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Photo-Cured Polymeric Insulating Materials Having High-Performance Electrical Properties

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Photo-Cured Polymeric Insulating Materials Having High-Performance Electrical Properties

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Chemically and thermally stable, durable, photosensitive polymeric insulating materials are in great demand for fabrication of electronic devices. In this study, we have synthesized photosensitive polymers by mixing a host polymer and photosensitizer, and explored their chemical and electrical properties. Uniform, chemically stable, mechanically flexible pinhole-free films can be formed by spin-coating, baking and photolithography at a relatively low temperature (<150°C); these films are clearly defined by photolithography technique. Their electrical properties showed excellent electrical performance as insulators which depend on chemical structure of a host polymer used and photosensitizer (DAST) concentration. In particular, the insulating property was improved after photo-cross-linking reaction, which is adequate for plastic-based electronic devices such as organic thin-film transistor and flexible display.

Keywords: electrical properties; photosensitivity; polymer insulator

INTRODUCTION

Polymeric materials for insulating electrical equipment/device have received increasing attention recently in place of inorganic insulating materials because of their advantages in flexibility, low weight, the ability to form intricate shapes, and low manufacturing cost. Processing steps for most polymer insulators require a relative low temperature that allow a wide range of substrate possibilities and make them attractive materials for many plastic-based electronic applications

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such as smart cards, electronic tags, and flexible displays [1,2]. For these electronic devices, polymeric insulating materials must be pinhole-free and have a high dielectric strength, insulation resistance, and good long-term stability. Other typical requirements for this material are: it must have good adhesion to a substrate used; it must be able to be applied by conventional techniques such as spin coating and inkjet printing; it must be compatible with subsequent processing; it must be insoluble to organic solvents/etchants that will be used in processing. Additionally, if it could be patterned by conventional photolithography, it is obviously advantageous for various electronic devices.

Electrical properties in polymers, which are their response when an electrical field is applied to them, depend on their chemical composition [3–5], environment, physical state, purity, and types of electrodes used. In particular, chemical structures of these polymers affect their physical state and sensitivity to the environments. The electrical properties of polymer relate to an extremely diverse range of molecular phenomena. Therefore, to achieve the optimum performance of electrical properties, understanding of the electrical insulating phenomena and a proper selection of polymer as an electrical insulating material are desired.

There is growing interest in a few polymer insulators, such as polyimide [6–10], poly-p-xylene [5], poly(vinyl phenol) (PVP) [11–15], poly(methyl methacrylate) (PMMA) [13,16–19], and poly(vinyl alcohol) (PVA) [20], due to their inexpensive manufacturing cost and prospective for integration into large area and flexible electronic applications. These polymers have the disadvantages, however, of a poor chemical stability and/or difficulty in high-resolution patterning for defining an insulator layer. Therefore, chemically stable, durable, photosensitive polymer as an insulating material is in great demand for fabrication of electronic devices.

In this study, we have prepared photosensitive polymer insulators, which are prepared by mixing a conventional polymer and photosensitizer, and explored their chemical, physical and electrical properties.

EXPERIMENTAL

Materials

PVA, PVP, and poly(vinyl pyrrolidone) (PVPr) were purchased from Sigma-Aldrich and Tokyo Chemical Industry Co., Ltd., and used as host polymers without purification. Dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) used as solvents without purification,

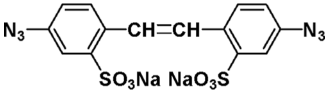


FIGURE 1 Chemical structure of 4,4′-diazidostibene-2,2′-disulfonic acid disodium salt (DAST) used in this study.

which were purchased from Tokyo Chemical Industry Co., Ltd. 4,4′-Diazidostibene-2,2′-disulfonic acid disodium salt (DAST, see Fig. 1) as a photosensitizer was supplied from Tokyo Chemical Industry Co., Ltd.

Formation of Photo-Cured Polymer Insulator

Glass substrate, with dimensions of $10 \times 10\,\text{mm}^2$, was washed with acetone and deionized water in an ultrasonic bath and then dried in a stream of nitrogen. For characterization of insulating properties of photo-cured polymers, we fabricated a device with metal-insulator-metal (MIM) structure. Figure 2 shows a schematic diagram of a device used for evaluation of electrical behavior.

The device is formed as follows: A 50-Å-thick Ti and a 500-Å-thick Au layer as a bottom electrode were deposited on the glass by e-beam evaporation, which was defined using a shadow mask during vapor deposition in a high vacuum of $<10^{-6}$ Torr. Photo-curable blends were prepared by mixing the host polymer and DAST. PVA-DAST blend was obtained from PVA (10 g) and DAST (0.5 g) in DMSO (125 g) at ambient temperature. First PVA was dissolved in DMSO, and then DAST added to the solution. PVP-DAST was similarly prepared from PVP (10 g) and DAST (1.6 g) in DMF (62.5 g). PVPr-DAST was prepared by mixing PVPr (10 g) and DAST (1.0 g) in deionized water (200 g). To form the polymeric insulating films, the photo-curable blends were spin-coated onto the Au/Ti/glass and then heated at $140 \sim 150$°C to evaporate the solvent. The dried films were

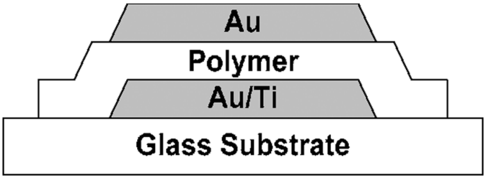


FIGURE 2 A cross-section of the device of used for evaluation of electrical behavior.

subsequently irradiated to form the photo-cured polymer film (exposed light energy, $56 \sim 84\,\mathrm{mJ/cm^2}$). Photo-reaction was performed using a high-pressure mercury (Hg) lamp with a light intensity of $7\,\mathrm{mW/cm^2}$ (at 366 nm). Finally, an Au top electrode with a thickness of 800Å was also evaporated via a shadow mask directly onto the polymer film.

Characterization

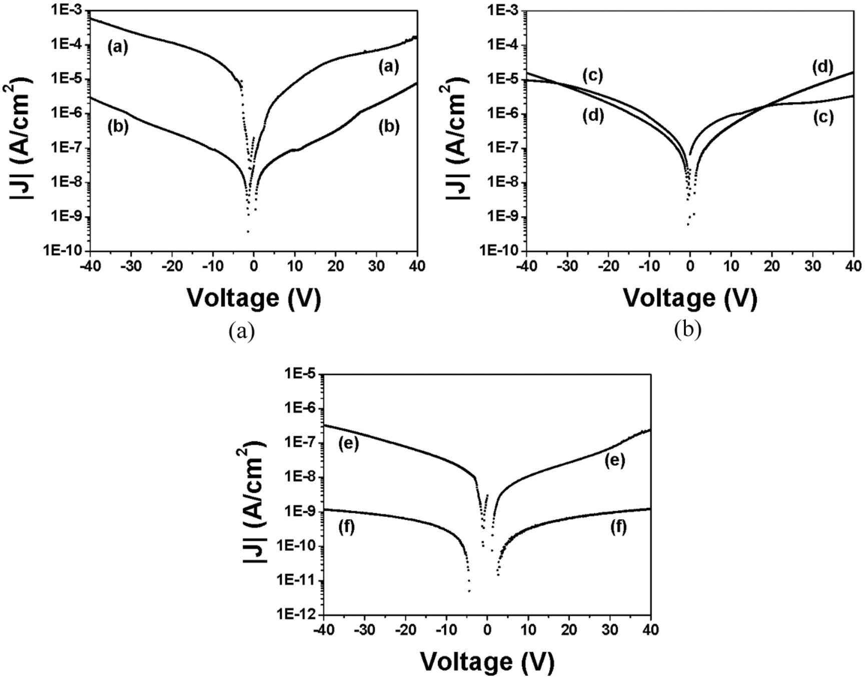
Surface roughnesses of these polymers, which are basis for subsequent processing, were studied by atomic force microscopy (AFM). Resolution of the photo-cured polymer patterned by photolithography was evaluated with SEM (FEI, SIRION). The polymer thickness was measured using a Tencor Instrument Alpha-Step 500. For electrical measurements of the fabricated device, a parameter analyzer (HP 4145B, Hewlett Packard) was used as a voltage source and current measurement unit. Dielectric constants were obtained from capacitance-frequency (C-F) and impedance measurements carried out with HP 4194A impedance analyzer.

RESULTS AND DISCUSSION

The photo-cured films exhibit good adhesion to a glass substrate. By AFM, the surface of all photo-cured polymers appears almost completely unstructed. The films possess root-mean-square (rms) roughness of $<1\mathrm{nm}$ and the maximum difference in height (peak-to-valley) are about 10 nm.

Effect of Photo-Cross-Linking Reaction

To compare electrical characteristics of the host polymer before and after the photo-cross-linking reaction, we investigated current-voltage (I-V) characteristics of the photo-cured polymers and their host polymers; the results are shown in Figure 3. The I-V measurements were recorded in accumulation region while a positive/negative voltage (from 0 to $\pm 40\,\mathrm{V}$) was applied across the device. As is evident, the leakage current density (J) of the photo-cured polymer decreases by $2 \sim 3$ orders of magnitude compared to that of its host polymer. At a voltage of 10 V applied across the photo-cured PVA layer (corresponding to an electric field of 0.27 MV/cm), we measure a current density of $8.6 \times 10^{-8}\,\mathrm{A/cm^2}$. At 40 V the current density is $7.9 \times 10^{-6}\,\mathrm{A/cm^2}$. The current density of the photo-cured PVP and PVPr are $5.0 \times 10^{-7}\,\mathrm{A/cm^2}$ (PVP; thickness, 7000 Å) and $3.1 \times 10^{-8}\,\mathrm{A/cm^2}$ (PVPr, thickness, 2800 Å) at 10 V. It is known that a stress in polymer film caused by



(a) (b)

(c)

FIGURE 3 Leakage current density (J) versus voltage for various polymers: (a) only PVA (thickness, 3720 Å); (b) PVA (10 g)/DAST (0.5 g) (thickness, 3670 Å); (c) only PVP (thickness, 7000 Å); (d) PVP (10 g)/DAST (1.6 g) (thickness, 5750 Å); (e) only PVPr (thickness, 10350 Å); (f) PVPr (10 g)/DAST (1.0 g) (thickness, 2800 Å).

photo-crosslinking reduces the insulation in many cases. However, according to our results, although the change in the I-V profiles of the photo-cured PVP was smaller than those of the other photo-polymers, the insulating property was improved after the photo-reaction. This result might be related to a decrease in the free volume and an increase in the molecular weight of the photo-cured polymer [21].

We next investigated dielectric properties from frequency measurements performed on Au/polymer/Au structures. The area of the capacitor is 1 mm^2. The result obtained for the capacitor structure with the photo-cured PVA (thickness, 3670 Å) is displayed in Figure 4. Dielectric constants of polymers, in general, are known to decrease gradually with increasing frequency. The photo-cured PVA has a dielectric constant of approximately 5.59 at 1 KHz and 4.25 at

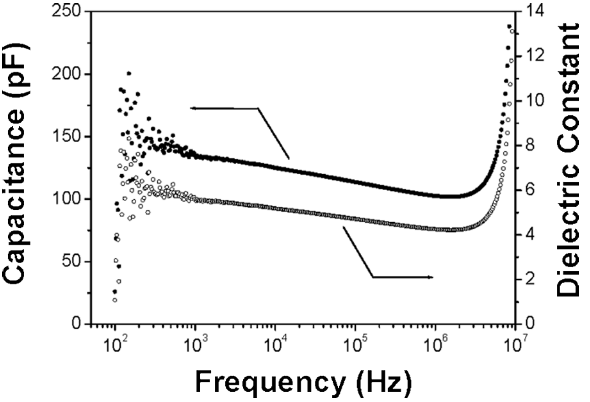


FIGURE 4 Capacitance-frequency characteristic and dielectric constant for photo-cured PVA at room temperature.

1 MHz. This variation in dielectric constant is attributed to the frequency dependence of the polarization mechanisms [4].

Table 1 presents the measured dielectric constants for both the host and photo-cured polymers. A small reduction in dielectric constant is observed by incorporating a cross-linking unit to the host polymer. Chemical/physical properties of polymers are a basic factor in the determination of dielectric behavior. Dielectric behavior of a polymer is determined by the charge distribution and the statistical thermal motion of polar groups [3]. Cross-linking tends to decrease the effective dipole moment caused by thermal motion of polar groups [22]. A relative flexible polar group, on the other hand, tends to increase the effective dipole moment [22]. Therefore, such changes in the dielectric constants (see Table 1) might occur mainly by the different behavior of thermal motion of polar groups.

To evaluate a quality of the photo-cured insulating film, we have also investigated a capacitance-voltage (C-V) characteristic during measurement sweeps at 1 MHz. Figure 5 shows a C-V plot of the photo-cured PVA. From the result displayed in Figure 5, we did not observe a significant hysteresis shift of capacitance behavior while sweeping the voltage from positive (+10 V) to negative (−10 V) and back again. Although no known polymer is completely free of conduction process, this result indicates that the photo-cured PVA is not influenced by impurities that provide small concentrations of charge carriers in the form of ions and/or electrons and new charge carrier injected through the electrode during measurement sweeps at 1 MHz. MHz. The C-V characteristics of the photo-cured PVP and PVPr were

TABLE 1 Dielectric Properties of the Host Polymers and Photo-Cured Polymers

	Mw	Solvent (wt %)	DAST content (g/10 g of polymer)	Soft-baking	UV expose (exposed light energy)	Developer	Post-baking	Thickness (Å)	Dielectric constant (at 1 MHz)
PVA	124,000 ~ 186,000	DMSO (8%)	0	150°C/10 min	0	–	0	3720	4.4
			0.5		56 mJ/cm^2	Water	150°C/10 min	3670	4.2
PVP	20,000	DMF (16%)	0	145°C/10 min	0	–	0	7000	6.2
			1.6		84 mJ/cm^2	Acetone	150°C/10 min	5750	4.7
PVPr	630,000	Water (5%)	0	140°C/10 min	0	–	0	10350	3.4
			1.0		56 mJ/cm^2	Water	150°C/10 min	2800	2.8

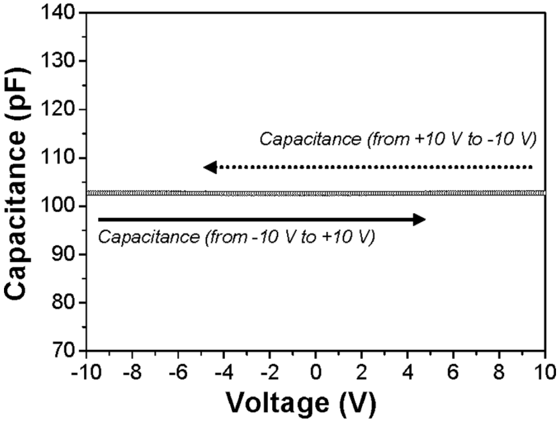


FIGURE 5 Capacitance-voltage characteristic for photo-cured PVA.

also investigated, which exhibited similar behavior to that of the photo-cured PVA.

These photosensitive films are clearly defined by lithography technique. Figure 6 shows SEM image of the photo-cured PVA patterned. It shows the good resolution results obtained under optimized conditions. The minimum feature of the photo-cured polymers are about 2 μm.

Effect of DAST Concentration

To confirm effects of DAST, we investigated electrical properties of the photo-cured polymers as a function of DAST concentration. We prepared four devices with the photo-cured PVA layer of differing

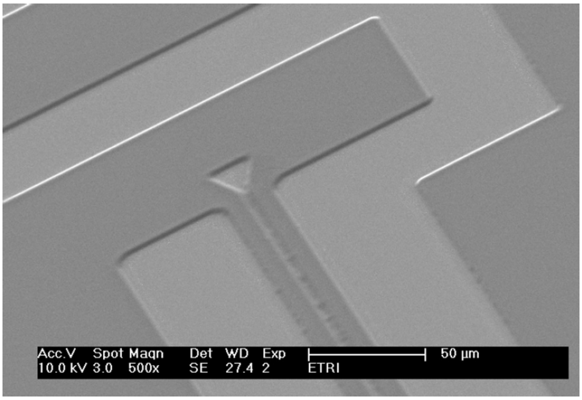
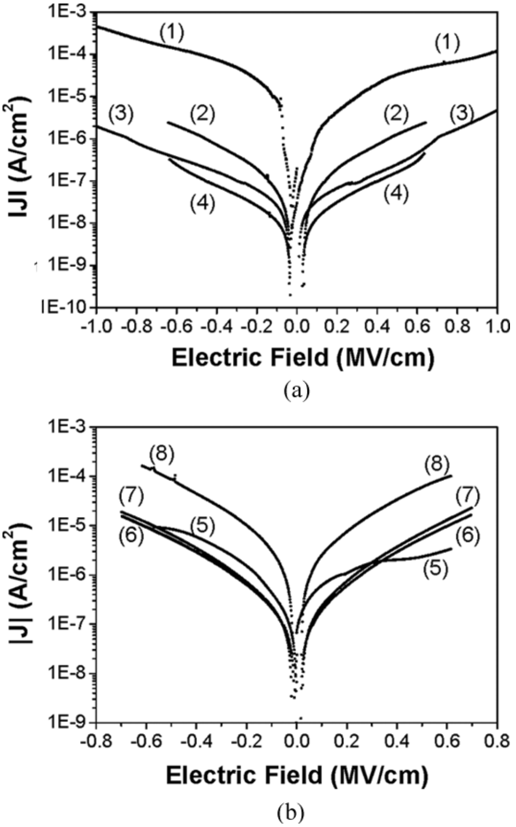


FIGURE 6 SEM image of photo-cured PVA.

DAST content: device 1, PVA (10 g)/DAST (0 g) (thickness, 3720 Å); device 2, PVA (10 g)/DAST (0.3 g) (thickness, 6240 Å); device 3, PVA (10 g)/DAST (0.5 g) (thickness, 3670 Å); PVA (10 g)/DAST (1.0 g) (thickness, 6300 Å). In this experiment, the same light energy (56 mJ/cm^2) used to form the cross-linked insulating film. As shown in Figure 7(a), at an electric field of 0.5 MV/cm, the current densities are 3.3×10^{-5} A/cm^2 (device 1), 1.2×10^{-6} A/cm^2 (device 2), 2.4×10^{-7} A/cm^2 (device 3), and 1.6×10^{-7} A/cm^2 (device 4), respectively.



(a)

(b)

FIGURE 7 (a) Dependence of DAST concentration on insulating property of photo-cured PVA: (1) only PVA (thickness, 3720 Å); (2) PVA (10 g)/DAST (0.3 g) (thickness, 6240 Å); (3) PVA (10 g)/DAST (0.5 g) (thickness, 3670 Å); (4) PVA (10 g)/DAST (1.0 g) (thickness, 6300 Å). (b) Dependence of DAST concentration on insulating property of photo-cured PVP: (5) only PVP (thickness, 7000 Å); (6) PVP (10 g)/DAST (1.6 g) (thickness, 5750 Å); (7) PVP (10 g)/DAST (2.5 g) (thickness, 5730 Å); (8) PVP (10 g)/DAST (4.0 g) (thickness, 6500 Å).

TABLE 2 Dielectric Constants as a Function of DAST Concentration

	Solvent (wt%)	DAST content (g/10 g of polymer)	UV expose (exposed light energy)	Thickness (Å)	Dielectric constant (at 1 MHz)
PVA	DMSO (8%)	0	0	3720	4.4
		0.3	56 mJ/cm^2	6240	4.3
		0.5		3670	4.2
		1.0		6300	4.2
PVP	DMF (16%)	0	0	7000	6.2
		1.6	84 mJ/cm^2	5750	4.7
		2.5		5730	4.2
		4.0		6500	4.1

It was observed that the insulating property enhanced with increasing DAST content.

We next explored the I-V characteristics of the photo-cured PVP of differing DAST concentration, as shown in Figure 7(b). It was observed that with increasing DAST content, however, the I-V profile shifted to a high current density. The molecular weight and molecular weight distribution are fundamental properties of polymers which affect a polymer's bulk density, crystallinity, morphology, and conductivity. In general, the molecular weight effect is very evident in the low molecular weight region [23]. PVP used has a relatively low molecular weight (Mw, 20000). Moreover, in this case, high DAST concentration (>13.7 wt% of PVP) is necessary for photo-cross-linking of PVP. Therefore, such change in the insulating property might be caused by unreacted residual PVP and low molecular fractions because of low molecular weight of PVP and high DAST concentration, independently of the photo-crosslinking. However, this remains unclear at present. Dielectric constants as a function of DAST concentration is shown in Table 2. The chemical structures of the host polymer and DAST concentration make it possible to control dielectric constants of the photo-cured polymers.

CONCLUSIONS

We found that the photosensitive polymeric insulating materials, which were prepared by mixing host polymers and DAST, exhibit good chemical, physical and electrical properties. They can be formed by a relatively low temperature (<150°C). These polymer films formed by spin-coating method exposed to radiation undergo photo-cross-linking and the corresponding image is developed by dissolving the unexposed polymer with water or acetone. The photo-cured polymer showed very low current density compared with that of its host polymer, indicating that its photo-cross-linking reaction using DAST improved the insulating property of the host polymer. This behavior is affected by the chemical structure of the host polymer used and DAST concentration. Dielectric constant decreases with increasing DAST content, however, the photo-cured polymer shows a high dielectric constant which is suitable to plastic-based organic device fabrication such as organic thin-film transistor. Photo-reaction using DAST might be applied to various polymers with the aim of development of new photosensitive polymer insulator having high dielectric constant.

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