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All-polymer capacitor fabricated with inkjet printing technique

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Abstract

All-polymer capacitors have been fabricated only by the inkjet printing technique. A conductive polymer, poly(3,4-ethylenedioxythiophene), has been employed as the electrode material of the capacitor. A precursor-route polyimide was applied as the insulator of the device. The fabrication process of the inkjet printed all-polymer capacitor has been demonstrated. The electrical characteristics of the polymer capacitor, analogous to that of the common parallel plate capacitor, are discussed in detail. The all-polymer capacitor has been applied to the polymer RC filter circuits. The characteristics of the inkjet printed polymer RC filter are also demonstrated.

Keywords: Inkjet printing; All-polymer capacitor; RC filter

1. Introduction

The discovery of high conductivity in the doped polyacetylene in 1977 [1] has aroused considerable interests in the applications of polymeric semiconductor devices. The first organic thin film transistor (TFT) was reported in 1983, in which polyacetylene was the active layer [2]. Following that, the first all-polymer thin film transistor was reported in 1990 [3]. In 1994, Garnier et al. [4] reported the first all-polymer transistor by screen-printing technology. Organic microelectronic devices are attracting considerable attention due to their processing advantages over traditional inorganic devices. They are potentially useful in a number of applications such as electronic luggage tags [5] and gas sensors [6].

Many techniques have been used in the fabrication of organic and polymer microelectronic devices such as lithography, spin coating, thermal evaporation, and printing. Various printing techniques including screen-printing [4,7,8], microcontact printing [9,10], and inkjet printing (IJP) [11,12], are of great interest. Among these printing techniques, the IJP has been gaining more attention because polymer devices fabricated by the IJP technique have the advantages of simplicity of fabrication, compatibility with various substrates, availability of non-contact and no-mask patterning, low temperature processing, no vacuum processing, and low cost. IJP has been used to fabricate the all-polymer transistor [11–14], polymer light emitted diode (PLED) [15–17], and nanoparticle microelectromechanical systems [18]. The polymer capacitor only by IJP has not been reported, possibly because it is difficult to print out the insulating polymers, most of which are insoluble or are solutions but easy to cause clogging problems [17]. Our approach to overcome this problem is to print the insulating layer of polyimide (PI) through the soluble precursor without clogging the nozzle. Combined with the inkjet printed conductive polymer of poly(3,4-ethylenedioxythiophene) (PEDOT) as the electrodes of the parallel plate capacitor, the all-polymer capacitor has been fabricated and characterized.

2. Experiments

The inkjet printer used was a commercial Epson Stylus color 480 SXU printer with the resolution of

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720×720 dpi. The printing head uses a piezoelectric ceramic, which squirts the ink droplets from the nozzle by piezo crystal deformation [19]. For IJP technique to work, the polymer must be air-stable and solution processable. For the all-polymer capacitor, PEDOT doped with poly(styrene sulfonic acid) (PSS), (Baytron P from Bayer Company) acts as the top and bottom electrodes owing to its high conductivity. PEDOT is a type of polythiophene that has received much attention during the last several years. In its doped state, PEDOT can be transparent, light blue with high conductivity up to 500 S/cm and has a particularly high stability in this doped state [20]. This enables it to be used in the applications such as the electrodes for photodiodes [20], all-polymer transistors [12], as well as our capacitor. Viscosity is one of the important characteristics that should be considered for the materials used in the printing process. Our experiments show that the solution with viscosity higher than 5 mPa s would be hard to be printed out through the tiny nozzle. The original PEDOT/PSS water solution with viscosity of 80 mPa s is diluted with water so that it could be printed out from the commercial printer without clogging the printer head. As for the insulating material, we have tried many insulating solutions, such as polytetrafluoroethylene (PTFE) and poly(4-vinylphenol) (PVP), but they all block the printer nozzle after being printed out once or twice. Finally, the poly(biphenyltetracarboxylic dianhydride-co-phenylenediamine) (PBPDA-PD) (from Aldrich company) was chosen because PBPDA-PD will form insoluble PI upon heating [21], a very good insulator that has been widely used in thin films due to its high dielectric strength of 22 kV/mm. Fig. 1 shows the structure of PEDOT/PSS and PI, respectively.

Fig. 2a shows the cross-section of the all-polymer capacitor. First, two layers of PEDOT were printed on the substrate to act as the bottom electrode. Each layer of PEDOT is heated on a hot plate at 50 °C for 2 min to dry it completely and make it more uniform. After printing the bottom PEDOT layer, three layers of PBPDA were printed out on the top of the previous pattern. The annealing temperature for PBPDA at 50 °C will make PBPDA polymerized into PI [21]. Three layers of PBPDA were printed to make sure that no pinholes exist in the insulating layer and thus avoid a short circuit between the two electrodes. After that, two layers of PEDOT were printed on top of the PI layer at the same annealing condition. Fig. 2b shows the photo of a fab-

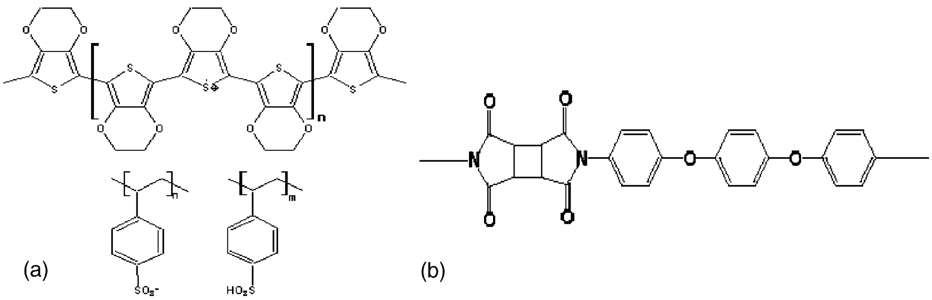

Fig. 1. (a) The chemical structure of PEDOT/PSS. (b) The chemical structure of PI.

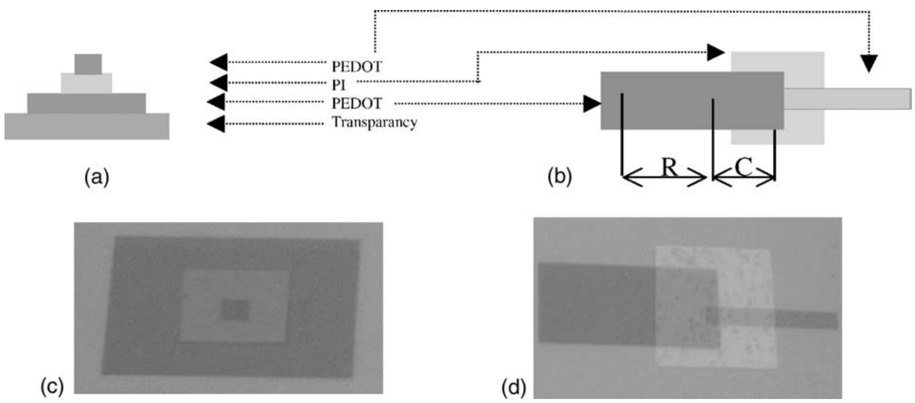

Fig. 2. (a) The cross section of the all-polymer capacitor. (b) The structure design of the RC filter. (c) Picture of the fabricated polymer capacitor. (d) Picture of the fabricated polymer RC filter.

ricated all-polymer capacitor. The effect area of the capacitor (overlapped area between the top electrode and the bottom electrode) is 2 mm by 2 mm. RC filter circuits have also been fabricated based on the all-polymer capacitor. Fig. 2c shows the design of the RC circuit, in which the resistor was also made of PEDOT/PSS. Conductive glue (epoxy) is used to attach three metal wires as the electric leads on the two electrodes of the capacitor as well as the resistor in order to connect the RC circuit to a function generator and an oscilloscope. Fig. 2d shows the printed polymer RC filter.

3. Results and discussions

The *C–V* characterization of the printed capacitor was measured by the Keithley 595 *C–V* system in an air environment, as shown in Fig. 3. It shows that the *C–V* curve is almost a straight line, which is similar to the *C–V* curve of a typical parallel plate capacitor [22].

Charge storage and transport in polymers are the key issues to explain electrical characteristics of the all-polymer capacitor. Unlike the conventional charge storage in semiconductors, charges injected into the valence and conduction bands are not expected to remain in the band states. The structural relaxation around the charges occurs when charges are added to the polymer chains. The processing of conducting polymers degenerate ground state with a preferred sense of bond alternation, and the localized states are the bond alternation defects known as solitions, polarons, and bipolarons [23]. The capacitance is the change in charge density at an interface between the insulator and the conducting polymer. These added charges are stored in solution-like states, thus $\partial Q/\partial V$ can represent the capacitance. The electrical conductivity of conducting polymers results from mobile charge carriers introduced into the conjugate chains through doping. At low doping levels, these charges self-localize and form the nonlinear configurations (solitons, polarons, and bipolarons), which behave as charge carriers. At high doping levels, a transition to a degenerate Fermi sea can be observed, with an associated metallic behavior [24]. Since the PEDOT/PSS used in the experiment is highly doped (about 1×10^{20} cm^{-3}), it is a heavily doped p-type semiconductor. With extra bias voltages applied onto the device, the charges will be accumulated or depleted at the interfaces. The accumulation or depletion rate of positive polarons or bipolarons at the top PEDOT/PI interface is the same as the rate of that at the bottom interface since the top and bottom electrode are the same conductive polymers. Therefore the *C–V* curve would be a straight line, similar to the behavior of the common parallel plate capacitor [22]. Fig. 5 shows that the measured *C–V* curve is almost a straight line except for two peaks which might be due to dust contamination from the air. From this figure, the capacitance of the capacitor is about 53 pF. The thickness of the PI layer is 355 nm measured by a roughness surface tester (From Veeco Company). The equation $C = \varepsilon_0 \varepsilon_r A/d$ is normally used to calculate the common parallel plate capacitor made from metal electrodes such as aluminum. Using this equation (with the area of 4 mm^2 and the PI's dielectric constant of 3.4), the capacitance can be calculated as 338 pF. The capacitance difference between the experimental result and the calculated result is due to the different charge carriers and

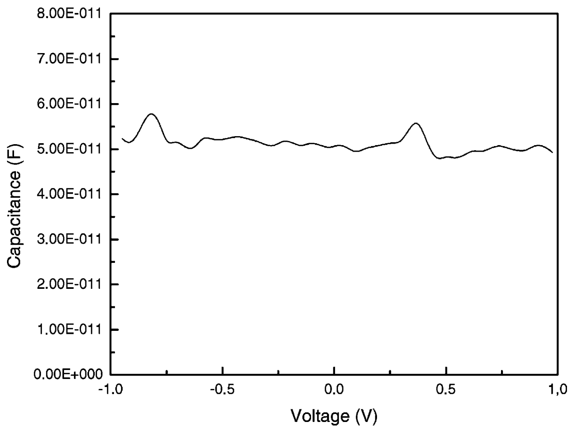

Fig. 3. *C–V* measurement of the printed polymer capacitor.

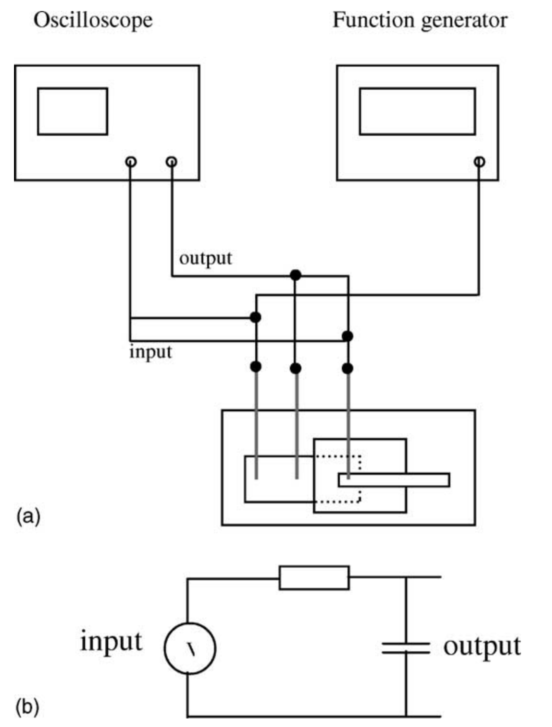

Fig. 4. (a) RC filter test set-up, (b) equivalent circuit of the testing RC filter.

transport mechanism in different electrode materials during the charging and discharging process. For the common parallel plate capacitor, the charge carriers are electrons or holes, which have a much higher mobility than polarons or bipolarons [25]. In addition, unlike the metal in which the charge transport occurs in the delocalized state, charge transport in conductive polymer, such as PEDOT, takes place by hopping between localized states and carriers are scattered at every step [26]. These result in much lower charging and discharging speeds ($\partial Q/\partial V$) of a polymer capacitor than the common parallel plate capacitor, and therefore lead to lower capacitance. A similar lower capacitance can also be observed in the solid electrolytic capacitor where PEDOT acts as a counter electrode [27].

Furthermore, the all-polymer capacitor has been applied to RC filter circuits that were fabricated with the IJP technique. For one of the RC filters, the resistance is 17 MΩ and the capacitance is 50 pF. Thus its RC time constant is 0.85 ms. Fig. 4a shows the testing set-up of the RC filter circuit, and Fig. 4b is the equivalent circuit.

For the low-pass filter configuration, as shown in Fig. 4, it is expected from the simulation result (Fig. 5a) that the amplitude of the output voltage will decrease with the increasing frequency of input signal when keeping the amplitude of the input signal constant. In addition, when the input signal was a square wave at the low frequency of 800 Hz, the transient characteristics of the output signal will be an integral curve from our simulation result (Fig. 6a). The output voltage and transient characteristics of the PEDOT/PSS RC filters were measured by the HP54653A digital oscilloscope. Figs. 5b and 6b shows the experimental results of the low-pass output frequency characteristics and the low-pass filter transient response, respectively. Experimental results are in agreement with what we expect and prove that the RC filter is fully functional. Details about the inkjet printed all-polymer RC filter circuits, their simu-

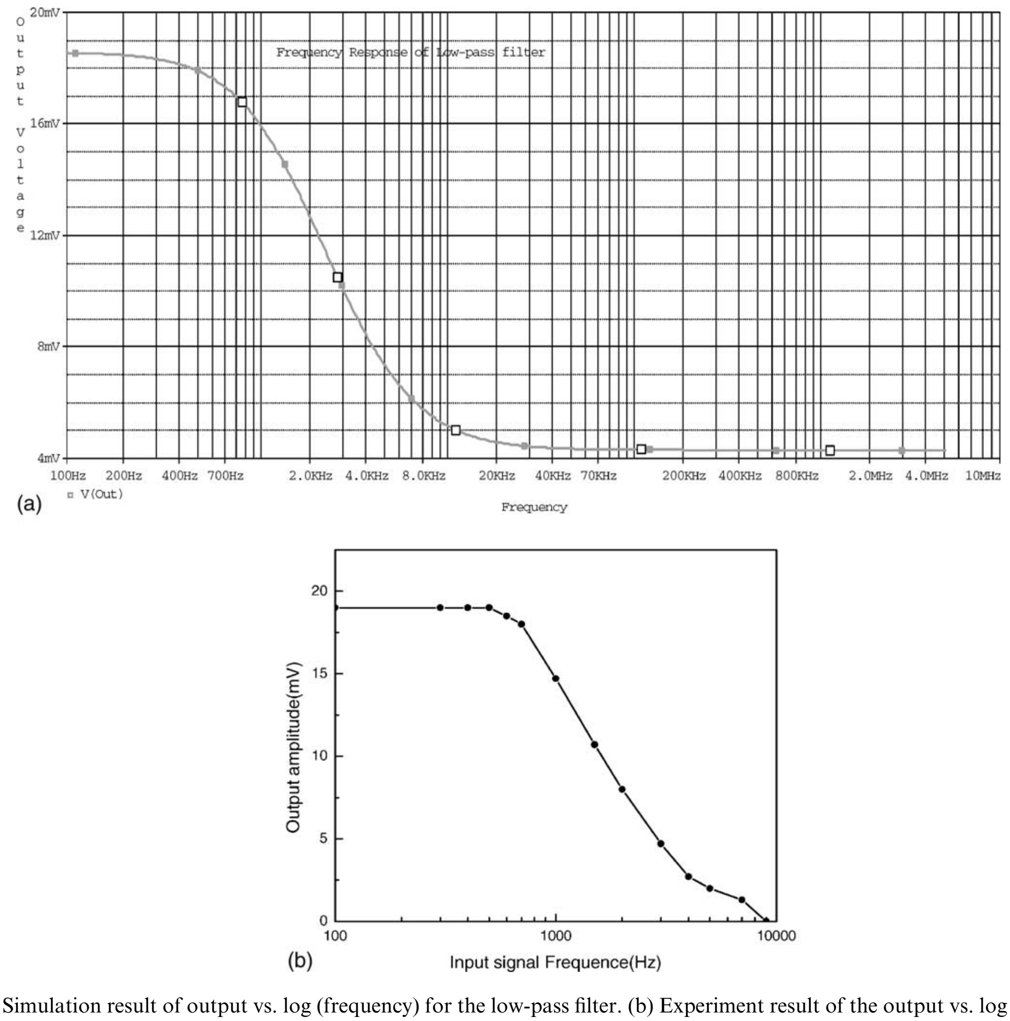

Fig. 5. (a) Simulation result of output vs. log (frequency) for the low-pass filter. (b) Experiment result of the output vs. log (frequency) for the all-polymer low-pass filter.

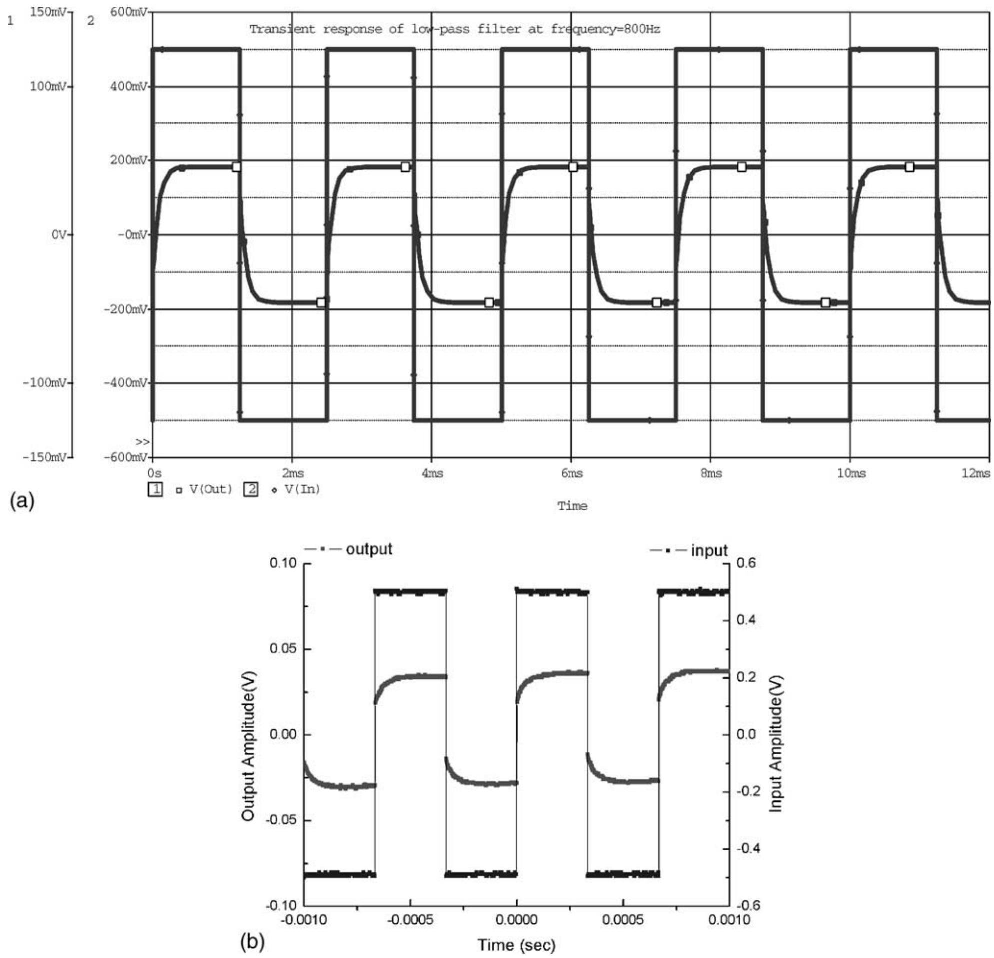

Fig. 6. (a) Simulation result of transient characteristic of low-pass filter at 800 Hz. (b) Experiment result of transient characteristic for the all-polymer low-pass filter at 800 Hz.

lation results, and degradation characteristics have been discussed elsewhere [28].

4. Conclusions

This paper demonstrates the possibility of using the IJP technique to fabricate the all-polymer capacitors as well as the RC filter circuits, in which precursor-route PI is the key to printing out the insulating layer of the capacitor. The inkjet printed polymer capacitor functions similarly as the traditional parallel plate capacitor. The characteristics of the inkjet printed all-polymer RC filter have been tested, which are in agreement with our expectations. From a processing standpoint, the procedures described here are attractive because it does not require high temperatures, low pressures, and masks, therefore providing a very low-cost approach to fabricate the passive electrical components. The polymer capacitor demonstrated here can further find its application to the low-cost all-polymer IC circuit industry [29].

Acknowledgements

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