

Porphyrin-Containing Polyimide Films Deposited by High Vacuum Co-Evaporation

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INTRODUCTION

Porphyrins are macrocyclic compounds which have been arousing increasing interest in the last decade due to their peculiar properties. Particularly interesting are their optical properties such as the intense absorption of visible light, the high fluorescence quantum yield in the visible region and the large Stokes' shift. Recently, much attention has been focused on porphyrins containing polyimide systems, since they can be potentially used as wavelength shifting materials.

Aim of this work was to produce thin films of a novel hybrid material consisting of a porphyrin embedded in a fluorinated polyimide by means of vacuum co-evaporation. The optical properties of the produced films have been tested in view of applying the porphyrin-containing films to enlarge the spectral sensitivity of semiconductor-based radiation detectors [1].

EXPERIMENTAL

Porphyrin-containing polyimide films have been produced by using commercially available chemicals: 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA) and 3,3'-diaminodiphenyl sulfone (DDS) were chosen as the precursor monomers in order to obtain a highly optically transparent polyimide and 5,10,15,20 meso-tetraphenyl porphyrin (TPP) was selected as the porphyrin owing to its high fluorescence yield.

The porphyrin-containing polyimide films were produced by high vacuum co-evaporation of 6FDA, DDS and TPP. The experimental equipment used for the evaporation is described elsewhere [2]. After the deposition the films were cured at temperatures ranging from 120 °C to 240 °C. The optical properties of the films after curing were studied by measuring their light absorption and emission. The light emission of the TPP-containing films was stimulated both by directly exciting TPP molecules at wavelengths around 420 nm (Soret band) and by exciting the film matrix in the near-UV range, in order to study the chemical state of TPP molecules and the occurrence of an energy transfer between matrix and TPP.

RESULTS

Figure 1 shows the absorption spectra of 6FDA-DDS and 6FDA-DDS-TPP films cured at 180 °C for 4 hours. As can be seen, the film without TPP is completely transparent in all the visible range, as could be expected. In the TPP-

containing film the absorption peaks fall at 422 nm (B band) and 518 nm, 553 nm, 595 nm and 648 nm (Q band). The appearance of this spectrum highlights that the incorporation of TPP molecules in the polyimide matrix has been achieved; moreover, the position of the B and Q bands is very close to that of TPP dissolved in CHCl₃. This finding indicates that the TPP molecules are incorporated in the matrix in the neutral monomeric form. Moreover the close resemblance between the spectra of TPP-containing film and TPP dissolved in CHCl₃ shows that the thermal treatments do not affect the optical properties of TPP molecules and do not induce their aggregation. The lack of aggregation in the film is also well highlighted by the narrowness of the B band: the FWHM is only 20 nm, which is much lower than that of an evaporated film of only TPP (FWHM = 69 nm) [2]. It is also noteworthy that the strong absorption of these films in a relatively narrow wavelength range make them interesting for such applications as the production of wavelength-selective filters and optical filter coatings of LCD displays [3].

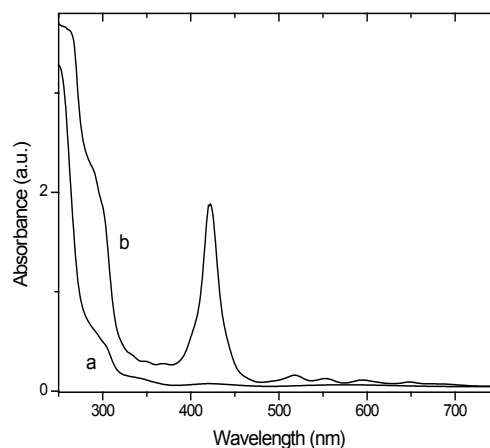


FIG. 1. Optical absorption spectra of cured films: (a) 6FDA-DDS; (b) 6FDA-DDS-TPP.

Excitation and emission spectra of cured films are shown in figure 2. For the excitation spectra the emission wavelength was $\lambda_{em} = 660$ nm and for the emission spectra the excitation wavelengths were $\lambda_{ex} = 300$ nm and $\lambda_{ex} = 420$ nm. For the pure 6FDA-DDS film the excitation spectrum was also collected at $\lambda_{em} = 440$ nm in order to study the emission of the polyimide matrix. The latter spectrum shows an intense band peaked at about 300 nm. The 6FDA-DDS film excited at 300 nm exhibits a broad band between 400 and 600 nm, which is typical for this polyimide [4], with two maxima at 447 nm and 517 nm. On the other hand, by exciting at 420 nm only a weak band centred at 520 nm appears and no emission is found above 600 nm.

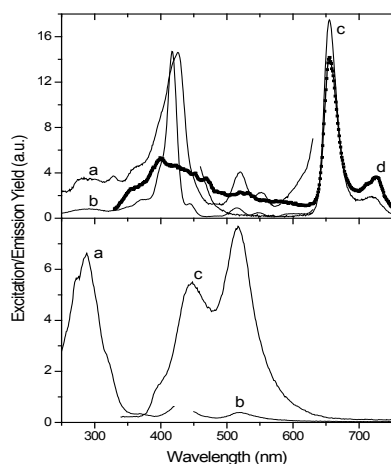


FIG. 2. Top: Excitation spectra of: (a) cured 6FDA-DDS-TPP film ($\lambda_{em}=660\text{nm}$); (b) TPP dissolved in CHCl_3 (10^{-6}M) ($\lambda_{em}=660\text{nm}$); Emission spectra of cured 6FDA-DDS-TPP film: (c) $\lambda_{ex}=420\text{nm}$; (d) $\lambda_{ex}=300\text{nm}$ (the ordinate of this spectrum is magnified four times (4x)). Bottom: (a) Excitation spectrum of cured 6FDA-DDS film ($\lambda_{em}=440\text{nm}$); Emission spectra of cured 6FDA-DDS film: (b) $\lambda_{ex}=420\text{nm}$; (c) $\lambda_{ex}=300\text{nm}$.

In the 6FDA-DDS-TPP film the emission spectrum excited at 420 nm shows the two typical peaks of the TPP molecule. The peaks are placed at 655 nm and 719 nm. The position and the relative intensity of these peaks show that the TPP molecules are in the neutral, monomeric form. This finding confirms that after curing no aggregation of TPP molecules occurred. It is interesting to observe the emission spectrum excited at 300 nm: the emission of the polyimide matrix is shown by the appearance of the broad band between 350 nm and 550 nm. On the other hand, the two emission peaks of TPP also appear, although their intensity is lower as compared to the intensity of the same peaks when the excitation wavelength is 420 nm. In order to study in more detail the occurrence of the energy transfer process between polyimide and TPP when the film is excited at 300 nm, the excitation spectrum of TPP dissolved in CHCl_3 (10^{-6}M , $\lambda_{em}=660\text{nm}$) has been also reported in Figure 2. As can be seen, in the latter spectrum the yield at 300 nm is very low as compared to that of the Soret band, i.e. $Y_{300}/Y_{417}=0,05$. On the other hand, this ratio becomes almost five times higher in the 6FDA-DDS-TPP film ($Y_{300}/Y_{426}=0,24$). Taking into

account that the excitation spectrum of 6FDA-DDS film ($\lambda_{em}=440\text{nm}$) exhibits an intense band at about 300 nm, this shows that the energy transfer between polyimide and TPP occurred. The energy transfer process is still less effective than the direct excitation of the Soret band of TPP, as shown by the low value of the ratio Y_{300}/Y_{426} (less than unit), maybe due to non-radiative de-excitation processes of the polyimide chains.

CONCLUSIONS

Porphyrin-containing polyimide films have been produced by co-evaporating 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA), 3,3'-diaminodiphenyl sulfone (DDS) and 5,10,15,20 meso-tetraphenyl porphyrin (TPP) and by curing the as-deposited samples to complete the polyimide condensation reaction.

Optical analysis highlights that curing does not induce any damage in the TPP-containing films and that the aggregation of TPP molecules in the cured films does not occur. This last feature is an important goal as it allows TPP molecules to preserve their optical properties, in fact: (i) self quenching of the fluorescence intensity due to aggregation is prevented; (ii) the broadening of the absorption peaks, particularly the Soret band, does not occur. The occurrence of an energy transfer process between polyimide matrix and TPP has been pointed out by exciting the films in the near-UV range. The energy transfer is less effective than the direct excitation of TPP; therefore, when the emitted light has to be maximized, the excitation of the Soret band must be preferred. For instance, in optical gas and chemical sensors where LEDs are used as light sources, the excitation of the Soret band allows to enhance the signal/noise ratio and then to improve the detection limit of the sensing device. On the other hand, in applications like radiation detection and solar cell power generation, the collection of light from the near-UV range becomes particularly important.

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