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XPS Study on J-Aggregate of Merocyanine Film Prepared by Vacuum Deposition

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Thin film of J-aggregate of merocyanine (MD-18) was prepared by exposure the vacuum-deposited MD-18 film to dimethyl amine (DMA) aqueous vapor. The structure of J-aggregate of MD-18 was investigated by X-ray photoelectron spectroscopy (XPS). The intensity of N1s and O1s spectra increased by DMAaqueous vapor treatment. J-aggregate of MD-18 contained hydrated DMA. MD-18 molecules were combined each other with hydrogen bonding through hydrated DMA.

Keywords merocyanine; vacuum deposition; J-aggregate; XPS spectroscopy

INTRODUCTION

J-Aggregates are characterised by narrow, excitonic absorption band. The narrow absorption band of J-aggregates opens new fields in optical data storage in multicolour technique. Through J-aggregation the first and second optical hyperpolarisability is strongly enhanced as compared to monomeric molecules due to the excitonic energy delocalisation thus allowing second and third harmonic generation (SHG, THG) applications in minimal sizes. There have been many reports on formation and characterization of J-aggregates in concentrated aqueous solution and Langmuir-Blodgett film but few reports on preparation of J-aggregates using

vacuum-deposited film. In a previous paper, we have studied the formation of J-aggregates in vacuum-deposited merocyanine film[1].

In this work, the structure of J-aggregate of merocyanine dye in thin film was investigated by X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

3-Carboxy-methyl-5-[2-(3-octadecyl-2-bennzothiazolinylidene)-ethylidene]-2-thioxo-4-thiazolidinone (MD-18) was evaporated onto a pyrex glass substrate kept at 20℃ from a fused silica glass crucible in a vacuum of 1.33×10^{-3} Pa. The deposition rate and film thickness were controlled about 12 nm min^{-1} and 20nm. MD-18 film on a glass substrate was exposed to a vapor of 10v/v% dimethylamine (DMA) aqueous solution in a petri dish. The visible spectra and X-ray photoelectron spectra (XPS) of the film was recorded using Shimadzu UV-2200 spectrometer and PHI Quantum 2000 X-ray photoelectron spectrometer. The binding energy was calibrated by a thin gold film vacuum-deposited on the sample, taking the Au(4f7/2) peak as a reference at 83.8eV.

RESULTS AND DISCUSSION

MD-18 film is composed of continuous amorphous layer. Figure 1 shows the spectral change of MD-18 film during DMA/H_2O vapor treatment. The absorption spectrum of as-deposited MD-18 film exhibits two absorption peaks at 516 nm (dimeric band) and at 546 nm (monomeric band). When the MD-18film is exposed to DMA/H_2O vapor, the intensity of these peaks decreases immediately and a new absorption peak appears at 620nm on the red side of the spectrum. The red-shift of absorption peak means the formation of J-aggregate.

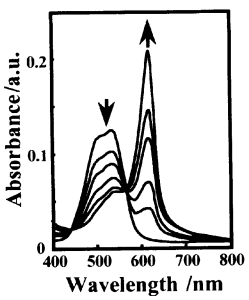


FIGURE 1 Sspectral change of MD-18 film during vapor treatment of DMA/H_2O.

Figure 2 shows C(1s) XPS spectra of MD-18 film before and after DMA/H_2O vapor treatment. The spectra were deconvoluted to the four bands shown with fine lines; the data are summarized in Table 1. The intensity ratio of band 1/band 2 is about 18/(6+2). The band 1 and 2 corresponding to the lowest and

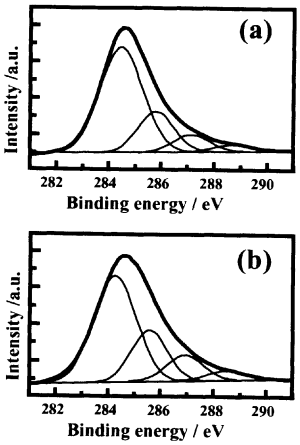
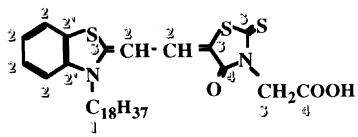


FIGURE 2 C1s photoelectron spectra of MD-18 film before (a) and after vapor treatment (b).

TABLE 1 XPS data of C1s photoelectron spectra of MD-18 film.

	Peak No.	B.E. eV	FWHM eV	Integrated area (%)
as-deposited	1	284.6	2.0	57.7
	2	285.8	1.8	23.2
	3	287.1	1.7	11.9
	4	288.7	1.7	7.2
treated	1	284.5	2.0	51.1
	2	285.6	1.8	22.7
	3	286.9	1.7	18.6
	4	288.5	1.7	6.5



the second lower binding energy are attributed to the carbon atoms in the chain and those in the benzene ring and the ethylidene group, respectively. Another bands are assigned as shown under part in the table refering to XPS data book, i.e. carbon atoms bonding to nitrogen, sulfur and so on (band 3) and in the carbonyl group (band 4). It is noted that the intensity of band 3 increases slightly after DMA/H_2O vapor treatment.

Figure 3 shows N(1s) and O(1s) XPS spectra of the film before and after DMA/H_2O vapor treatment. After vapor treatment, the intensity of N(1s) peak also increases slightly. Remarcable change in the peak intensity is observed in the O(1s) spectrum. In order to trace the origin of the change of intensity, O(1s) spectra are deconvoluted. The spectrum of as-deposited film is deconvoluted to two bands with an intensity ratio of about 1:2. The

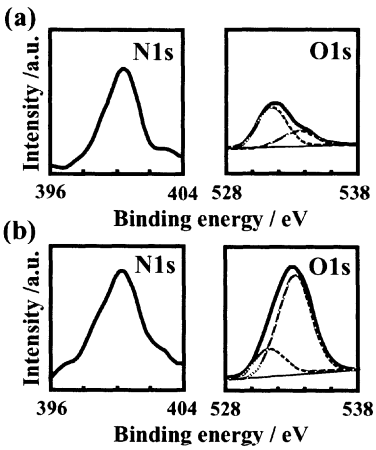


FIGURE 3 N1s and O1s photoelectron spectra of MD-18 film before (a) and after DMA/H_2O vapor treatment (b).

bands with high and low energy are assigned to oxygen atom in hydroxy group and 2 oxygen atoms in carbonyl group, respectively. The spectrum of the film after vapor treatment is also deconvoluted to two bands with simillar binding energy to that of as-depsited film. It is noted that the intensity of hydroxy band increases remarkably. The results of XPS measurement are summarized as follow; the intensity of the bands of the carbon atoms bonding to nitrogen atom and that of the nitrogen peak increase slightly and that of hydroxy band increases remarkably by vapor treatment. These indicate that MD-18 film after DMA/H_2O vapor treatment include both DMA and H_2O molecules.

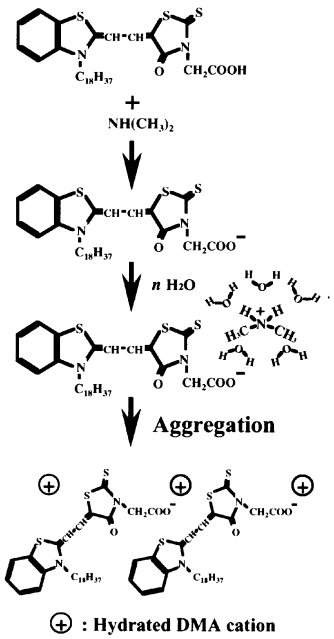


FIGURE 4 Aggregation model of MD-18 with DMA/H_2O.

Figure 4 shows the J-aggregate formation model in MD-18 film by exposure to DMA/H_2O vapor. At initial step, the dimethyl ammonium salt is formed by the acid-base reaction with MD-18 and DMA. Then H_2O molecules seem to hydrate with dimethyl ammonium salt. Neighboring MD-18 anions are combined each other with hydrogen bonding through hydrated dimethyl ammonium cations and these cations stabilized three-dimensional structure.

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References

[1] Y.Ueda and K.Nitta,Jpn.J.Appl.Phys., in prress