

Organic p-type/ntype/piezoelectric tricolor superlattice for photo-responsive actuator

Takashi Yanase, Taro Nagahama, Toshihiro Shimada

Hokkaido Univ.

Division of Applied Chemistry

Kita 13, Nishi 8, Kita-ku, Sapporo, 060-8628, Japan

Phone: +81-11-706-6576 E-mail: shimadat@eng.hokudai.ac.jp

Abstract

In order to combine the photovoltaic and piezoelectric activities in a single film, we fabricated tricolor superlattices consisting of an organic p-n junction and a piezoelectric polymer with sub-nm thickness control. The photovoltaic response of each repeating unit was saturated at 10 nm each as a function of the layer thicknesses. The capacitance across the 50 periods of superlattice changed by 0.009 pF upon photo-irradiation, which corresponds to a 2 nm thickness change of a 1- μm thick film. The characteristic time dependent behaviors of the capacitance of the superlattice consist of photocarrier generation, electrostriction, and poling of the piezoelectric polymer.

1. Introduction

Organic molecular materials are made of molecules that have atomically designed structures with various functions. They can be used in an amorphous form as seen in organic light emitting diodes. Amorphous films can be very quickly deposited because the deposition rate can be increased without being limited by the crystallization rate. This feature of organic materials opens the possibility of making macroscopic superlattice materials with useful functions.

In this paper, we report the fabrication of an organic superlattice with three components (tricolor superlattice, Fig. 1(a)) consisting of a p-type semiconductor, an n-type semiconductor, and a piezoelectric polymer aimed at forming a photo-responsive actuator. Although there are various types of photo-responsive actuators including photochromic molecules in the literature, there are no reports of piezoelectric materials combined with p-n junctions. We examined the photovoltaic performance of the superlattice and the displacement induced by the application of an electric field and photo-irradiation.

2. Experiments

We used a fully automated rapid multisource deposition system developed in-house[1]. Organic molecular materials were deposited by infrared light heating combined with mechanical turning of the carousel to speed up the change in the source materials. The power source and the shutter were controlled in conjunction with a quartz crystal thickness monitor. It can make superlattices with 150 different layers within 3 h. The superlattice structures consisting of the p-type semiconductor, N,N0-di(1-naphthyl)-N,

N0-diphenylbenzidine(NPB), n-type semiconductor, tris hydroxyquinoline aluminum (Alq3), and piezoelectric polyurea were fabricated on an ITO substrate. The polyurea has electric dipoles in the urea bond, of which one exists in every repeating unit in the polymer chain. The substrate surface was cleaned by a UV-ozone treatment. The surface root-mean-square roughness of the substrate was 2.1 nm. NPB was first deposited, then polyurea was synthesized on surface by an alternating deposition polymerization,9–11 then Alq3 was deposited. This sequence was repeated 50 times with different layer thicknesses. The sequence is schematically shown in Fig. 1(b). Aluminum was deposited as the top electrode for the electrical measurement. Since the as deposited polyurea does not show a piezoelectricity due to the random orientation of the molecular dipole, it was processed by poling, i.e., applying a high electric field at an elevated temperature.

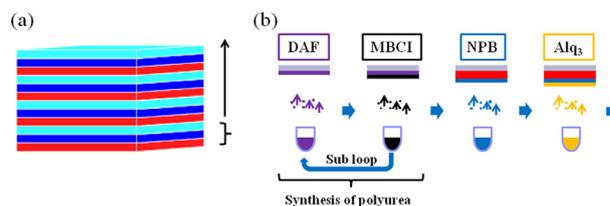


Figure 1. Device fabrication

The photovoltaic properties were studied by light irradiation from a 150W Xe lamp focused onto a 20 mm² area by a quartz lens. The size of the device between the Al and ITO electrodes was 2mm x 2mm. The photons were irradiated from the ITO side. A capacitance meter (NF 2345) was used in the four probe mode at 0.2–20 kHz. The results in the following were analyzed as a series CR circuit because the parallel component was negligible due to the four probe measurement scheme.

3. Results and discussions

AFM images of a superlattice sample with 50 repeating units (thickness: 1000 nm) before the final deposition of the Al electrode showed the RMS roughness of 4–6 nm, which corresponds to 0.1 nm per repeating unit. The deviation in the thickness is negligible when compared to the thickness of each layer (2–10 nm).

Figure 2 shows the photovoltaic response of the tricolor superlattice. The samples are as follows:

- (a) (NPB (10 nm)/polyurea (2.0 nm)/Alq3 (10 nm))₅₀,
- (b) (NPB (10 nm)/polyurea (2.7 nm)/Alq3 (10 nm))₅₀,

(c) (NPB (10 nm)/polyurea (3.4 nm)/Alq₃ (10 nm))₅₀,
 (d) (NPB (15 nm)/polyurea (2.7 nm)/Alq₃ (15 nm))₅₀.

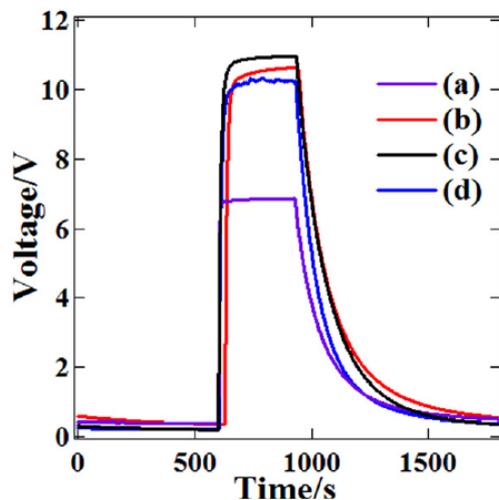


Figure 2. Photovoltaic response of the superlattice samples

It seems that the photovoltage is almost saturated as a function of the semiconductor (NPB and Alq₃) layers with a 10-nm thickness, while the thickness of the polyurea should be greater or equal to 2.7 nm. The mechanism governing the effect is as follows. If there is a through-hole or conduction in the polyurea layers, the asymmetry of the tricolor superlattice will be lost, and no photovoltage will be observed. The photovoltage of 50-period sets was ~ 11 V, corresponding to 220mV at each p-n junction. This value is very low compared to the band offset (2.5 eV) estimated from ultraviolet photoemission spectroscopy measurement. This is probably due to the effect of the input impedance of the voltmeter measuring the sample that contains insulating polyurea. The resistance of a 200-nm polyurea film was separately measured, which was greater than 100MW both in the dark and under illumination. The behaviors when the illumination started and stopped have important implications. It was found that they could be well fit by simple exponential functions, although the rise time when the illumination started and the fall time when the illumination ended were very different. It is consistent with various device parameters obtained from the insulating properties of the polyurea.

We estimated the actuator function or the photo-responsible thickness change from the device capacitance. Figure 3 shows the characteristics of (NPB(10 nm)/polyurea (2.7 nm)/Alq₃(10 nm))₅₀ sample with forward and reverse pre-biasing for poling of piezoelectric polyurea under illumination. Although they show a slow change with the time constant of ~ 100 s (Fig. 3 (a)), clear displacement was observed by taking difference (Fig.3(b)). This means that the pristine signals in Fig. 3(a) consist of the following three components: (i) spike-like rise and fall when the photo-irradiation starts and stops, respectively; (ii) exponential decay, and (iii) step-like capacitance change corresponding to the photoirradiation. Since the fastest spike-like rise and fall disappears in the difference (Fig. 3(b)), it comes from the part of the tricolor superlattice that

is not related to the poling of the polyurea. This part is the p-n junction and it is presumed that (i) is due to the change in the photocarrier concentration in the p-n junction. Since the time constant of the exponential decay, (ii) is high and symmetrical in capacitance, it is considered as the poling effect, that is, a change in the electric dipole of polyurea chain induced by the electric field. The step-like change in capacitance (iii) probably corresponds to the change in the thickness, i.e., an electrostriction effect induced by the photovoltage. The amount of the step-like capacitance change is 0.009 pF, which corresponds to the thickness change by 2 nm of a 1000 nm thick film. Although this value is very low, it amounts to 0.2%. If we use a lever mechanism, the change will be magnified. The problem of this material system is the poling effect induced by the photovoltage. It is characteristic of polymer piezoelectrics and it should be solved in the future by selecting more appropriate piezoelectric polymers that have a higher poling temperature.

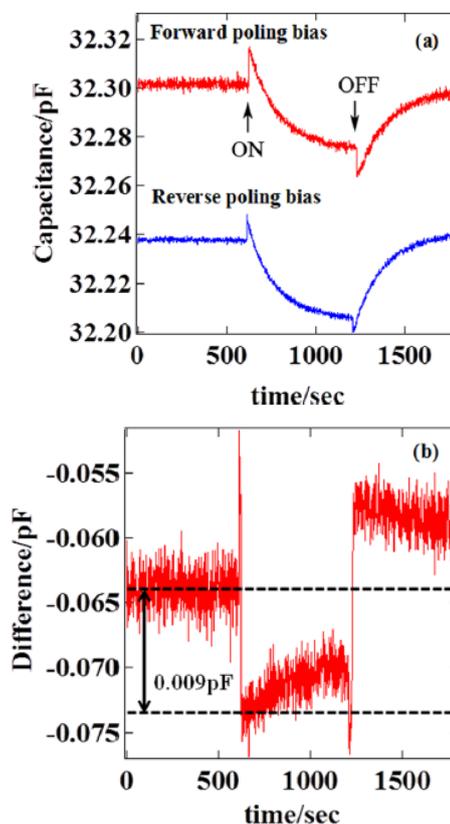


Figure 3. Photoresponse of capacitance change (a) raw data (b) difference between opposite poling

4. Conclusion

It was demonstrated that tricolor superlattices of organic p-type/ntype/piezoelectric layers exhibited a photoresponsive capacitance change. It corresponds to 0.2% change in the thickness and provides a promising pathway to fabricate photoactuators.

References

[1] T. Yanase, T. Nagahama, T. Shimada, *Appl. Phys. Lett.* 103, 133305 (2013).