

Apparatus for solution jet beam deposition of organic thin films and *in situ* ultraviolet photoelectron spectroscopy

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We report an instrument with the combination of solution jet beam deposition method and ultraviolet photoelectron spectroscopy (UPS). 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, e.g., ionic organic solids such as cyanine dyes. The present instrument combines this method with UPS, which is a powerful method for investigating the electronic structure of solids. Using this instrument, the UPS spectra of cyanine dye films deposited by the solution jet beam method were measured without exposure to air. The observed spectra were clearer than those of spin-coated films exposed to air. © 2006 American Institute of Physics. [DOI: 10.1063/1.2185132]

I. INTRODUCTION

Recently there is much interest in the use of organic thin films in relation to their possible applications to organic thin film electronics¹ and various types of nanostructure fabrication.² Various methods have been used to fabricate organic thin films, but each method has some disadvantage. Vacuum evaporation is one of the most common methods, but it cannot be applied to materials which are decomposed at evaporation. Examples of such class of compounds are ionic dyes, polymers, and biorelated molecules. Spin coating can be applied to ionic materials and polymers, but it is difficult to avoid the effects from ambient gases and to finely control the film thickness.

For overcoming such difficulty, we have been developing the solution jet beam method as a technique to prepare 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 is generally applicable 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; Fig. 1(a)].³ The apparatus used in this work was based on the cluster beam apparatus for studying hydrate clusters in aqueous solution.⁴ Recently other similar or related techniques have also been reported with applications to polymers,^{5,6} DNA,⁷ liquid crystals,⁸ and thermally unstable materials.⁹

An attractive extension of this method is the combination with another technique where the contact with ambient air may cause some difficulty. 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 such as spin coating. An example of such a technique to be combined is the ultraviolet photoelectron spectroscopy (UPS), which is a powerful technique to probe the electronic structure of solids. Since the escape depth of photoelectrons is rather small, it is surface sensitive and the results can suffer from the surface modification at the contact with ambient gases.

In this article we report a newly designed and constructed apparatus for measuring the UPS spectra of the films prepared by the solution jet beam method. The films of Alq₃ and some cyanine dyes in Fig. 1(b) prepared by this method were characterized by atomic force microscopy (AFM), and the UPS results for cyanine dyes are reported as an application of this apparatus to compounds which cannot be vacuum evaporated.

Cyanine dyes, with structure such as Fig. 1(b), play an important role in the spectral sensitization of photographic emulsion¹⁰ and organic solar cells.¹¹ As they are organoionic compounds with strong intermolecular interaction due to the electrostatic attractive force among the cations and anions, they cannot be evaporated, and spin-coating method has been

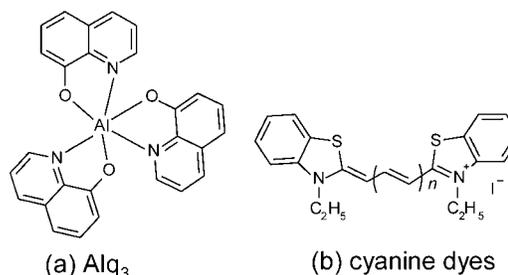


FIG. 1. Molecular structures of the compounds used in the present study.

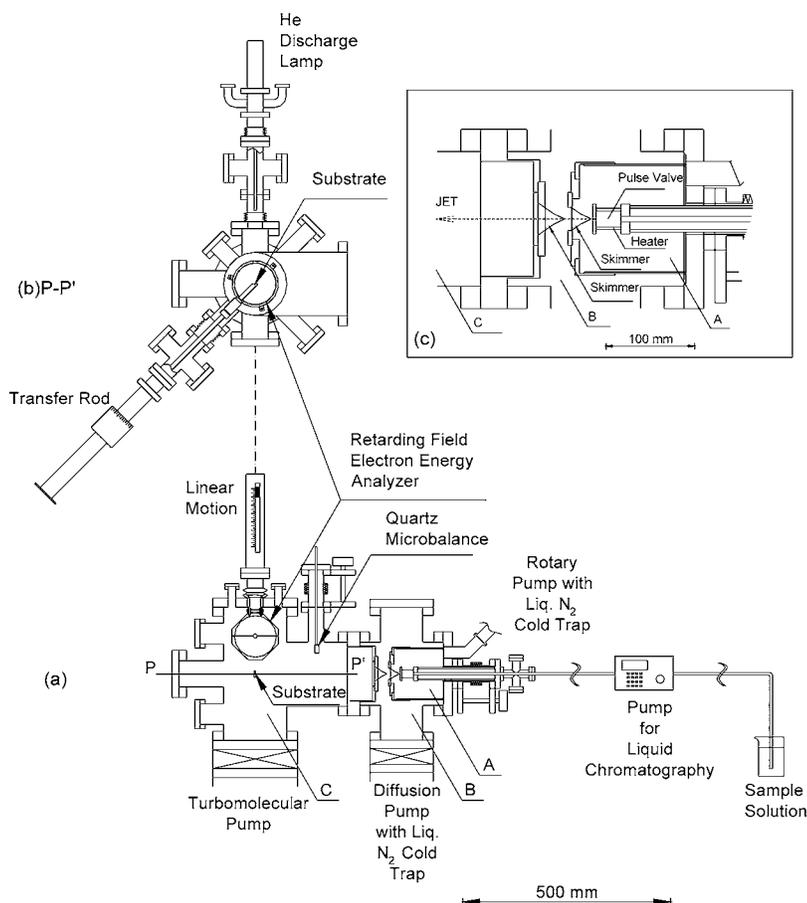


FIG. 2. Apparatus for the solution jet beam method. (a) A cross sectional side view of the whole apparatus. The apparatus is separated into three chambers A–C by two skimmers. (b) A cross sectional top view of the chamber along the line P–P' in (a). (c) Expansion of the jet production part.

almost the only way to fabricate their thin films. A few UPS measurements were reported for spin-coated cyanine dye films,^{12,13} but the sample preparation was carried out in ambient atmosphere, and the surface of the films might be affected by air. Actually the present results indicated that the UPS spectra of the films fabricated by the solution jet beam method show sharper features than those in the spectra of spin-coated films prepared in air.

II. EXPERIMENTAL SETUP

A. Vacuum system and solution jet beam part

Figure 2 shows the experimental apparatus. As shown in Fig. 2(a), 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. The internal and external angles of the skimmers are 25° and 30°, respectively. These skimmers are made of Cu and are coated by Au to avoid chemical reaction with sample compounds and solvents. Chamber A is evacuated by a rotary pump (BOC Edwards, E2M28, 9.2 L/s) through a liquid nitrogen cold trap. Chamber B is evacuated by a diffusion pump (BOC Edwards, DIFFSTAK160/700F, 760 L/s), also through a liquid nitrogen cold trap. Chamber C is evacuated by a turbomolecular pump (Mitsubishi, PT-300, 300 L/s). The base pressures of the chambers A, B, and C are $<10^{-2}$, 7×10^{-4} , and 1.5×10^{-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) operated by an IOTA-ONE controller (General Valve Co.) [Fig. 2(c)]. The pulse valve is heated with a silicone rubber heater (Watlow, Silicone rubber heater, 25 W) to help the solvent evaporation and prevent the freezing of the solution due to the cooling by the heat of evaporation of the solvent. The temperature of the pulse valve is monitored by an alumel/chromel thermocouple [Fig. 2(c)]. The droplets of the solution sprayed into vacuum 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 placing a quartz microbalance (Inficon, Bakable Crystal Sensor with XTM/2 controller) attached to a linear motion on the line of the solution jet beam, as shown in Fig. 2(a). After measuring the deposition rate, the quartz microbalance is pulled away from the solution beam line, and the film deposition onto the substrate can be started. Typically it takes about 30 min to fabricate several nanometer thickness films. The characterization of the morphology of the prepared films is described later in Sec. III.

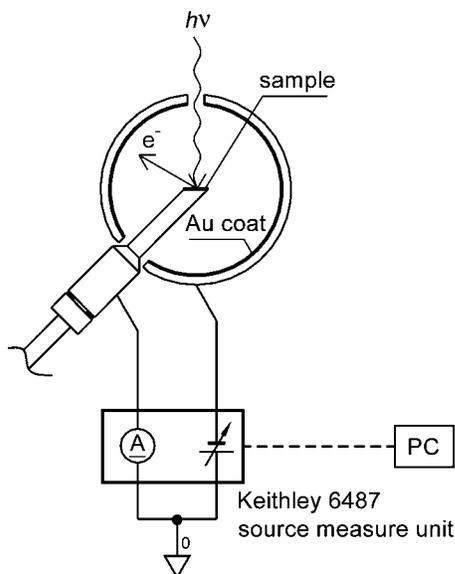


FIG. 3. Schematic illustration of the retarding-field electron energy analyzer.

B. *In situ* UPS system

The UPS apparatus consists of a He discharge lamp (SPECS UVS 10/35) with two differential pumping stages which emits the He I line ($h\nu=21.22$ eV) and a spherical retarding-field electron energy analyzer¹⁴ installed in the chamber C [Fig. 2(a)]. Typical working conditions of the He discharge lamp have a discharge current of 80 mA, a discharge voltage of 450 V, and a He gas pressure of 10 Pa.¹⁵

During the fabrication of the organic films, the analyzer is placed at the upper part of the chamber C as illustrated in Fig. 2(a) to avoid disturbing the solution jet beam, and the substrate is placed at the center of C for the deposition of the organic material. After the fabrication of the film, the setting is changed for the UPS measurements as follows: (1) the substrate with organic film is once put back using a transfer rod, (2) the analyzer is set to the center of the chamber C, and (3) the substrate with the film is inserted into the analyzer, as shown in Fig. 2(b). Thus we can measure UPS without exposing the film to the air. The spherical electron energy analyzer of internal diameter of 100 mm is made of stainless steel (SUS304), and its internal surface is plated with gold by vacuum evaporation. Photoelectrons emitted from the sample are collected by this collector electrode, to which retarding voltage from a source measure unit (Keithley Model 6487 picoammeter/voltage source) under the control of a personal computer is applied. When the retarding voltage is large, all photoelectrons are pushed back to the sample, and the photocurrent is zero. As the retarding voltage is decreased, at first photoelectrons with large kinetic energy overcome the potential barrier, then arrive at the collector, leading to increasing photocurrent. When the retarding voltage is further decreased, all the photoelectrons are collected, and the photocurrent becomes finally saturated. In this apparatus, the photocurrent is measured as the drain current due to the flow of holes from the substrate by using the same source unit of measure as described above. The UPS spectrum, which is the kinetic energy distribution of photoelec-

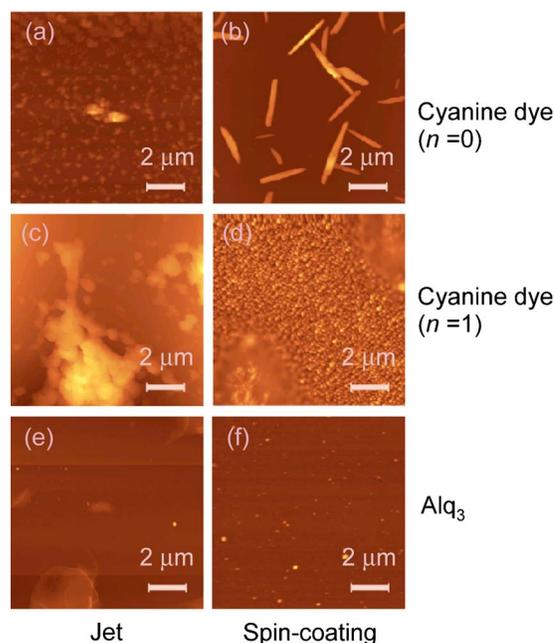


FIG. 4. AFM images of the cyanine dyes ($n=0,1$), and Alq_3 films fabricated by the solution jet beam method and the spin-coating method.

trons, is obtained by digitally differentiating the photocurrent-voltage curve with respect to the retarding voltage (Fig. 3). The resolution of the spectrum is 0.2 eV full width at half maximum (FWHM), as judged from the Fermi edge of gold. Typically, it takes 20 min to measure one UPS spectrum with the sample current of several hundreds of picoamperes.

III. FILM DEPOSITION AND MORPHOLOGY

Cyanine dyes with the numbers of the methine group $n=0$ and $n=1$, [Fig. 1(b); purity of 97% and 95%, respectively] and Alq_3 [Fig. 1(a); purity of 99.995%] were purchased from Aldrich, and they were used without further purification. Acetone solution of these compounds with a concentration of 10^{-4} mol/L was used for the film preparation. The morphology of the films prepared by the solution jet beam method is 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,³ and the results are used 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 on Si(111) wafer of $10 \times 15 \times 0.5$ mm³. The substrates of Pt and Cu were also tried.

In Fig. 4, the AFM images of the films prepared by the solution jet beam method are compared with those of the spin-coated films for the cyanine dyes and Alq_3 . Spin coating was carried out on similar substrates to those for UPS at 2000 rpm from ethanol solution for cyanine dyes and from acetone solution for Alq_3 . The spin-coated film was inserted

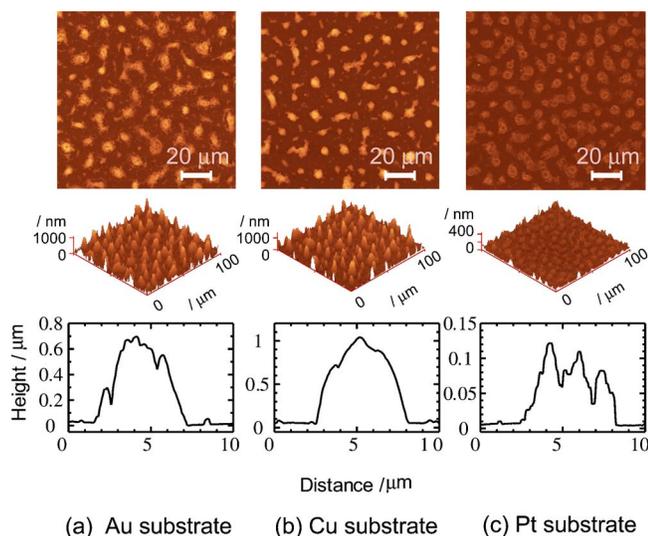


FIG. 5. AFM images and height profiles of cyanine dye ($n=1$) films on (a) Au, (b) Cu, and (c) Pt substrates. Each film shows fine islandlike structure, and the height profile of a representative island is also shown at the bottom.

in vacuum within a few minutes. The UPS measurements were started typically 30–40 min after the start of evacuation.

Spin-coated film of cyanine dye ($n=0$) shows an AFM image with a needlelike structure as shown in Fig. 4(b), while the image for the jet film [Fig. 4(a)] with the average thickness of 8 nm is quite different, showing sea-island-like structure. As described later, the UPS spectrum of the jet film of similar thickness did not show the spectral features due to photoelectron emitted from the substrate. Considering the surface sensitivity of UPS resulting from the short escape depth of photoelectrons, we can deduce that the substrate is fully covered with the dye molecules even at the sealike area. On the other hand, the UPS spectrum of the spin-coated film showed the Fermi edge due to the emission from the Au substrate, indicating that the spin-coated film was not fully covered.

The spin-coated film of cyanine dye ($n=1$) had grains of submicrometer size [Fig. 4(d)], while jet film had a few micrometer-sized islandlike structure [Fig. 4(c)]. In the case of Alq_3 , both spin-coated and jet films [Figs. 4(e) and 4(f)], had basically similar structures with fine islands, but the jet film [Fig. 4(f)] showed a few traces of droplets. Jet and spin-coated films of cyanine dye ($n=1$) and Alq_3 did not show UPS spectral feature of substrate, showing that the substrate is fully covered by the organic layer.

Comparing Figs. 4(a), 4(c), and 4(e), we found that the morphology of the films of cyanine dyes ($n=0$ and $n=1$) and Alq_3 fabricated by solution jet beam method is quite different. This suggests that the morphology of the films depends on factors such as the interaction between the substrate and the solute and between the substrate and the solution concentrated by the evaporation of the solvent. For getting further information about this point, we also examined the substrate dependence of the morphology of films deposited by the solution jet method.

Figure 5 shows the AFM images and the height profiles of cyanine dye ($n=1$) films deposited by the solution jet

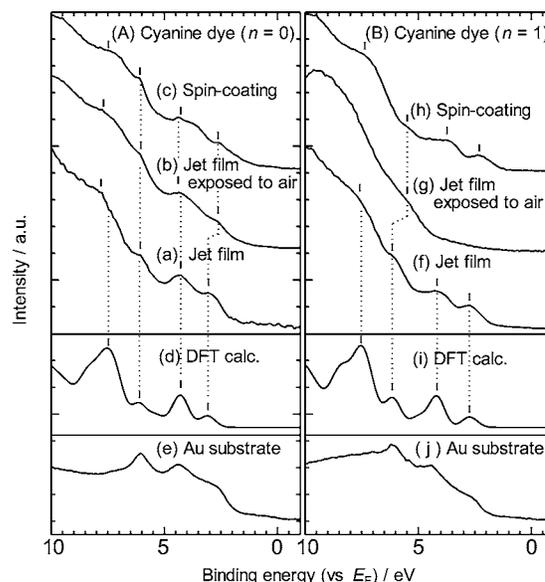


FIG. 6. UPS spectra of cyanine dyes [$n=0$ (A) and $n=1$ (B)] deposited on gold substrates; as prepared by the solution jet beam method, [(a) and (f)]; after exposing to air [(b) and (g)]; spin-coating method [(c) and (h)]. The spectra [(d) and (i)] show the simulated spectra by DFT calculations. The bottom lines [(e) and (h)] show the UPS spectra of Au substrates.

beam method on (a) Au, (b) Cu, and (c) Pt substrates. Each film shows fine islandlike structure, and the height profiles of a representative island are also shown at the bottom. The UPS spectra showed that the surfaces are fully covered, indicating that various metals can be used as the substrate for UPS studies using the solution jet beam method. We still note that the shapes of the islands are slightly different depending on the substrate. On the Au substrate, islands of the dye show some extended branches, suggesting wetting nature of the solution to the substrate. On the other hand, the films prepared on the Cu and Pt substrates show shrunken islands, suggesting that the solution was repelled by the substrate. Such difference in wetting properties suggests the variation of the interaction of cyanine dyes and the substrates.

According to the AFM images shown in Fig. 5, the size of the island is typically a few micrometers. We speculate that the film is formed on the substrate through repeated cycles of drying and dissolving into newly arrived droplets. The size of the droplets at the arrival at the substrate should be about few micrometers or less, because larger droplets should form rougher films as shown in our previous report.³

IV. UPS OF CYANINE DYES

Figure 6 shows the UPS spectra of the films of cyanine dyes ($n=0$ and $n=1$) fabricated by the solution jet beam method and prepared *in situ* measured in vacuum [(a) and (f)], jet films exposed to air [(b) and (g)], and the spin-coated films [(c) and (h)]. 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 before depositing the dye samples.

To interpret the observed spectra, the density of states of cyanine dyes was simulated by molecular orbital (MO) calculations by density functional theory (DFT) [B3LYP/6-31G(d)] using the GAUSSIAN 98 program package. The calculated line spectra were convoluted with a Gaussian function with a FWHM of 0.8 eV to fit to the observed spectra. The geometrical optimization and the MO calculation were performed on the cations, since the energy levels of the anions are expected to be deeper than those in Fig. 6. The simulated spectra are shown in Figs. 6(d) and 6(i). These simulated spectra are shifted for the best fit to the observed spectra. The spectral features observed for the jet films [Figs. 6(a) and 6(f)] are more clearly observed than those for the spin-coated films [Figs. 6(c) and 6(h)]. The observed and simulated 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.¹⁵ The UPS spectra of the Au substrates are shown in Figs. 6(e) and 6(j). The UPS spectra of the Au substrates are shown in Figs. 6(e) and 6(j). These spectra show Fermi edge features. Similar feature is seen in the spectrum of spin-coated film of cyanine dye ($n=0$) (c), indicating that the film is not fully covered. This is consistent with the AFM image shown in Fig. 4(b) that exhibit a rodlike structure.

To examine the advantage of the present apparatus enabling the UPS measurements without exposure to air, the effect of air exposure was also examined. In Fig. 6, the UPS spectra of the cyanine dyes after exposure to air are also shown. The jet film of cyanine dye ($n=0$) [Fig. 6(b)] was not clearly changed even after the exposure to air, while the spectral features in the spectrum of cyanine dye ($n=1$) [Fig. 6(g)] disappeared completely. 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 an unexpected result, since the film preparation was carried out in the air. The reason of the difference in the sensitivity to air between the jet and spin-coated films is not clear at present. We may speculate that the surface of the jet film was rougher than the spin-coated film, enabling the air to penetrate deeper in the jet film, but this needs further examination.

V. DISCUSSION

An instrument combining the organic film preparation by the solution jet beam method and *in situ* UPS measurements of the prepared film is reported. The films of two cyanine dyes and Alq₃ were fabricated by the solution jet beam method, and they were characterized by AFM. The AFM measurements revealed that the morphology of the films de-

pends on solutes and substrates, and this variation may be related to the wetting property of the solution. The UPS spectra of cyanine dye 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, demonstrating the advantage of the apparatus and enabling the *in situ* measurement of the UPS spectrum.

As described in the introduction, there are many classes of materials such as ionic dyes, biorelated molecules, and polymers, which cannot be vacuum evaporated. So far it was difficult to measure UPS without air exposure, although they are important. With the type of instrument described in this article, more detailed and precise studies of the electronic structure and effect of air on it will become possible for these materials.

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