Structural and electrical characterization of spin-coated polyurea thin films

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A B S T R A C T

Thin-film fabrication of polyurea is hindered by poor solubility in most organic solvents. We fabricated spin-coated thin films of polyurea and investigated the structural and electrical properties of the films. The as-spun films had rough surfaces and relatively high crystallinity with 4.5 nm grains, while melt-quenched films were smooth and lower in crystallinity with 2.7 nm grains. Residual solvent remained in the films at temperatures above the boiling point of the solvent. The quenched polyurea films exhibited large current peaks originating from activated impurity charges from the residual solvent in the current density-electric field curves. The pyroelectric coefficient of the spin-coated polyurea films was estimated to be 4.13 $\mu C/m^2 K$. The polyurea films maintained pyroelectricity even after the application of an electric field, thereby exhibiting potential applicability in pyroelectric devices with annealing to remove the impurity charges.

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1. Introduction

Ferroelectric materials exhibit spontaneous electric polarization that can be reversed by external electric fields. Several ferroelectric materials, including those with pyro- and piezoelectric properties, have been applied in nonvolatile memory devices, infrared sensors, and piezoelectric elements. Inorganic ferroelectric materials such as lead zirconate titanate (PZT) and barium titanium oxide ($BaTiO_3$) have been widely commercialized [1,2]. Organic ferroelectric materials have recently attracted great interest because they have excellent flexibility, optical transparency, and environmental friendliness, without toxic lead or rare metals and widely usable in large-area electronics. Poly(vinylidene fluoride) (PVDF) and the copolymer poly(vinylidene fluoride/trifluoroethylene) [P(VDF/TrFE)] are popular organic ferroelectrics among those developed for applications [3–9]. Other organic ferroelectric materials, such as croconic acids [10] and benzimidazoles [11], have also been studied.

Polyureas exhibit excellent water, chemical, and thermal resistance and good machining characteristics. Consequently, they have been employed as water-resistant protective coating materials and fire-resistant building materials. They are expected to have good ferroelectric properties because of the large dipole moment of the urea bond (NHC=ONH) (4.9 debyes) [12], which is more than twice that of P(VDF/TrFE) (2.1 debyes). The ferroelectric behavior of aromatic polyureas [13–16] and aliphatic polyureas with an odd number of CH_2 groups [12,17–19] have been studied. These studies reported remnant polarizations (P_r) of odd-numbered aliphatic polyureas of 440 mC/m^2 [17]. The ferroelectricity of amide polymers, in which the amide bond (NHC=O) is structurally similar to the urea bond, such as odd-numbered nylons [20–23] and even-numbered nylons, has also been studied [24].

For fabricating polyurea films, melt-pressing [17,25], vapor deposition polymerization (VDP) [13,19,26], and molecular layer deposition [27,28] are the most common techniques. Thin films fabricated by these methods have disadvantages of a minimum thickness greater than 20 μm and chemical and physical impurities regarding the chemical structure or degree of polymerization. This is attributed to the poor solubility of polyureas in most organic solvents, which inhibits thin film fabrication by wet processing. Very few studies have reported on the wet-process fabrication of polyurea thin films [29]. In this study, we spin-coated thin films of odd-numbered aliphatic polyurea and investigated the film structures. In addition, the current density-electric field (J-E) curves were measured to evaluate the basic electrical properties of the films. The polarizing conditions in the films were confirmed by measuring the pyroelectric coefficient.

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2. Experimental methods

The polymer used in this study was the odd-numbered poly-undecylurea (PUA11, M_w: 13000, M_n: 7000) supplied by Unitika Limited. PUA11, synthesized from carbon dioxide and 1,11-diaminoundecane, has a linear polyurea structure (Fig. 1) with polar urea (NHC=ONH) and aliphatic (-(CH$_2$)$_n$-, n = 11) components. Thus, the polymer dipole moment is normal to the chain axis. PUA11 was dissolved in 4.0 wt% hexafluoroisopropylalcohol (HFIP; Tokyo Chemical Industry), which, while not a popular organic solvent, has been used in similar structural nylon solutions [22]. The solution was spin-coated at 2500 rpm for 30 s onto an Al (bottom electrode)-coated quartz glass substrate under N$_2$ at 25 °C. The PUA11 films were annealed at 260 °C, above the melting point of PUA11 (Fig. 2), for 30 s under N$_2$ before being quenched in a liquid nitrogen bath. In the differential scanning calorimetry (DSC) curve from − 20 to 260 °C (Fig. 2), only one peak is observed at the PUA11 melting point during the heating and cooling processes; phase and glass transition peaks are not observed. The Al top electrode was vacuum evaporated. The surface morphology of the PUA11 film was observed using an atomic force microscope (AFM) in tapping mode (JSPM-5200, JOEL). The scanning area was 25 × 25 μm and the scan speed was 1.0 ms/point. Si cantilevers (Olympus) with resonant frequencies of ~300 kHz and spring constants of ~42 N/m were used. The structure of the PUA11 films were elucidated by an out-of-plane X-ray diffraction (XRD) pattern, obtained with a Rigaku Ultima IV Protectus operated at 40 kV and 40 mA, with Cu-Kα radiation. The urea bonding conditions and chemical structures of the thin films were evaluated using Fourier transform infrared spectroscopy (FT-IR); spectra were obtained using a reflection absorption spectroscopic (RAS) method in ambient atmosphere with a JASCO FT/IR-660Plus. The resolution and cumulative number of measurements were 4 cm^{-1} and 512 cycles, respectively.

The *J-E* curves of the PUA11 films were measured at temperatures from 25 to 160 °C using a current−voltage (*I/V*) converter (Model 6252 Rev. C, Toyo Corporation), an arbitrary waveform generator (Biomation 2414B), and an analog-to-digital converter (WaveBook 516E). The pyroelectric coefficient *p* was obtained by applying a triangular thermal wave to the PUA11 films after applying an electric field of 110−160 MV/m at 160 °C. The pyroelectric current of the polyurea films in response to this applied triangular temperature oscillation around 40 °C was measured using an electrometer (Model 4200-SCS, Keithley).

3. Results and discussion

3.1. Morphology and structure of the PUA11 thin films

The thickness of the spin-coated PUA11 thin films was controlled between 0.5 and 2.0 μm PUA11 films with 4.0 wt% solution were ~1.2 μm thick. Fig. 3(a) and (b) depict AFM images of the as-spun and quenched PUA11 thin films, with average roughnesses of 44.0 and 3.9 nm, respectively. The relative smoothness of the quenched films results from fluidization by annealing above the melting point of the materials. As seen in Fig. 3(a), the as-spun
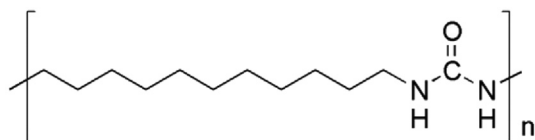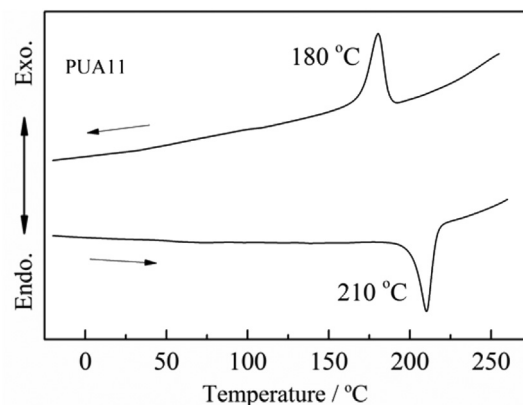

Fig. 2. DSC curves of PUA11 at heating and cooling rates of 10 °C/min.

PUA11 film has a rough surface with large undulations of ~300 nm height and ~4 μm width. Fig. 3(b) shows the large flat surface of the quenched PUA11 film with some bumps of approximately 30 nm height and 200 nm width. Because of the roughness, the as-spun films could not be electrically characterized in this study because of electrical short-circuiting. This suggests that annealing at temperatures exceeding the melting point of the films is necessary after spin-coating for electrical applications.

The XRD patterns of the as-spun and quenched PUA11 films clearly differ (Fig. 4). The XRD pattern of PUA11 powder exhibits diffraction peaks at $2\theta = 7.00°$ (1.26 nm), 21.05° (0.422 nm), and 23.00° (0.387 nm), corresponding to the (001), (100), and (010) reflections, respectively [30,31]. The broad diffraction peak observed in the quenched PUA11 films at 20.35° (0.436 nm) is associated with the (100) reflection, suggesting the formation of small crystallites of PUA11 by quenching the molten films. The as-spun PUA11 films exhibit higher diffraction peak intensities, and thus are higher in crystallinity, than the quenched films. The crystal grain sizes of the as-spun and quenched films are ~4.5 and ~2.7 nm, respectively, according to the Scherrer equation $L = K\lambda/(\beta \cos \theta)$, where L is the crystal grain size, K is the shape factor and equal to 0.89 here, λ is the X-ray wavelength, and β is the full width at half-maximum for the diffraction peak [30]. The higher crystallinity of the as-spun films arises from the dipole interactions of urea groups in the PUA11 molecules. However, the as-spun thin films must be annealed to remove residual solvent. Devices using annealed films may show better performances if smooth film surfaces form during annealing.

The FT-IR spectra of the as-spun PUA11 films measured at temperatures between 30 and 150 °C are shown in Fig. 5. Remarkable changes in the absorption peaks with changes in the temperature are observed at 1620, 1570, 1375, 1282, 1181, and 1100 cm^{-1}, corresponding to C=O stretching; ν(C=O), N−H in-plane bending; δ(NH), COH in-plane bending; δ(COH), C−F asymmetrical stretching; ν_{as}(CF), ν_{as}(CF), and C−O stretching; ν(C−O), respectively. Other peaks at 1475, 1465, 1270 and 1240 cm^{-1} correspond to the alkyl chain, namely, δ(CH$_2$), δ(CH$_2$), CH$_2$ rocking; r(CH$_2$), and r(CH$_2$), respectively. Peaks at 1620 and 1570 cm^{-1} originate from the urea groups [32−35], With increasing temperature, the ν(C=O) and δ(NH) peaks shift from 1620 to 1630 cm^{-1} and from 1575 to 1567 cm^{-1}, respectively. The increased wavenumber of ν(C=O) indicates weakening of the carbonyl bonds [12,34−36]. This suggests that the polyurea intermolecular distance widens and that the hydrogen bonds of polyurea films become disordered with increasing temperature. The peaks at 1375, 1282, 1181 and 1100 cm^{-1} originate from the HFIP solvent [37−39], and disappear at 80 °C. HFIP remains in the PUA11 films at 80 °C, above

Fig. 1. Chemical structure of polyundecylurea.