

Printed polymeric passive RC filters and degradation characteristics

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Received 28 July 2003; received in revised form 9 November 2004

The review of this paper was arranged by Prof. C. Hunt

Abstract

Ink-jet printed thin films of conductive polymers such as polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrene sulfonate) and polymer dielectric material poly(4-vinylphenol) (PVP) were used to make RC filters. Both high-pass and low-pass filters were tested. The fabrication process and device characteristics of the RC filters have been demonstrated. Degradation of the ink-jet printed RC filters has been investigated, and the results indicate that PEDOT/PSS RC filters are more stable than those made from PANI.

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Keywords: Filter; Frequency; Polymer; Ink-Jet Printing

1. Introduction

The discovery of polyacetylene conductivity in 1977 by Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa has broken ground for new microelectronic materials and devices, and has earned the three scientists the 2000 Nobel Prize in Chemistry [1,2]. From then on, numerous microelectronic devices made from polymer materials have been fabricated or reported [3–8]. The electrical characteristics, solubility, and processibility of conductive polymers have also been greatly improved. The conductivity of some conjugated polymers has been made comparable to that of copper [2,9]. All of these achievements in polymer science and technology have presented us a brighter promise of polymer-based microelectronics. Low cost, easy processing, versatility,

and flexibility are the benefits that we can obtain from the applications of conductive polymers. Polymer devices can be fabricated using lithography, thermal evaporation, spin coating, dipping coating, printing, layer-by-layer self-assembly, and spraying coating [10–14]. Among all these fabrication techniques, ink-jet printing (IJP) [15–17] has been gaining more and more popularity due to its unique characteristics, such as stability, simplicity, compatibility with a lot of substrates, non-contact and no-mask patterning, room-temperature fabrication (much lower than traditional semiconductor fabrication techniques), no need of vacuum, and especially low cost. All-polymer transistors [15–19], polymer light emitting devices (PLED) [20–24], and nanoparticle microelectromechanical systems [25] have been fabricated by ink-jet printing or hybrid spin-coat/ink-jet printing techniques.

Conductive polymers have unique characteristics far different than their solid-state counterparts (e.g., silicon). Many of them are easily subject to degradation due to different reasons (such as photochemical effects [26], electrochemical effects [27,28], interface interactions

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[29], structural configuration [30], etc.), resulting in the characteristics of polymer devices getting worse with time. This drawback always is one of the major points of consideration for device engineering. When handling these kinds of polymers, dependent on their oxidation states, it is required to be in an inert environment and to provide good hermetical packaging to the devices. This fact shows the necessity of performing degradation test of some potential working materials, such as polyaniline (PANI), poly(3,4-ethylenedioxythiophene)

(PEDOT/PSS), and cyano-substituted poly(phenylene vinylene) (CN-PPV).

Similar to silicon-based integrated circuits (ICs), polymer ICs will face the same problems such as crosstalk, power dissipation delay, etc. To solve these upcoming problems, systematic investigations on the fundamental behaviors and characteristics of polymer-based integrated circuits (such as RC filters) are very necessary. Given the importance of frequency response (functionality) and device degradation (stability), we

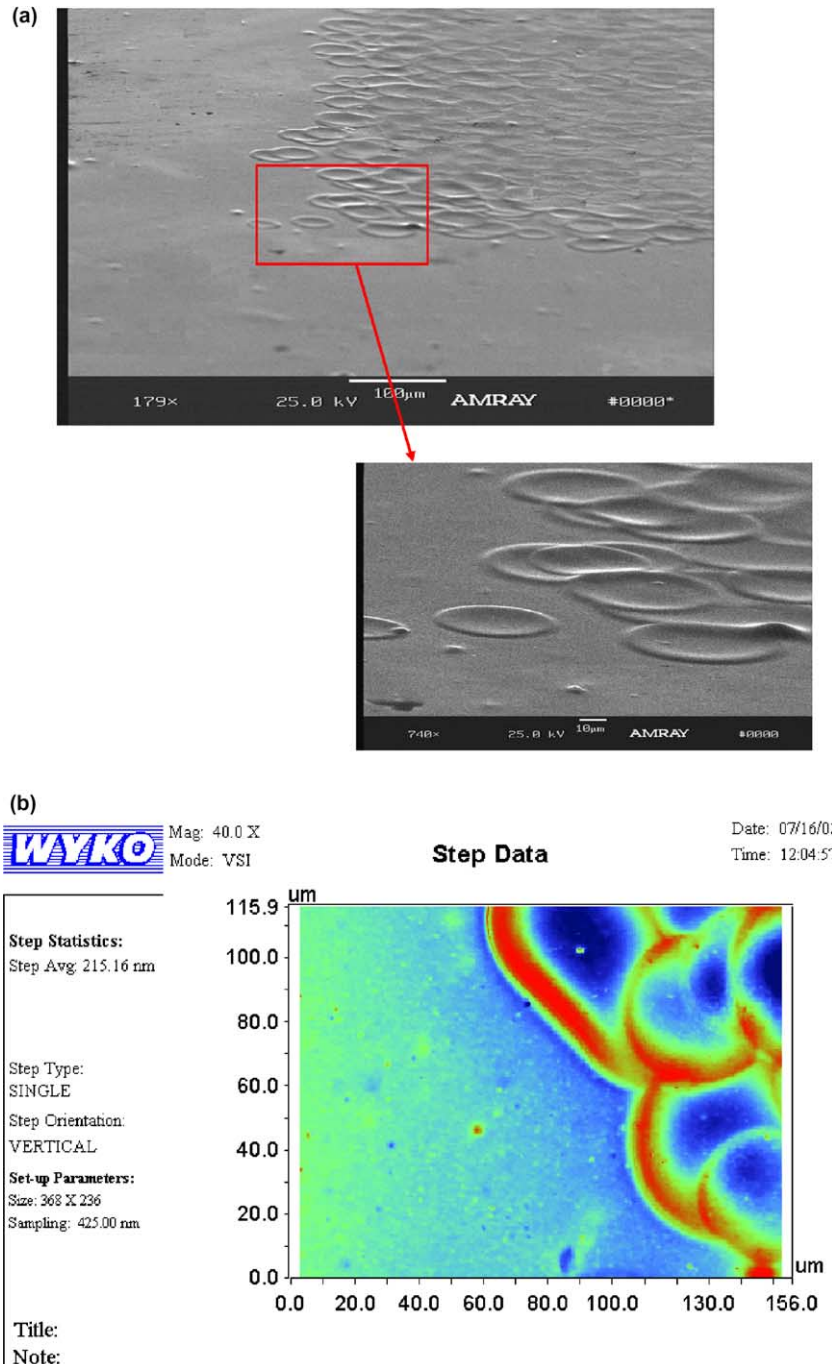


Fig. 1. (a) SEM picture of PEDOT/PSS thin film. (b) RST step profile of PEDOT/PSS bilayer.

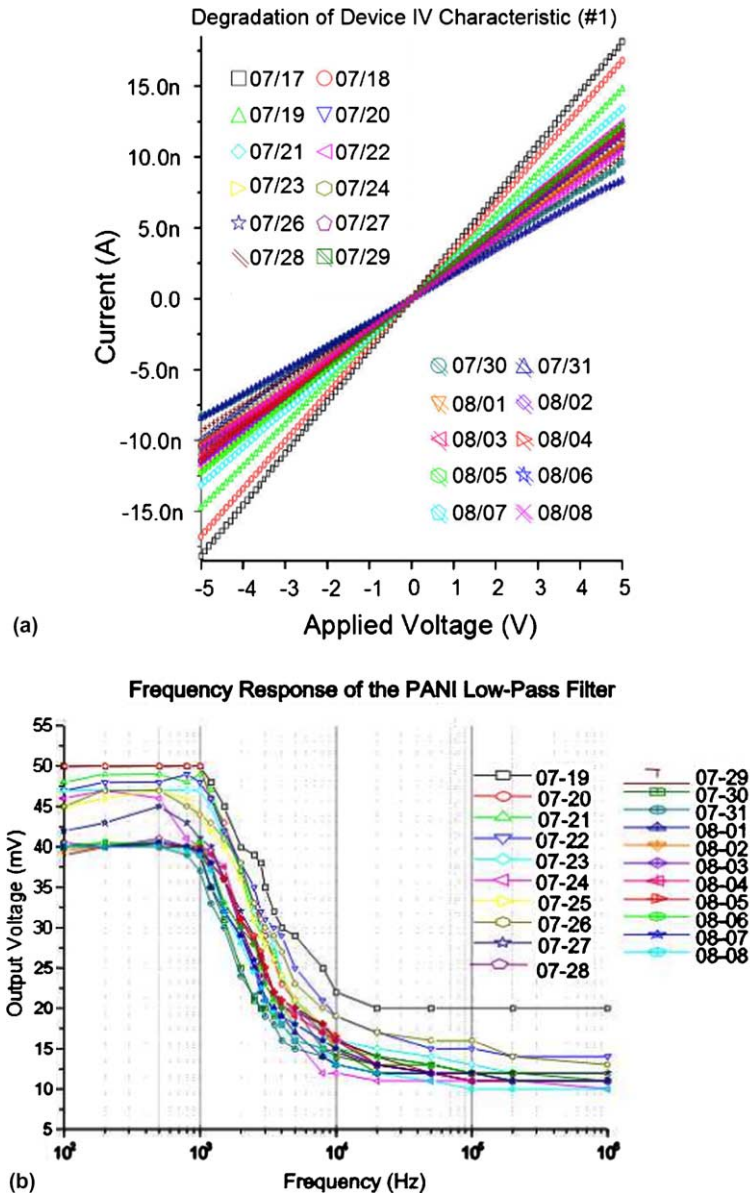


Fig. 2. (a) IV characteristic of PANI thin film. (b) Frequency response of PANI low-pass filter.

paid much attention to these two behaviors. As polymer ICs being fabricated, an early report of polymer RC filters and device degradation characteristics in this paper as well as the easy fabrication technique, ink-jet printing, will facilitate the fabrication of more practical and functional polymer ICs.

2. Experiments

Two types of commonly used conductive polymers, PEDOT/PSS (Baytron P^{\circledR} from Bayer) and PANI (from Aldrich) are selected for ink-jet printing in our experiment. The Baytron P^{\circledR} is water-soluble and PANI is fine water dispersion of nanoparticles (10–15 nm). Carter

et al. reported that using PEDOT/PSS or PANI as transparent anodes in polymer light emitting diode (PLED), they had greatly improved the quantum efficiency and brightness of their PLEDs [31]. PEDOT and PANI also have been successfully used in many other applications, such as antistatic and electrostatic coatings, metallization of insulators [32] and battery electrodes, conductive coatings for electrostatic speakers, capacitor electrolytes, and transparent conductive coatings.

Two layers of PEDOT or PANI were printed to act as the bottom electrode. Each layer of PEDOT or PANI is heated on a hot plate at 50 °C for 2 min not only to dry it completely, but also to make the thin film continuous. Next, 3 layers of poly(4-vinylphenol) (PVP) dissolved in alcohol were printed sequentially on top of

the previous PEDOT/PSS or PANI layers as the insulating layer. Finally, PEDOT/PSS or PANI layers were printed again. Conductive glue (epoxy) was used to attach three metal wires as the electric leads on the two electrodes of capacitor as well as the resistor.

Fig. 1(a) is the SEM picture of the PEDOT/PSS thin film printed on a commonly used transparency. The whole device was printed out by a commercial ink-jet printer from Epson [Stylus C40]. The surface profile of the printed PEDOT/PSS thin film is quite acceptable, even though some stray satellite droplets were found at the edge of the pattern.

The thickness of the thin film was measured by RST (Roughness/Step Tester from WYKO Corporation). The calculated thickness of the printed PEDOT/PSS bilayer is about 220 nm. The step height measured by RST is 215.16 nm. Fig. 1(b) shows the step data of the thermally evaporated aluminum thin film, and one may observe the PEDOT/PSS droplets under the aluminum thin film.

The fabricated RC filters were stored in a covered wafer box at 300 K room temperature and 41% humidity. The devices were tested under normal air conditioning with fluorescent light and the same temperature and humidity as mentioned above. KEITHLEY TEST SYSTEM (236 Source Measure Unit) and HP54653A digital oscilloscope [33] were utilized for the measurements of IV characteristics and frequency responses, respectively.

3. Results and discussions

One of the PANI RC low-pass filters was first investigated for 23 days. The IV characteristics and the frequency response of the filter are shown in Fig. 2(a) and (b), respectively. The calculated average voltage current slope and extracted output voltage at certain frequencies are illustrated in Fig. 3(a) and (b). Fig. 3(a) shows that the surface resistance of the PANI thin film continuously increased in the first 10 days, and decreased until the end of the test to reach a relatively stable status. Correspondingly, the frequency response curves show the same degradation trend. The IV characteristics of the PANI device were continuously changing within the range defined by the first day's and the 15 day's measurements as the boundary. This changing pattern is reflected by the cutoff frequencies of the device, which are within a range from about 1 kHz to 2 kHz. Even though the exact reasons of the measured degradation are not determined, several reasons can cause the degradation as mentioned above, among which electrochemical effects are significant and investigated widely [34,35]. Since the devices were stored and tested under normal air conditioning, polymer materials will absorb the water in the environment. The absorption would affect the behaviors of devices. Another important effect is

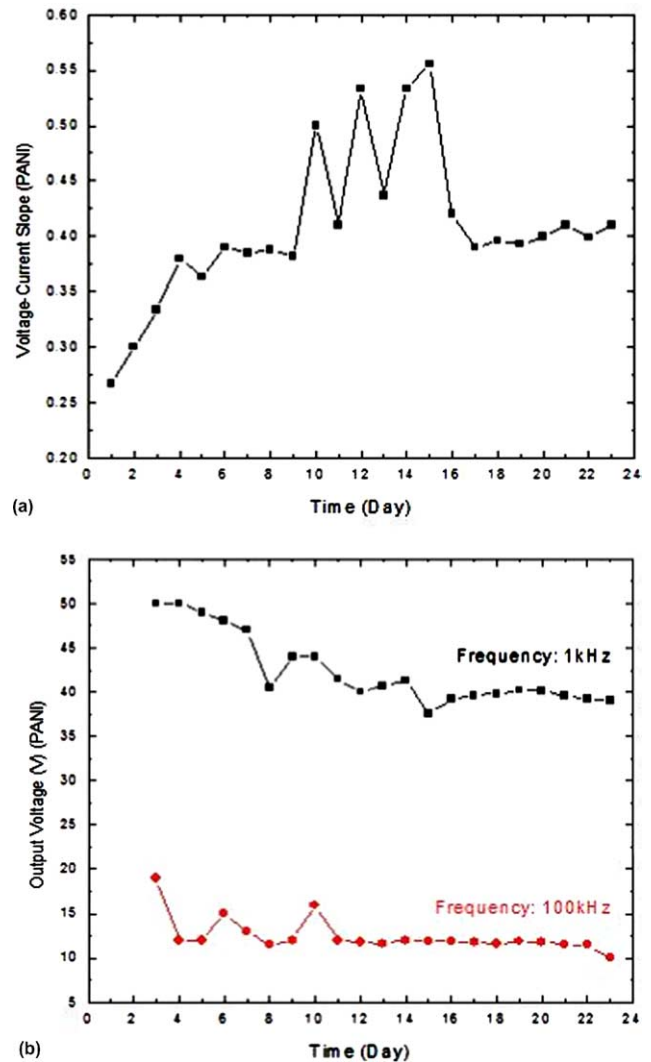


Fig. 3. (a) Voltage versus current slope of PANI thin film. (b) Output voltage at certain frequencies of PANI low-pass filter.

the interaction at the interface of two polymers. The interaction can change the profile and composition at the interface, and thus influence the functionality of devices. Moreover, the results of this interaction may raise the change of the electrode (PANI and PEDOT/PSS here) potential, and therefore make conducting polymer much easier to degrade. How to improve the stability of PANI will be considered in the future for improved performance in its applications.

Similar results were also obtained for PEDOT/PSS RC filters. Compared to the PANI-based RC filter, we can see that both the IV characteristics and the frequency response show relatively smaller fluctuation in their IV characteristics and frequency response, as shown in Fig. 4(a) and (b). The slope of IV curve versus time and the output voltage at certain frequencies versus time are also extracted in Fig. 5(a) and (b). From the aspect of statistics, the standard deviation of the surface

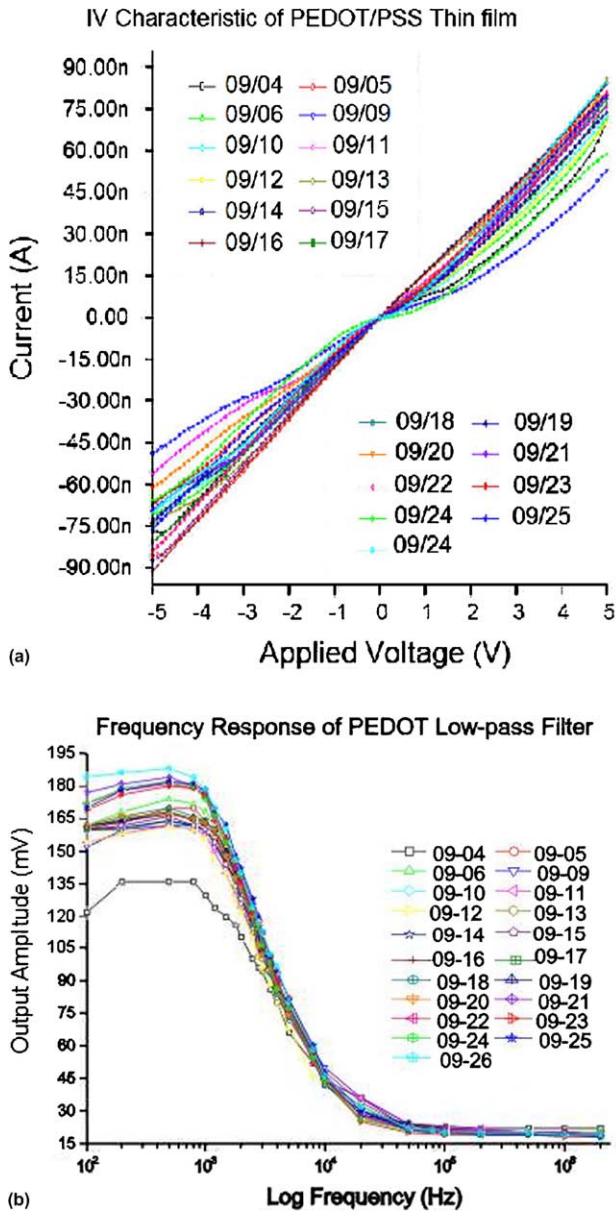


Fig. 4. (a) IV characteristic of PEDOT thin film. (b) Frequency response of PEDOT low-pass filter.

resistance is $1.11E + 9$ and $1.17E + 8$ ohms for PANI and PEDT/PSS, respectively. The standard deviation reflects the stability of devices by the fluctuation of parameters. From the results of the degradation measurement of PANI and PEDOT/PSS RC filters, PANI degrades slightly larger than PEDOT/PSS demonstrated by our experimental results. Both PANI and PEDOT/PSS shows some fluctuation and degradation which can not be negligible, though both of them are reported having excellent stability [32,36]. It also indicates that PEDOT/PSS and PANI are suitable for the fabrication of RC filters and OLEDs with the consideration of good stabilities.

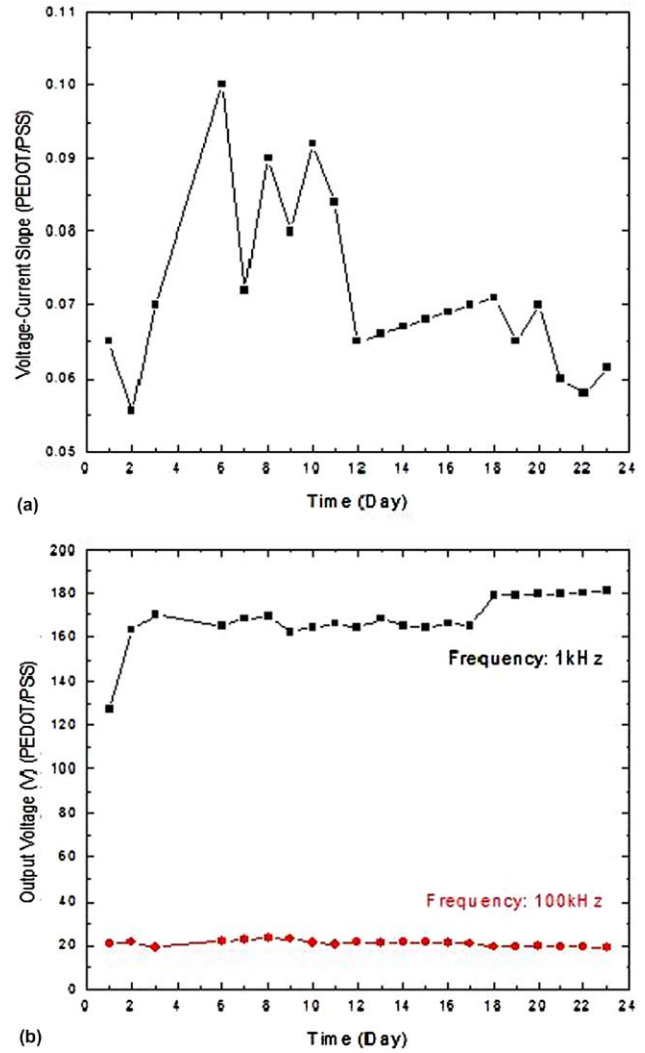
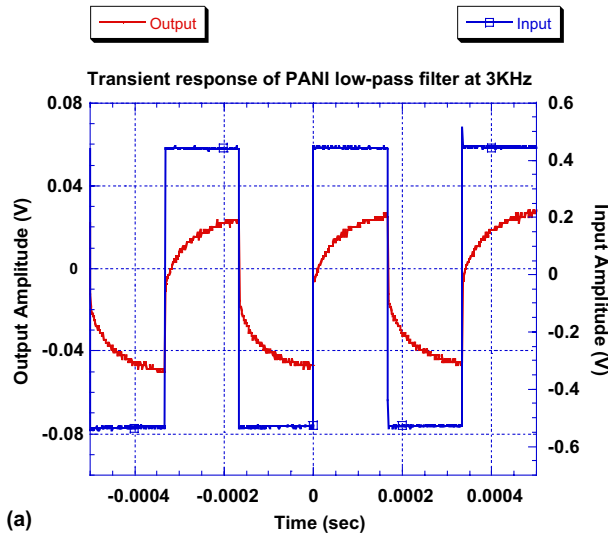


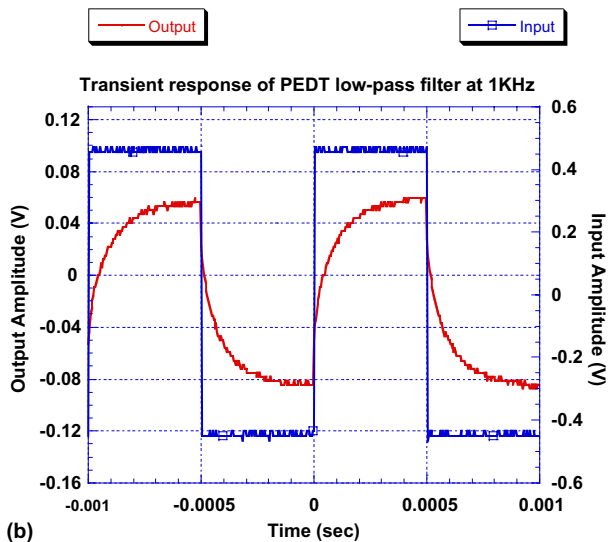
Fig. 5. (a) Voltage current slope of PEDOT thin film. (b) Output voltage at certain frequencies of PEDOT low-pass filter.

The transient characteristics of the PEDOT/PSS and PANI RC filters were also measured by HP54653A digital oscilloscope. In Fig. 6(a) and (b), PANI and PEDOT/PSS RC integral circuits show low-pass characteristics, while in Fig. 7(a) and (b) the two RC differential circuits present high-pass characteristics. The devices made from different polymers have the same circuit behaviors.

The repeatability of the RC filters based on PEDOT/PSS is better than PANI RC filters. This is because PEDOT/PSS is more stable than PANI in normal atmosphere, and the ambient has much more oxidation effect on PANI. After passivation with polyimide, both PEDOT/PSS and PANI RC filters show very similar IV characteristics and repeatability. Due to uneven polymer thin film deposited by ink jet printing, both PEDOT/PSS and PANI RC filters have fringe capacitances at the edge, which is another reason resulting in the repeatability of polymer RC filters. Annealing as well



(a)



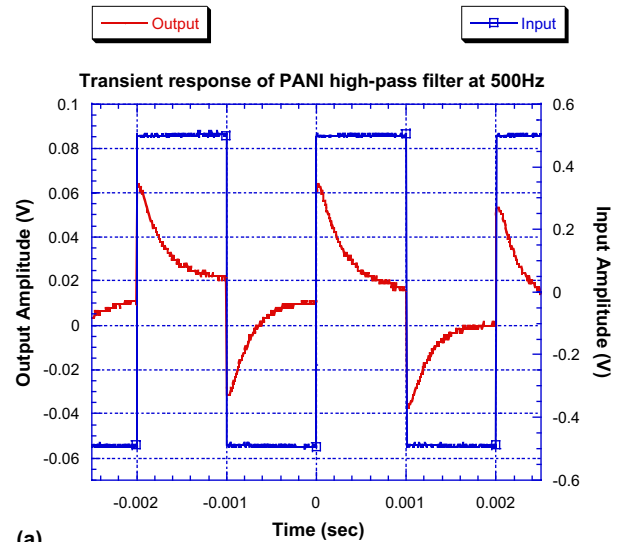
(b)

Fig. 6. (a) Transient response of PANI low-pass filter to a 3 kHz square input. (b) Transient response of PEDOT/PSS low-pass filter to a 1 kHz square input.

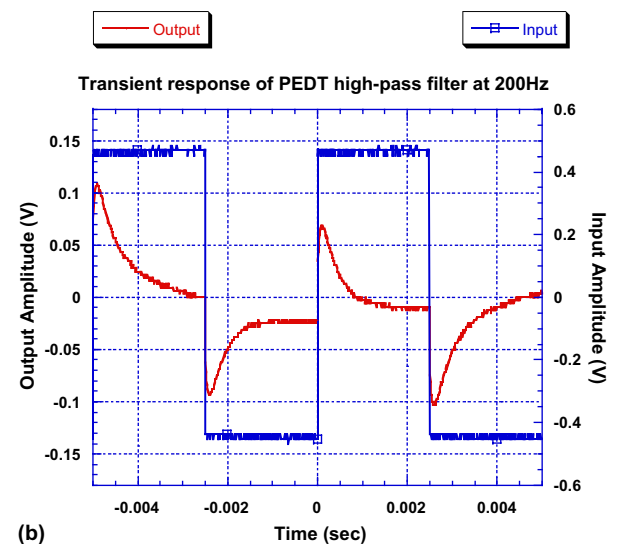
as optimizing the ink-jet printing parameters are possible good approaches to improve the deposition quality of polymer thin films and to improve the repeatability of ink-jet printed polymer RC filters.

4. Conclusion

Commercial ink-jet printers were successfully used in fabrication of all polymer RC filters. Commonly used conductive polymers, such as PEDOT/PSS and PANI, have been investigated in the fabrication of passive RC components. The all-polymer devices can work as both low-pass and high-pass filters with specific cut-off frequencies. The degradation test results indicate PEDOT/PSS has more stable characteristics over PANI.



(a)



(b)

Fig. 7. (a) Transient response of PANI high-pass filter to a 500 Hz square input. (b) Transient response of PEDOT/PSS high-pass filter to a 200 Hz square input.

Acknowledgment

This work was partially supported by the DARPA and CENIT seed grant at Louisiana Tech University.

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