Electric and Pyroelectric Properties of spin-coated Polyurea Films

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Abstract

Electric and pyroelectric properties of polyurea spincoated films with superior chemical and thermal stability were investigate. Ferroelectric-like current peaks were observed in current density-electric field curves, and the measured value of electric displacement of 17000 mC/m² is much higher than expected one. One of possible reason of the too much value is residual solvent in the spin-coated films. However, pyroelectric current was clearly responded to temperature variation of the thin films. The pyroelectric coefficient of spin-coated polyurea films was estimated to be 4.13 μ C/m²K.

1. Introduction

Polyureas have attracted much interest because of superior durability such as water, chemical and thermal resistance, and good machine characteristic, therefore they have been using as fire-resistance building materials and water-resistance protective coating materials. In addition, they have been expected to show the excellent ferroelectric property, because the urea bond (NHC=ONH) has the large dipole moment (4.9 debyes), which is more than double for that of P(VDF/TrFE) (2.1 debyes) as the typical organic ferroelectric materials.

Ferroelectric materials have the spontaneous electric polarization and it can be reversed by external electric field. They have used for various application fields, such as nonvolatile memories, infrared sensors, piezo elements and so on, to their ferro-, pyro-, and piezoelectric properties. Organic materials have attracted great interest owing to their flexibility, optical transparency, and their wide use in large area electronics. Moreover using the organic materials, the eco-friendly devices can be developed due to the toxic lead and the rare metal-free. Using aromatic polyureas and aliphatic polyureas with an odd number of CH_2 groups, the ferroelectric behavior have been previously reported. These reported that the values of them were larger than that of VDF-related materials. However, the reported P_r was too larger even if all of the dipoles in polyurea are completely oriented. The too large value of P_r could not be explained by the only urea groups, therefore it has been inferred the effects of hetero-charges in crystal region, charge trapping in amorphous region, and ionic components due to partial ionized functional groups, i.e. the urea groups. The interpretation of such effects has not been always clear, because it is difficult to distinguish each charges from the charge compensation due to the orientational polarization.

In this study, we prepared the spin-coated films using odd-numbered aliphatic polyurea and investigated ferroelectric-like behavior of polyurea thin films by current densityelectric field (*J-E*) curves. In order to explain the effects of residual solvent, the temperature dependence of *J-E* curves on typical ferroelectric film added solvent films were examined. The polarizing condition in polyurea thin films was confirmed by measuring the pyroelectric coefficient.

2. Experimental

The odd-numbered polymer used in this study was polyundecylurea (PUA11) (Mw: 13000, Mn: 7000) which was obtained from Unitika Limited. Organic capacitors were fabricated as Al top electrodes/ polyurea/ Al bottom electrodes on the quartz substrates. PUA11 dissolved in 4.0 wt% of hexafluoroisopropylalcohol (HFIP) was spin-coated onto the substrates, and then melted it at 260 °C for 30 s under a nitrogen atmosphere. The molten films were quickly quenched



Fig. 1 The *J-E* curves of PUA11 thin films at a) 25 °C and b) 165 °C. The amplitude and frequency of the applied triangular voltage were 160 V and 1 Hz, respectively.

in a liquid nitrogen bath. To verify the effects of residual solvent in PUA11 films, the typical organic ferroelectric polyvinylidenefluoride (PVDF) thin films added HFIP solvent were fabricated. PVDF solution was prepared that the weight ratios of PVDF : N,N-dimethylformamide : HFIP were 1 : 19 : 5. The mixed solution was spin-coated onto the substrates at 60 °C, followed by heat treatment at 130 °C for 2 hours to obtain highly crystallized films. A series of the *J-E* curves of the PUA11 films were measured. For pyroelectric coefficient measurement, the as-quenched PUA11 films were applied DC 160 V at 150 °C, subsequently the dynamic pyroelectric current in response to an applied triangular temperature oscillation was measured.

3. Results and discussion

Figure 1 shows the *J*-*E* curves at 25 and 165 °C. The amplitude and frequency of the applied triangular voltage were 160 V and 1 Hz, respectively. At 25 °C [Fig. 1(a)], the PUA11 thin film behaves as the dielectric state, on the other hand at 165 °C [Fig. 1(b)], it obtains the clear switching of current peaks at positive and negative voltages. The integral value of the current peak indicates the electric displacement, which is estimated to be 17000 mC/m². This value is much larger than that of the other organic ferroelectric material (220 mC/m²)[1] and that of the practical inorganic ferroelectric displacement of PUA11 probably causes by some factor except the spontaneous polarization of polyurea.

The temperature dependence of *J-E* curves using PVDF thin films added HFIP solvent are shown in Fig. 2. With increasing temperature from 25 to 140 °C, the current peaks gradually become broad, and the area of peaks, i.e. the electric displacement, increase from 3.95 to 11.9 mC/m². At 120 °C, the two peaks are shown. Both the peak position and area, which are observed at the low electric field, decrease with increasing temperature, thus it is considered that the peak cause to the polarization reversal of PVDF (a solid arrow line in Fig. 2). On the other hand, both the peak position and area, which are observed at the higher one, increase with increasing temperature, it is considered that the peak cause to the HFIP solvent in the PUA11 films (a dashed arrow line



Fig.2 The temperature dependence of *J*-*E* curves using PVDF thin films added HFIP solvent.

in Fig. 2) because the peak behavior is similar to the temperature dependence of PUA11. Therefore, one of possible reasons in the large electric displacement of polyurea thin films is the effects of residual solvent in PUA11 films.

Figure 3 shows the pyroelectric current of PUA11 thin films. The range and gradient of the applied triangular temperature were from 38 to 43 °C and 0.966 °C/min, respectively. The relationship between pyroelectric coefficient *p* and current *I* is defined as the temperature derivative dT/dt and the active area *S*, and it is indicate by the following as I = pS(dT/dt). The pyroelectric coefficient is estimated to be 4.13 μ C/m²K. As discussed above, the large electric displacement in the PUA11 films can be affected by the residual solvent, however the polarization of PUA11 is aligned unidirectionally with applied external electric field, namely the PUA11 films indicate the pyroelectric state.



Fig.3 The pyroelectric current of PUA11 thin films with applied triangular temperature from 38 to 43 $^{\circ}$ C and the rate of 0.966 $^{\circ}$ C/min.

4. Conclusion

The polyurea thin films were fabricated by spin-coated and observed the ferroelectric-like behavior. The electric displacement of as-quenched PUA11 films was estimated to be 17000 mC/m². Too much value was affected residual solvent (HFIP) in the PUA11 films. However, the pyroelectric coefficient of PUA11 was estimated to be 4.13 μ C/m²K. This means that the PUA11 films observed ferroelectric-like state caused the HFIP solvent, therefore the polarization of PUA11 is aligned, namely it indicate the pyroelectric state.

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