Ultraviolet Photoelectron Spectroscopy (UPS) Measurements of Cyanine Dye Films Fabricated by Solution Jet Beam Deposition Method

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We report ultraviolet photoelectron spectroscopy (UPS) measurements of cyanine dye films fabricated by solution jet beam method without exposure to air. The solution jet beam method is a novel technique to fabricate organic thin films in vacuum, where solution of the organic material is sprayed in vacuum. This method can be applied to organic materials which cannot be vacuum-evaporated due to thermal decomposition, as in the case of cyanine dyes. The observed spectra were sharper than those of spin-coated films exposed to air, demonstrating the advantage of the present approach. The spectra were compared with the results of density functional theory (DFT) calculations.

Keywords: Photoelectron spectroscopy; Vacuum science and technology; Growth; Solution jet beam deposition; cyanine dye

I. INTRODUCTION

Cyanine dyes, with structure such as Fig. 1, play an important role in the spectral sensitization of photographic emulsion [1] and organic solar cells [2]. But organoionic compounds such as them cannot be vacuum-evaporated, because they decompose at evaporation. Therefore, spin-coating method has been almost the only way to fabricate their thin films. There have been several works studying the spin-coated cyanine dye films using ultraviolet photoelectron spectroscopy (UPS), which is a powerful technique to probe the electronic structure of solids [3, 4], but the sample preparation was carried out in ambient atmosphere, and the surface of the films might be affected by air.

We have been developing the solution jet beam method, which is a novel technique to fabricate organic thin films. In this method, the film is fabricated by spraying the solution of the sample material, dissolved in a volatile solvent, onto the substrate in vacuum. This method can be generally applied to all samples which can be dissolved in a volatile solvent. The film preparation is carried out in vacuum, enabling to avoid the effects of the ambient gases. We have shown that films prepared by this method had sufficiently high quality to fabricate organic light emitting diodes using tris(8-hydroxyquinoline) aluminum (Alq3) [5]. The apparatus used in this work was based on the cluster jet apparatus for studying liquid clusters prepared by the ejection of liquid into vacuum [6]. Recently similar other techniques have also been reported with applications to polymers [7, 8], DNA [9], liquid crystals [10], and thermally unstable materials [11].

In this paper, the solution jet beam method is combined with UPS. Since the escape depth of photoelectrons are rather small, it is surface sensitive and the results can suffer from the surface modification at the contact with ambient gases. Such contact can be avoided in solution jet beam method, where the film is prepared in vacuum, while it is generally not easy to avoid for the case of alternative methods like spin coating. The films of some cyanine dyes with structure in Fig. 1 were characterized by atomic force microscopy (AFM) and UPS. Actually the present results indicated that the UPS spectra of the films fabricated by solution jet beam method show sharper features than those in the spectra of spin-coated films prepared in air.

II. EXPERIMENTAL

Figure 2 shows the experimental apparatus. The details are described elsewhere [12]. It consists of three chambers (A, B, and C) separated by two skimmers with diameters of 1 mm (between A and B) and 2 mm (between B and C), respectively. Chamber A is evacuated by a rotary pump (9.2 L/s) through a liquid nitrogen cold trap. Chamber B

![Cyanine Dyes](http://www.sssj.org/ejsnt)
FIG. 2: Apparatus for the solution jet beam method. The apparatus is separated into three chambers A to C by two skimmers.

is evacuated by a diffusion pump (760 L/s), also through a liquid nitrogen cold trap. Chamber C is evacuated by a turbomolecular pump (300 L/s). Base pressures of the chambers A, B, and C are $< 10^{-2}$ Pa, $7 \times 10^{-4}$ Pa, and $1.5 \times 10^{-6}$ Pa, respectively.

The sample solution which is pressurized by a pump for liquid chromatography (LC-10AT VP; Shimadzu Co.) is injected into vacuum through the pulse valve (General Valve Co., 9-279-900). The pulse valve is heated to help the solvent evaporation. The droplets of the solution fly through the two skimmers and reach the substrate in the chamber C. The solvent is almost dried up during the flight. During the film fabrication and the following measurements, the substrate is at room temperature. The distances among the pulse valve, the two skimmers, and the substrate are adjustable, with typical working distances of 5 mm (the pulse valve - the first skimmer), 35 mm (the first skimmer - the second skimmer), and 315 mm (the second skimmer - the substrate), respectively. The deposition rate is measured by a quartz microbalance.

AFM measurement was carried out in air by SPI3700 (Seiko Instruments Inc.) with dynamic force mode. Si cantilever of 40 N·m$^{-1}$ spring constant was used.

The UPS apparatus consists of a He discharge lamp (SPECS UVS 10/35, $h\nu = 21.22$ eV) and a spherical retarding-field electron energy analyzer [13] installed in the chamber C. It enables UPS measurements without exposure of the film to the air. The internal surface of the spherical electron energy analyzer is plated with gold by vacuum evaporation. Photoelectrons emitted from the sample are collected by the spherical collector, to which the retarding voltage from a source-measure unit (Keithley Model 6487 picoammeter/voltage source) was applied, and the collected electrons are measured as the photocurrent by the same source-measure unit. The resolution of the spectrometer is 0.2 eV (FWHM), as judged from the measured Fermi edge of gold.

Cyanine dyes with the structure shown in Fig. 1, with the number of the methine group $n = 0$ and $n = 1$, (purity of 97% and 95% respectively), were purchased from Aldrich, and they were used without further purification. Acetone solution of these compounds with the concentration of $10^{-4}$ mol/L was used for film preparation. Morphology of the films prepared by solution jet beam method depended on parameters such as material, solvent, substrate, temperature of the pulse valve, rate of solution pumping, frequency of ejection, and pulse width of ejection. We reported the trial of optimizing some of these parameters for the films of the best uniformity [5], and the results are used to prepare the films in the present study. The deposition conditions in the present film preparation are as follows: rate of solution pumping: 0.5 mL/min, pulse width: 10 ms, pulse repetition rate: 1 Hz, temperature of the pulse valve: 443 K. The substrates were Au evaporated films of 20 nm thickness on Si(111) wafer at a deposition rate of 0.05 nm/s.

FIG. 3: AFM images of cyanine dye ($n = 0$) films deposited by (a) solution jet beam method and (b) spin-coating method.
III. RESULTS AND DISCUSSION

Morphology of the cyanine dye \((n=0)\) film prepared by the solution jet beam method is compared with those of the spin-coated film by AFM in Fig. 3. Spin-coating was carried out on similar substrates to those for UPS at 2000 rpm from ethanol solution in air. The film prepared by solution jet beam method with average thickness of 8 nm shows AFM image with sea-island-like structure (Fig. 3(a)), while the image for spin-coated film shows needle-like structure (Fig. 3(b)). Although the solution-jet film is taken out into air, this comparison gives some idea about the morphology of the films prepared by this method.

Figure 4 shows the UPS spectra of the films of cyanine dyes \((n=0)\) and \((n=1)\) fabricated by solution jet beam method ((a), (e)), jet films exposed to air ((b), (f)), and spin-coated films ((c), (g)). The rightmost peak corresponds to the electron emission from the highest occupied molecular orbital (HOMO), and features at the left are due to deeper electronic levels. The origin of the binding energy is the Fermi level of the Au substrate, which is determined as the Fermi edge of the gold substrate measured before each set of the measurements of the dye samples.

For the interpretation of the observed spectra, the density of states of cyanine dyes were simulated by DFT MO calculations (Gaussian98, B3LYP/6-31G(d)). The geometrical optimization and the MO calculations were performed on the cations, since the energy levels of the anions are expected to be deeper than those in Fig. 4. The simulated spectra are shown in Figs. 4(d) and (h). These simulated spectra were shifted for the best fit to observed ones. The spectral features observed for the jet films (Figs. 4(a) and (e)) are more clearly observed than those for the spin-coated films (Figs. 4(c) and (g)). The observed and simulated spectra correspond well, enabling the assignments of the spectral features to various electronic energy levels. The detailed analysis of the electronic structure, including the chain length dependence, will be reported elsewhere [14].

The effect of air exposure was also examined. In Fig. 4, the UPS spectra of the cyanine dyes after exposure to air are also shown (Figs. 4(b) and (f)). The peak position of the HOMO in the spectrum of the jet film of cyanine dye \((n=0)\) (Fig. 4(a)) shifted toward lower binding energy after exposure to air (Fig. 4(b)). In the case of the cyanine dye \((n=1)\) (Fig. 4(e)), spectral features in the spectrum disappeared completely (Fig. 4(f)). This clearly shows the advantage of the present instrument for measuring the air-sensitive samples. On the other hand, the spectral features in the UPS spectrum of spin-coated film of cyanine dye \((n=1)\) did not disappear. This is somewhat unexpected result, since the film preparation was carried out in air. The reason of the difference in the sensitivity to air between the jet and spin-coated films is not clear at present.
IV. CONCLUSIONS

The films of two kinds of cyanine dyes were fabricated by solution jet beam method, and they were characterized by AFM and UPS. The UPS spectra of cyanine dyes films deposited by solution jet beam method were successfully measured. For one of the films, significant effect of air exposure to the UPS spectrum was observed, showing the advantage of the apparatus enabling the in-situ measurement of the UPS spectrum.

Several classes of materials such as ionic dyes, bio-related molecules, and polymers can not be vacuum-evaporated. Therefore, it was difficult to measure UPS without air exposure, although they were important for various roles, such as dopants into organic semiconductors for the case of ionic dyes. With the instrument described in this paper, density of states and effect of air of those materials can be measured also for other systems.

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