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Fabrication of Piezoelectric Polyurea Films by Alternating Deposition

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We demonstrate that polyurea films can be prepared by alternating deposition with automated deposition control involving quartz crystal microbalance monitoring and optical source heating. The thickness of the films was linearly controlled by changing the repetition time of deposition, and the stoichiometry obtained was much higher than $\pm$ 5%. The surface roughness of a 600-nm-thick film was 0.5 nm, which ensures the nm thickness control of the deposited polymers. The piezoelectricity of the films was confirmed by directly measuring the current transient induced by mechanical stress and by measuring the capacitance change induced by electric field.

1. Introduction

Piezoelectric polymers[1)], such as poly(vinylidene fluoride) (PVDF), and copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) have become increasingly important with respect to the development of flexible electronics. They are potentially applicable as key components of flexible memories [2-6)], transducers [7,8)], power sources[9,10)], and printable thermal sensors [11)].

Polyurea (PU) has unique characteristics among the piezoelectric polymers because it can be fabricated by vapor deposition polymerization without by-products [12-16)]. The high dipole moment (4.9 D) in its unit structure coming from the urea bond is also attractive because the strength of spontaneous polarization strongly depends on the dipole moment. Vapor deposition polymerization is suitable for fabricating ultrathin films with controlled thickness and morphology. These unique characteristics of PU have not been explored thoroughly, because a codeposition method has generally been used for synthesis, in which stoichiometry, i.e., the ratio of two monomers, cannot easily be controlled owing to the different adsorption coefficients of monomers. Here, we report an experimental study on the possibilities of using alternating deposition to improve stoichiometry and thickness control for the fabrication of PU films. We developed an apparatus for the optically heated deposition of organic materials, which is suitable for the alternating deposition as well as

fabricating organic superlattices. We used it for the synthesis of PU films consisting of 2,7-diaminofluorene (DAF) and 4,4'-methylenebis (2-chlorophenyl isocyanate: MBCI). We examined the controllability of thickness, surface morphology, and piezoelectric properties of the films.

2. Experimental Procedure

We used a newly developed apparatus particularly designed for the fully automated fabrication of amorphous superlattices with PU sublayers fabricated by the alternating deposition. Figure 1 shows the schematic illustration of the apparatus. It uses a halogen lamp heater (75 W) for source heating. Up to six different materials can be set to a source carousel, which is precisely positioned using a stepping motor. Silicon powder was mixed with the source materials for rapid infrared absorption and heating. The thickness of each layer was monitored using a quartz crystal microbalance (QCM). The temperature of QCM and the substrate was kept at approximately 20 °C by cooling water circulation. The substrate was rotated to ensure the uniformity of the films.

The operation of this apparatus is as follows. The first source material is heated with a certain preset power and the QCM reading is monitored continuously. When the QCM reading becomes the preset value, the power of the lamp heater is cut off and the source

carousel changes the source material and the timing is recorded in a log file. The choice of materials, the amount (thickness) of each layer, the heater power, and the time allowed for one layer can be arbitrarily programmed. If the deposition rate is insufficient compared with the preset value, the power of the lamp heater is gradually increased. If the power reaches the preset maximum or the time of one sequence becomes larger than the preset alert value, the apparatus stops with an error message. The specimens presented in the following were fabricated during the normal operation of the apparatus.

The reaction for the formation of PU is established[12-14], as shown in Fig. 2. It is notable that no by-product is formed by the reaction, which is suitable for deposition polymerization. DAF (Kanto Chemical) and MBCI (Aldrich) were used as purchased. They were evaporated alternately at a vacuum pressure lower than 5×10^{-4} Pa, adsorbed on the surface of the substrate, reacted with each other, and copolymerized. We changed the deposition amount in each alternating sequence and characterized the quality of the films. First, the films were optically examined to see the inclusion of particles and then evaluated by atomic force microscopy (AFM). The thickness of PU films was measured using a stylus-type profilometer (DEKTAK 6M). Infrared (IR) spectroscopy was carried out to investigate the degree of polymerization and the conditions of post-thermal treatment. A fourier transform (FT) IR microscope (JASCO IRT-3000N) was used in the reflectance

mode.

The piezoelectric properties of the films grown under optimal conditions were estimated after the poling treatment. We employed two types of measurement. One is the measurement of the current induced by mechanical stress, and the other is the measurement of the capacitance change induced by electric field. They will be explained in detail in the following section.

We used a substrate with a different structure suitable for each characterization technique. Si substrates with a thermal oxide layer (700 nm) and an aluminum layer (200 nm) ($Al/SiO_2/Si$) were used for IR measurement. Indium tin oxide (ITO) substrates were used for piezoelectric measurement. Since the poor wettability and roughness of the substrates cause problems, N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (NPB) and tris(8-hydroxyquinolinato) aluminum (Alq_3) were deposited on the substrates as buffer layers. These materials were chosen for the future fabrication of p-type semiconductor (NPB) - n-type semiconductor (Alq_3) - piezo (PU) superlattices. We have confirmed that smooth surfaces with excellent wettability to organic materials can be obtained by using these buffer layers of 20 nm thickness. To measure the piezoelectricity of the PU film deposited on the ITO substrate, aluminum electrodes were finally deposited on the PU film. The effective area of the polyurea layer between ITO and aluminum electrodes was

approximately 2×3 mm^2.

3. Results and Discussion

It was found that PU can be synthesized by alternating deposition and the supply ratio of two monomers is a critical factor for obtaining uniform and flat PU films. Judging from the reaction scheme shown in Fig. 2, the ratio of DAF to MBCI should exactly be 1:1. Figures 3(a)-3(c) show the optical microscopy images of a DAF-rich film (weight deposition ratio of approximately DAF:MBCI = 6:7), a monomer-balanced film (ratio 6:8), and an MBCI-rich film (ratio 6:9), respectively. We can see particles on the surface shown in Figs. 3(a) and 3(c), and the color of the films was white. This is probably caused by the aggregation of surplus monomers. On the other hand, the film shown in Fig. 3(b) was free from particles and optically transparent. It was found even by visual examination that the optimal stoichiometry region is narrow, i.e., $\pm$ 5%, from the optimal QCM-based ratio. Figure 3(d) shows the AFM image of the surface of the PU film shown in Fig. 3(b). The image shows a root-mean-square roughness of 0.5 nm and a PU film thickness of 600 nm. It also shows that very smooth surfaces can be prepared if the ratio of monomers is appropriate.

Figure 4 shows the relationship between the PU film thickness measured using a stylus-type profilometer and the repetition time of the alternating deposition. Each

sequence of the deposition consisted of 150 ng/cm^2 DAF and 210 ng/cm^2 MBCI. It was confirmed that the PU film thickness was strongly proportional to the repeating times of the alternating deposition. This result was almost identical to the results obtained when the amount of each sequence was doubled or multiplied five times, including AFM and FTIR (see below) results.

Next, we examined the degree of polymerization reaction. To obtain PU films with a large piezoelectric constant, two monomers, DAF and MBCI, should completely copolymerize because the NHCONH group has the major dipole moment. The degree of polymerization reaction can be evaluated by monitoring the absorption peak at around 2270 cm^{-1} in the FTIR spectrum formed by the stretching vibration of isocyanate groups. Figure 5 shows the IR spectra of (a) the PU film grown with the optimal monomer ratio after thermal treatment and (b) the as-deposited PU film. The absorption peak at around 2270 cm^{-1} formed by isocyanate groups is observed in (b), which shows MBCI molecules. Following the previous reports on the codeposited films[12-14], we applied thermal treatment (200 ^{o}C, 10 min). The isocyanate peak disappeared after the thermal treatment [Fig. 5(a)], showing the completion of the polymerization reaction[13]. The optical transparency and surface morphology of the film did not change after the thermal treatment.

Since we confirmed that the PU films can be prepared by alternating deposition with nm

thickness control, we examined the piezoelectric properties of the films. Figure 6 shows the measurement setup that directly measures the current (time derivative of charges) induced by mechanical stress. The mechanical stress can be applied and released to the PU films with a spring. A Si wafer and a rubber film were placed between the spring and the PU films to ensure the uniformity of the applied stress. A poling procedure was applied before the measurement. The poling conditions were 100 MV/m at a temperature of 200 ^{o}C for 10 min. Figure 7 shows the piezoelectric response obtained as spikelike current signals with a picoammeter (Keithley 6487) when stress was applied and released 10 times alternately to the poled PU films sandwiched by ITO and Al electrodes. The insets in Fig. 6 show an expansion of around 600 s when the PU films were pressurized and an expansion of around 660 s when the PU films were depressurized. The direction of current flow when stress was applied was opposite to that when stress was released, and such directions were consistent with the poling direction. This indicates that the signals are purely piezoelectric by definition[16-18].

In this technique, however, it is difficult to carry out quantitative analysis because the spring-induced pressure is expected to be spikelike and the time resolution of the picoammeter is not sufficient for estimating the total charge accurately. Therefore, in order to evaluate the piezoelectric constant, we used a capacitance technique to measure the

thickness change when an electric field is applied. Capacitance is formulated by

$$C = \varepsilon \frac{S}{d} \quad , \qquad (1)$$

where ε is the dielectric constant, S is the surface area, and d is the film thickness. After the electric field application, the capacitance and thickness would become C' and d', respectively. Thus, the new formulation of capacitance is as follows:

$$C' = \varepsilon \frac{S}{d'}. \qquad (2)$$

Subtracting eq. (1) from eq. (2), we obtain the following equations:

$$C' - C = \varepsilon S(\frac{1}{d'} - \frac{1}{d})$$

$$\Delta C = -\varepsilon S \frac{\Delta d}{dd'} \cong -\varepsilon S \frac{\Delta d}{d^2} = -\frac{C}{d} \Delta d,$$

where $\Delta C = C' - C$ and $\Delta d = d' - d$. Therefore, we can estimate the piezoelectric constant d_{33} from $\Delta d/E$, where E is the applied electric field.

Figure 8(a) shows the capacitance measurements obtained when forward (+15 V, lower curve) and reverse (-15 V, upper curve) dc biases were applied to a 150-nm-thick PU film. Polarity was defined according to the definition of poling. The results clearly show the piezoelectric effect because the capacitance changes depending on the polarity of the bias. The difference in the absolute value of the change probably comes from the non-piezoelectric effect caused by bias application, such as the effect of induced carriers. To remove the non-piezoelectric effect, the difference between the different polarities was

calculated [Fig. 8(b)]. As shown in Figs. 8(a) and 8(b), $C \cong 170$ pF and $\Delta C \cong 0.090$ pF. Using these values and $d = 150$ nm, Δd was calculated as 0.079 nm. Finally, we obtained the piezoelectric constant d_{33} of 2.6 pC/N by dividing Δd by the applied voltage (30 V). This d_{33} value is smaller than the reported values (~5 pC/N)[13]. The observed difference may have come from the fact that the PU in the present experiment contains a large aromatic moiety and that the urea bond density of this PU is much lower than that of the simple aliphatic PU indicated in ref. 13.

4. Conclusions

We have demonstrated that polyurea films can be prepared by alternating deposition followed by thermal treatment. The thickness and stoichiometry of the films were effectively controlled by automated deposition control with QCM monitoring and optical heating. The piezoelectricity of the films was confirmed by directly measuring the current transient induced by mechanical stress, and the piezoelectric constant was estimated by measuring the capacitance change induced by electric field.

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Figure captions

Fig. 1. Apparatus used to fabricate the piezoelectric PU films by alternating deposition.

Fig. 2. Polymerization reaction of DAF and MBCI.

Fig. 3. Optical images of (a) DAF-rich, (b) monomer-balanced, and (c) MBCI-rich films. Particles are found on the surfaces of (a) and (c). (d) AFM image of the surface of (b). The oblique lines in (d) indicate the artifact formed by environmental vibration.

Fig. 4. Relationship between PU film thickness and repeating time of alternating deposition.

Fig. 5. FT IR spectra of (a) PU film after thermal treatment and (b) as-deposited PU film.

Fig. 6. Schematic drawing of piezoelectricity measurement setup.

Fig. 7. Spikelike current derived from piezoelectricity when strain was applied and released.

Fig. 8. (a) Changes in capacitance when dc bias voltages with different polarities were applied. (b) Difference between different polarities.

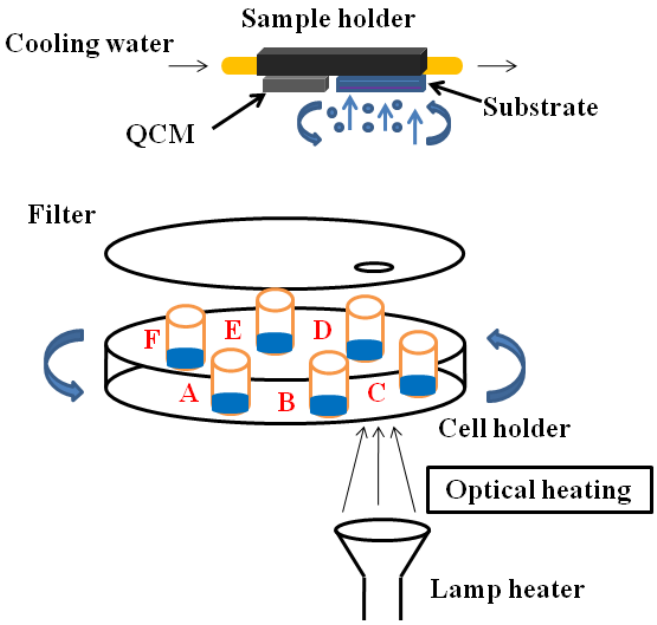


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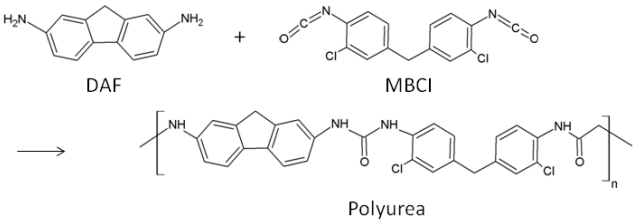


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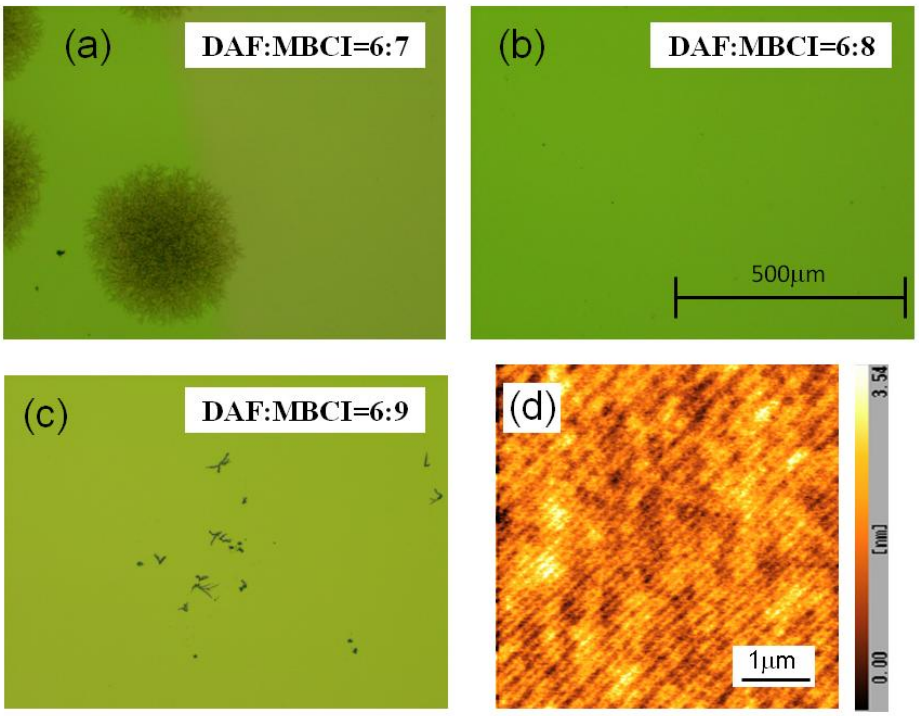


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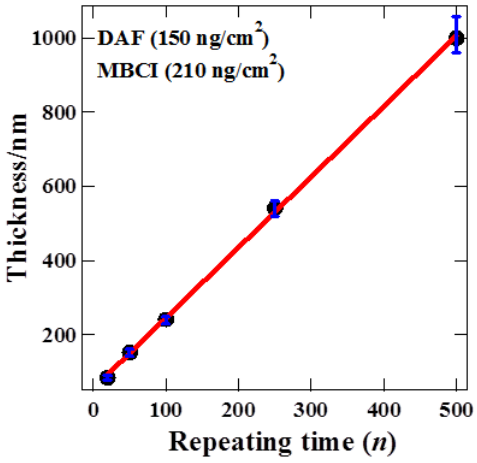


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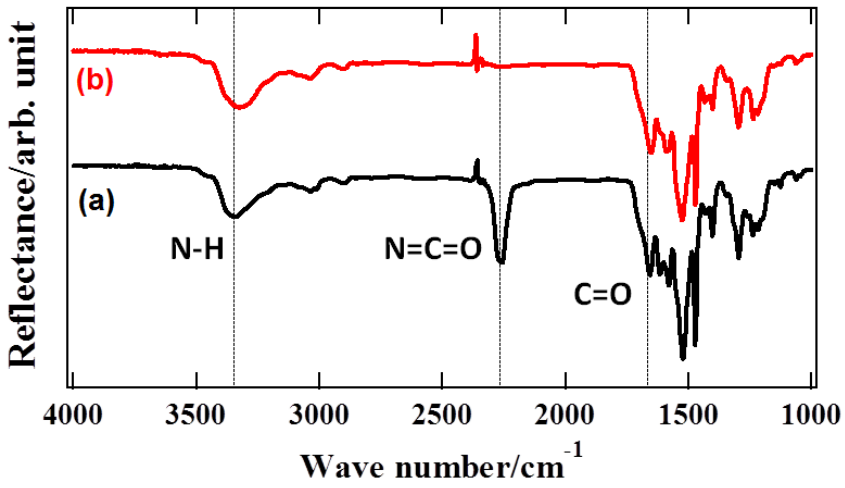


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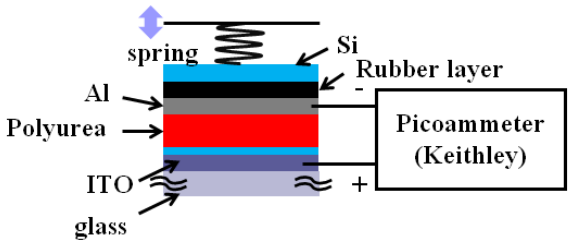


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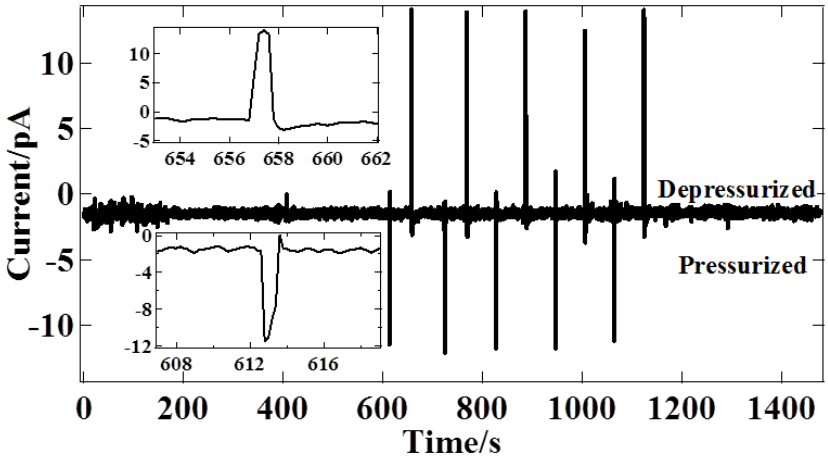


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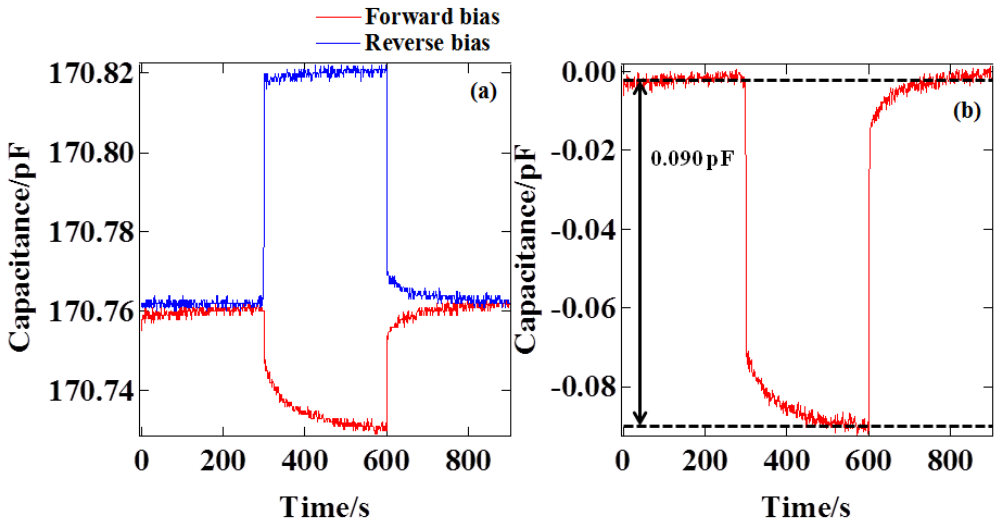


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