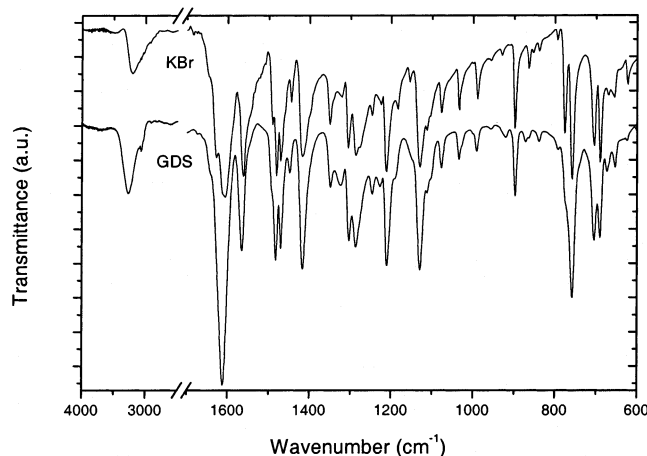
Figure 4. FT-IR spectra of 3-HF powder in KBr pellet (KBr, upper curve) and 3-HF coating deposited by glow discharge induced sublimation (GDS, lower curve).

plane deformation of 4 adjacent H) and between 704 and 690 cm^{-1} ($-$C$-$H out of plane deformation of 5 adjacent H). In the 4000 to 2500 cm^{-1} spectral range can be recognized a broad band centered at 3270 cm^{-1} ($-$O$-$H stretching) and a shoulder at 3070 cm^{-1} ($-$C$-$H stretching). The appearance of the main spectral features of the 3-HF molecule in the GDS coating suggests that the coating is mainly made of integer 3-HF molecules and that the incorporation of fragmentation products as detected by mass spectrometry is negligible.

3.2.3 Ion Beam Analyses. Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD) spectra are reported in Figure 5. Ion beam analysis points out the desorption of volatile species during the spectra collection as shown by the slow decrease of the carbon, oxygen, and hydrogen peak integrals at increasing ion fluence. The final desorption factors (i.e., the ratio between the expected peak integral and the measured integral) are 1.1 for carbon, 1.5 for oxygen, and 1.2 for hydrogen. By extrapolating the desorption curves, the film stoichiometry is calculated. The corrected molar ratios between carbon and oxygen and between carbon and hydrogen are 5.0 $\pm$ 0.2 and 1.5 $\pm$ 0.1, respectively. The average molecular formula of the GDS coating is then $C_{15}H_{9.7}O_3$, which agrees with the theoretical value, $C_{15}H_{10}O_3$, within the experimental error.

The coating deposition rate is 5 $\times$ 10^{14} molecules cm^{-2} s^{-1} as measured for the experimental conditions of 10 W RF power and 6 cm target$-$substrate distance.

3.2.4 Fluorescence Analysis. The fluorescence spectrum of a 3-HF deposited coating is reported in Figure 6. The excitation wavelength is 350 nm. A pronounced peak at 530 nm (green band) and an extremely weak one at 412 nm (blue band) appear in the spectrum: the green band is ascribed to the T* emission of the 3-HF molecule and the blue band to the N* emission. The T* peak position is very close to the position measured for 3-HF embedded in PMMA.[20] The appearance of these two bands in the emission spectrum shows the presence of integer 3-HF molecules in the deposited coatings, whose spectroscopic properties are preserved after the

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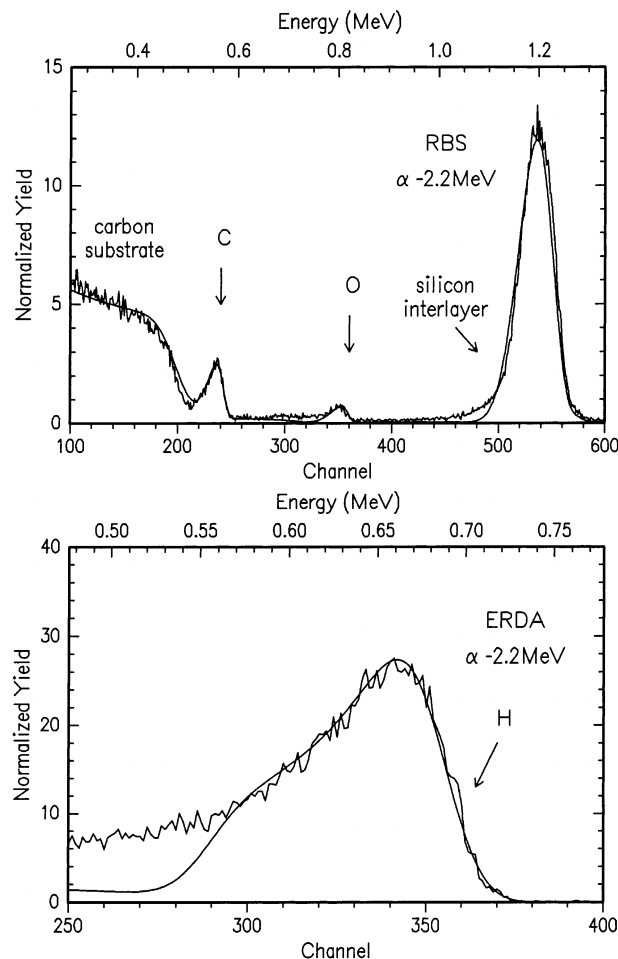
Figure 5. RBS and ERDA spectra of 3-HF coating deposited on silicon-coated graphite substrate.
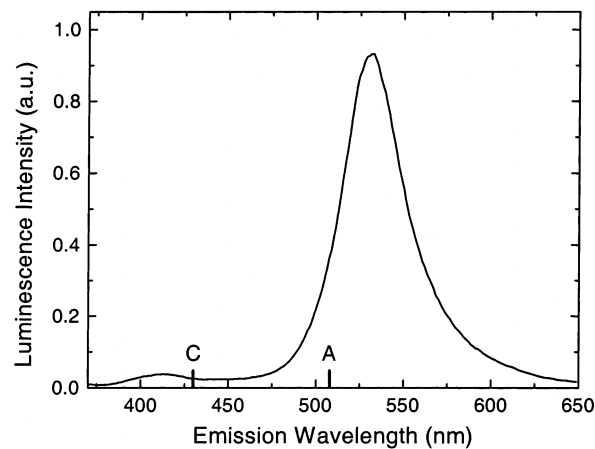
Figure 6. UV$-$Vis fluorescence spectra of a 3-HF coating deposited by GDS on silicon substrate (λ_{ex} = 350 nm). The position of the fluorescence peaks of the cationic (C) and anionic (A) forms of 3-HF is also shown.

GDS deposition route. The peak intensity ratio between the T* and N* bands, I_T/I_N, is about 32. As already reported,[9,21] the ratio I_T/I_N is strongly correlated to the chemical surroundings of the 3-HF molecule. The ESIPT kinetics can be severely perturbed by the presence of hydrogen bonding donor and acceptor molecules, due to the formation of chelate systems via intermolecular

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hydrogen bonds. In particular, the high I_T/I_N value of the deposited coating leads to the conclusion that the 3-HF molecule is embedded in an apolar and aprotic environment. The presence of fluorescent anionic or cationic forms of 3-HF can be also excluded owing to the absence of any emission feature at the wavelengths reported in the literature for these species, i.e., 508 and 430 nm.[22] This evidence shows that both gas phase ionized and protonated 3-HF molecules as detected by mass spectrometry stabilize in the optically active, neutral form during the condensation onto the substrate.

The excitation wavelength was also changed in the range 350 to 380 nm in order to point out the presence of different chemical environments of the dye molecule. Because the shape and the position of the T* peak was unaffected by the excitation wavelength it is inferred that the dye molecule is embedded in a homogeneous chemical medium.

The negligible incorporation of fragmentation products in the deposited film, as shown by FT-IR spectra and ion beam analyses and confirmed by the spectroscopic properties, suggests that most of these fragments are highly volatile compounds (such as benzene or CO/CO_2) and are pumped away during the deposition process.

4. Conclusions

A novel method for the deposition of organic dye thin coatings has been detailed. Glow discharge induced sublimation (GDS) has been used to grow thin coatings of 3-hydroxyflavone. The emission of volatile species from the target surface and their gas-phase interactions with the plasma components have been studied by mass spectrometry and optical emission spectroscopy. Mass spectra show that the ion bombardment gives rise to the emission of integer 3-HF molecules from the target surface. The sublimated 3-HF molecules interact with the glow discharge species (electrons and ions) and undergo different gas-phase reactions, i.e., ionization (both by electron impact and by charge transfer) and protonation. Fragmentation of 3-HF molecules also occurs because of both the ion bombardment of the target and the gas-phase reactions. Most of the molecular fragments are volatile species (such as benzene or CO/CO_2) which are not incorporated in the deposited coating as shown by FT-IR, RBS/ERDA, and fluorescence analyses. No neutral 3-HF molecule is detected by the mass spectrometer.

The optical emission spectra point out the emission of CO/CO_2 species, mainly due to the fragmentation of the 3-HF molecule. However, these species do not strongly affect the radiative processes of the excited Ar atoms.

The sublimated 3-HF molecules impinge on the substrate giving rise to homogeneous coatings, which mainly consist of integer 3-HF molecules as shown by FT-IR analysis.

Ion beam analysis of the deposited coatings gives a chemical composition corresponding to the 3-HF stoichiometry within the experimental error. The deposition rate of the 3-HF molecules is 5×10^{14} molecules $cm^{-2}s^{-1}$ (at 10 W RF power and 6 cm target−substrate distance), as determined by RBS/ERDA analysis.

Fluorescence analysis of the deposited coatings points out the typical emission feature of the 3-HF chromophore, showing that the spectroscopic properties of the dye molecules are preserved during the GDS process. This result shows that the GDS method is specifically suitable to the deposition of integer organic dye molecules in an inert environment, as the ESIPT mechanism of 3-hydroxyflavone is strongly affected by the chemical surroundings of the fluorescent molecule. The findings of the present work open new perspectives in the field of thin film deposition of chromophores where high purity and homogeneity are required.

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