Surface Potential Investigation of Fullerene Derivative Film on Platinum Electrode under UV Irradiation by Kelvin Probe Force Microscopy Using a Piezoelectric Cantilever

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Dynamic-mode atomic force microscopy (DFM) combined with Kelvin probe force microscopy (KFM) has been a powerful tool not only for imaging surface topography but also for investigating surface potential on a nanometer-scale resolution. We have developed DFM / KFM using a microfabricated cantilever with a lead zirconate titanate (PZT) piezoelectric thin film used as a deflection sensor. The observed sample can be in a completely dark environment because no optics are required for cantilever deflection sensing in our experimental setup, which is also equipped with a mechanism to irradiate ultraviolet (UV) light onto the sample. We prepared a platinum-on-silicon substrate and deposited fullerene-derivative (PCBM; [6,6]-Phenyl-C61-Butyric Acid Methyl Ester) film patterns by vacuum evaporation with two shadow masks in crossed directions. The energy band diagram with band-bending, it was created by simultaneously obtaining topographic and surface potential images of the same area using the developed DFM / KFM. [DOI: 10.1380/ejssnt.2015.102]

Keywords: Dynamic-mode atomic force microscopy (DFM); Kelvin probe force microscopy (KFM); Piezoelectric cantilever

I. INTRODUCTION

Scanning probe microscopy (SPM) is one of the most useful and powerful techniques in the field of surface science [1]. The SPM technique can be used not only for obtaining the surface topography by dynamic-mode atomic force microscopy (DFM) [2], but also for evaluating the surface potential by Kelvin probe force microscopy (KFM) [3]. In this study, we used the frequency modulation (FM) detection method [4] with precise probe control over a wide scanning area for highly sensitive, simultaneous measurements of the topography and surface potential of the same area on the micro- and nano-meter scales [5].

We have developed multifunction SPM using a microfabricated cantilever with a lead zirconate titanate (PZT) piezoelectric thin film used as a deflection sensor in the DFM [6–8]. The cantilever is referred to as a PZT cantilever. In conventional atomic force microscopy (AFM), it is possible that the scattered light of the laser beam used for the displacement sensing is a noise source [9]. In particular, it causes difficulty in the observation of photosensitive materials under the equilibrium conditions. That

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II. EXPERIMENTAL SETUP

A. Instrumentation

Figure 1 shows a schematic of the DFM/KFM with FM detection using the PZT cantilever. The instrumentation system was developed based on a commercial atomic force microscope (SII, SPA300HV).

The PZT cantilever beam was made of silicon, and the probe-tip, which was located at the end of the beam, was a hollow silicon nitride pyramid. The setup employed a 200-nm-thick platinum film as the lower electrode, an 800-nm-thick PZT film as a deflection-sensing layer, and another platinum layer as the upper electrode. In order to perform KFM measurement, a 20-nm-thick platinum film was sputter-deposited on the tip side to make the tip conductive. The radius of the apex and the tip angle were less than 50 nm and 40 degrees, respectively. The typical resonance frequency of the PZT cantilever ranged between 80 and 100 kHz, and the spring constant was calculated to be approximately 150 N/m, based on its dimensions.

The deflection of the PZT cantilever was detected by a current-to-voltage ($I-V$) converter and the resonance frequency shift ($\Delta f$) was detected using a laboratory-built FM detector [19]. The constant positive value of the frequency shift corresponds to a repulsive force between the cantilever probe and the sample surface. Consequently, the intermittent contact region was observed.

The KFM technique is capable of imaging the contact potential differences [3] between a PZT cantilever with a Pt-coated probe-tip and a PCBM film with a Pt electrode. To perform KFM measurements in this experiment, the signal was generated by the displacement of the resonant frequency of the cantilever when the modulation bias voltage (1 kHz, 2 V$_{p-p}$) was applied between the PZT cantilever with a Pt-coated probe-tip and the sample surface was detected by a lock-in amplifier (NF, LI5640). The obtained signal was based on the electrostatic force acting on the cantilever, which corresponded to the potential of the sample surface. The surface potential was measured by the null method, which compensated for with the bias feedback circuit according to the amount of the electric charge on the sample surface. The surface potential of the cross-point area of the deposited thin films was measured using the FM-DFM/KFM system [4].

The setup employed to irradiate the sample of interest with light of the selected wavelength was as follows. It is introduced into monochromator (Shimadzu, SPG-120S) by focusing light from a high pressure mercury lamp light source. The wavelength of the irradiated light was selected by the monochromator. Light having the selected wavelength was introduced via a slit (of width 100 μm) into a bundle fiber. Finally, the sample was irradiated through a quartz window. The advantage of this experimental setup is that we could simultaneously obtain a topographic image and surface potential image in the same area, under vacuum pressure conditions and in a completely dark environment, with or without the selected irradiation light. In addition, the area imaged by DFM/KFM could be precisely located using a charge coupled device (CCD) camera. The acquisition time for obtaining images was approximately 30 min. Thus, the energy band diagram for evaluating carrier behavior was derived from precisely measured film thicknesses and surface potentials.

B. Sample preparation for observation of DFM/KFM

Any contaminant on the Si-substrate was removed by ultrasonic cleaning with acetone and isopropyl alcohol solutions as well as by UV ozone cleaning. After cleaning, the substrate was placed in a vacuum evaporation system (Eiko, EO-5), where the PCBM thin films and Pt electrode were deposited on the Si-substrate. During Pt deposition on the Si substrate, the pressure in the vacuum chamber was 2×10$^{-3}$ Pa, and the evacuation rate...
of 0.5 nm/min was controlled by a crucible temperature around 1,000°C. The Pt thickness was about 50 nm.

After depositing the Pt electrode substrate without using a mask, we applied the mask intersection method [18, 20] to evaluate the surface potential, which is dependent on the thickness of the PCBM film. We purchased PCBM powder, from Frontier Carbon Corporation, to use as an n-type organic semiconductor molecule for which purification was not performed. A shadow mask, which was made of stainless steel, had line and space patterns with pitches of 100 μm (Toyo Precision Parts Mfg.) in the horizontal direction. The first layer of PCBM film was deposited by a PCBM source crucible using the shadow mask in a vacuum of 1.5 × 10⁻⁴ Pa. The temperature of the crucible was maintained at 300°C during deposition, and the deposition rate of PCBM was also adjusted to 1.5 nm/min.

Next, another shadow mask was used for the deposition of the second layer of PCBM film, which had line and space patterns perpendicular to those of the first mask and the same deposition conditions. As a result, two types of film were deposited in intersecting layers. Lastly, the sample was retrieved from the vacuum evaporation chamber and then placed in the DFM/KFM system.

Figure 2 shows an optical microscope image of the sample thickness across the PCBM area on the deposited Pt electrode. The intersection of the linear patterns resulting from the accumulated deposition of the molecules of each thin film can be confirmed. The position of the PZT cantilever under DFM/KFM observation was confirmed to match the part of the intersection point in each of the four areas in the CCD image: PCBM(1)/Pt, PCBM(2)/Pt, PCBM(2) + PCBM(1)/Pt, and Pt electrode alone.

An n-type organic semiconductor was used as the PCBM molecule, and evidence of the band bending that affects organic solar cell performance can be shown. To depict the energy band diagram, we prepared two kinds of samples: one with an extremely thin film, such as that shown in Fig. 3, with a thickness of rough equality to 35 nm, as obtained by a simple summation of the thicknesses of each PCBM film.

C. Absorption of PCBM film

Figure 3 shows the absorption spectrum of the deposited PCBM film by the vacuum evaporation method, with irradiated light of 340 nm wavelength and 0.5 mW output power, and the schematic diagram of the molecular structure of PCBM is shown in the inset. The values shown in Fig. 3 were normalized to each maximum peak value. The peaks in the PCBM film fabricated by vacuum deposition method were observed at 220 nm, 270 nm, and 340 nm. From this spectrum, it was suggested that there is no thermal decomposition in the side chain of the PCBM molecule obtained using the vacuum deposition method [21]. We have determined that irradiation with a wavelength of 340 nm facilitates compatibility with the absorption spectrum of the PCBM molecule, the wavelength of the high-pressure mercury lamp light source, and monochromator specification.

III. RESULTS AND DISCUSSION

A. Observation results

A topographic image of the PCBM film on the Pt electrode is shown in Fig. 4(a). In this image, the scanning area was 20 μm × 20 μm, and the resonance frequency shift (Δf) was +20 Hz. Four different scanning areas; PCBM(1)/Pt, PCBM(2)/Pt, PCBM(2) + PCBM(1)/Pt, and Pt electrode, are clearly observed. The thicknesses of the first, second, and first-second double-layered PCBM films were 12 nm, 23 nm, and 36 nm, respectively. Figure 4(b) is a simultaneously observed surface potential image of the same scanning area shown in Fig. 4(a). The surface potential of the PCBM films and the multi-layered area on the platinum electrode on silicon substrate are also observed. The numerical values show the mean surface potentials for each film in each area (approximately 10 × 10 μm²). Figure 4(c) is the surface potential image observed on the same area under UV light irradiation conditions.

First, as shown in Fig. 4(a), the first PCBM film thickness was 12 nm, the second PCBM film thickness was 23 nm, and the thickness of the double-layered area was 36 nm. Clearly, the film thickness in the double-layered area was roughly equal to 35 nm, as obtained by a simple summation of the thicknesses of each PCBM film.

Second, the Pt electrode region was measured to be +0.58 V, as shown in Figs. 4(b) and 4(c). Here, we have referred that the work function of the Pt electrode was 4.80 eV [22]. And we have confirmed the surface potential of the Pt electrode with UV-light irradiation did not change from the magnitude of the work function. It is well known that the energy corresponding to 340 nm-wavelength light is 3.65 eV, and this can be shown by a simple calculation; this value is less than the work function of Pt. The work function of the PZT cantilever probe tip is estimated to be 5.38 eV by comparison with the work function of the Pt electrode and the PZT cantilever with the Pt-coated probe tip. However, we must note the following two points. One is that the work function of the metal electrode is not determined uniquely. Another is that the work function of the Pt film is affected by the
shape of the probe tip, as the Pt film does not correspond to bulk metallic Pt [23].

Third, surface potential images, which depend on the thickness of the PCBM molecular film, are also shown in Figs. 4(b) and 4(c). It is confirmed that the surface potential depends on the thickness of the PCBM film on the Pt substrate. The mean surface potential and film thickness for each PCBM-film-patterned area were simultaneously observed over the same scanning area. As Fig. 4(b) shows, in conditions without UV-light irradiation, the surface potential of the PCBM thin film decreases from +0.32, +0.30, and +0.29 V as the thickness of the thin film increases from 12, 23, and 36 nm, respectively.

Lastly, as Fig. 4(c) shows, in conditions with UV-light irradiation, surface potentials of +0.26, +0.25, and +0.19 V corresponded to PCBM film thicknesses of 12, 23, and 36 nm, respectively. The thickness of the PCBM was compared to the surface potential in the presence or absence of ultraviolet radiation in the thickest region, it was confirmed that a change of 0.1 V in surface potential occurred only when UV-light irradiation was present. The lapse of about 24 hours after the UV-light irradiation was stopped, the value of the surface potential was set back to the same value as the initial condition. We have confirmed experimentally the reproducibility of such phenomena.

Under the thermal equilibrium with the UV-light irradiation, the wavelength of the UV-light (340 nm, 3.65 eV) is according to the onset of the absorption band corresponding to the electronic transition between the HOMO and the LUMO levels. The results suggest that the carriers generated by light absorption were existed in the film and/or moved to the Pt substrate by the local electric field at the interface [5]. The holes are trapped in the interface state due to the PCBM film and the electrode as substrate. Since the platinum has a large work function, it works as anode electrode. The holes might be traversed via the interface state by Pt electrode and the PCBM film. Conversely, the electrons are trapped on the surface level of the PCBM film, the surface state was indicated trend of negative potential.

**B. Energy band diagram with band bending in the PCBM layer**

In Fig. 5, the relationship between surface potential and film thickness is plotted based on the results obtained through the topographic and surface-potential images. The dotted line in the diagram shows the calculated surface potential variation curve [24, 25], assuming the existence of the space-charge layer [15]. Thus, in the PCBM film layer, both the width of the space charge and the decrease in surface potential with increasing thickness are in good agreement with the band bending [26, 27]. The magnitude of the contact potential difference calculated from the FM-DFM/KFM observation results is 0.39 V, which includes the upward band bending from the PCBM/Pt interface under UV-light irradiation.

Figure 6 presents an energy band diagram showing that the variation in the surface potential is related to the thickness of the PCBM film on the Pt electrode. First, the Fermi levels for the Pt electrode and the PZT cantilever with the Pt-coated probe tip are shown to be the same at thermal equilibrium. Second, the downward band bending [20, 27] towards the interface of the Pt electrode from the PCBM film side is the most important feature of carrier behavior. We demonstrated that the curvature of the band bending is changed by the presence or absence of UV irradiation.
FIG. 6. Energy band and molecular level diagram constructed from the KFM results and cited from Refs. [17] and [22].

IV. CONCLUSION

We prepared the sample by depositing a PCBM film on a Pt/Si substrate. We applied DFM/KFM combined with the FM detection method to simultaneously observe the same scanning area under vacuum pressure and completely dark conditions, obtaining clear topographic and surface potential images both with and without UV-light illumination. The energy band diagrams clearly illustrate the relationship between the thickness and surface potential of the PCBM film on the Pt electrode, which was deposited by the mask intersection method. By irradiating UV-light, the increasingly negative charge of the PCBM films was observed. Excitation and generation of photo-electrons by UV-light irradiation is suggested, as these phenomena are described by the resulting energy band diagram from the correlation of the film thickness and the surface potential.

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