Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thin Solid Films 450 (2004) 312–315
thin solid films
www.elsevier.com/locate/tsf

Thin film deposition of an n-type organic semiconductor by ink-jet printing technique

Yuming Ai[a], Yi Liu[a], Tianhong Cui[a,b,]*, Kody Varahramyan[a]

[a]*Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA 71272, USA*
[b]*Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, USA*

Received 14 January 2003; received in revised form 6 October 2003; accepted 13 November 2003

Abstract

An n-type organic material, 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTCDA), was successfully deposited and patterned on a SiO_2/Si wafer by the ink-jet printing technique. Dimethylformamide (DMF) was selected as the solvent in the processing of the ink-jet solution, NTCDA. After thermal annealing, the NTCDA thin film showed higher conductivity than the NTCDA thin film deposited by vacuum sublimation. Degradation of conductivity with time was found when the thin film was open to an ambient atmosphere.

Keywords: n-type polymer; Solution processing; Ink-jet printing; Conductivity

1. Introduction

Conductive organic and polymer materials have attracted much attention since the first conductive polymer was invented. They have been widely investigated for microelectronic and optoelectronic devices, such as organic light emitting diodes (OLEDs) [1,2], photovoltaic devices and photosensors [3], organic field effect transistors (OFETs) [4], and integrated circuits [5].

For low-cost polymer microelectronic devices, solution-processable materials are necessary for direct deposition to avoid the sublimation process at high vacuum. Stable and solution-processable p-type semiconductive polymer materials are commercially available [6]. However, thin films formed by stable n-type semiconductive polymer solutions are difficult to be developed [7].

The ink-jet printing technique attracts much attention in device fabrication due to its unique advantages including direct patterning, low cost, and low material waste [8]. Devices like OLEDs [9], thin film transistors [10], nanoparticle MEMS devices [11], and micro lenses [12] have been successfully fabricated by this technique. In this research, the ink-jet printing technique offers more options to the solvent selection than the traditional spin-coating technology. A uniform thin film could be obtained even with poor adhesion between the solution and the substrate.

In this paper, the deposition of an n-type semiconductor by the ink-jet printing technique is reported. An organic material, 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTCDA), is employed in the experiments. The fabrication process is found to produce a uniform thin film with a conductivity of 10^{-4}–10^{-5} S/cm after thermal annealing. This paves a new way to deposit an n-type polymer semiconductor, and provides the potential prospects for the fabrication of integrated circuits.

2. Experiments

NTCDA without further purification, from TCI Chemicals Incorporation, was dissolved in several types of solvents, including acetone, chloroform, dimethylformamide (DMF), or dimethylsulfoxide (DMSO), with ultrasonic vibration to obtain a saturated solution with excessive NTCDA appearing in the solution.

The SiO_2/Si wafers were from Silicon Quest Incorporation. Aluminum 1000-Å thick was deposited by thermal evaporation, and patterned by UV photolithog-

---

*Corresponding author. Tel.: +1-612-626-1636; fax: +1-612-625-9395.
E-mail address: tcui@me.umn.edu (T. Cui).

0040-6090/04/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2003.11.187

Fig. 1. Autodrop dispensing system with dispensing heads from Microdrop GmbH in Germany (1: *x*–*y*–*z* positing system; 2: camera 1; 3: solution reservoir; 4: substrate holder/hotplate; 5: camera 2; 6: temperature control system; 7: Driver electronics/pressure control; 8: Camera switch; 9: Monitor).

raphy. Electrodes fabricated by a lift-off process have different spacings.

The ink-jet printing system shown in Fig. 1 (an AutoDrop dispensing system with printing heads from Microdrop GmbH in Germany) was utilized in this experiment. An *x*–*y*–*z* axis positioning system was equipped with this system to control the movement of the dispensing head. A heating element was also installed on the substrate holder. The filtered NTCDA solution was filled in the printing head and printed between the two aluminum electrodes on the heated SiO_2/Si testing wafer, as shown in Fig. 2. The printed NTCDA dots and the single-layer thin film, with printing nozzles in different diameters, are shown in Fig. 3a,b, respectively. After printing, the substrate was placed on a hot plate and heated at 300 °C for solvent eliminating and thin film annealing.

When the printed thin film was cooled down to room temperature, the electrical characteristics were measured with a Keithley SMU236/237 system. One of the substrates was coated with the second layer of aluminum, 500-Å thick, to inspect the thickness of the NTCDA film. The thickness of the printed NTCDA film was measured by an interferometric roughness step tester microscope (WYKO RST Plus). All the fabrication and testing processes were undertaken in an ambient atmosphere, except for the aluminum deposition, which was done at 10^{-6} Torr.

3. Results and discussions

The NTCDA/DMF solution was finally selected as the 'ink' due to its high material solubility and relatively low surface tension, compared with the NTCDA/DMSO solution. A set of processing parameters of the Autodrop System, including the diameter of the printing head nozzle, the voltage, the pulse width, and the frequency, was optimized for the saturated NTCDA/DMF solution to obtain stable droplets.

For the continuous NTCDA thin film, the substrate temperature is one of the most important factors to control the deposition process. To obtain better patterns, higher temperatures were normally preferable for solidifying quickly and reducing the solution flow on the substrate. In the meantime, it was also preferred because the quasi-crystalline or polycrystalline structures are more likely to be formed at higher temperatures, while the amorphous structures are formed at lower temperatures. However, lower substrate temperatures may avoid frequent nozzle clogging, thus result in much more stable droplet flow and better thin film coverage. The substrates at room temperature, 20, 60, 100, 120, and 140 °C were investigated for the thin film deposition. The substrate temperature at 120 °C led to the best coverage and continuous semiconductor thin film. An optical image of NTCDA film with 10 times of printing, 4.5 mm by 1 mm, is shown in Fig. 3c.

The RST results showed the thickness of a single NTCDA film to be 20–50 nm. The conductivity can be calculated by the equation below [13].

$$\sigma = \frac{1}{\rho} = \frac{1}{R} \cdot \frac{L}{A} = \frac{I_n}{V} \cdot \frac{L}{A}$$

where σ is the conductivity ($\mathrm{S cm}^{-1}$), ρ is the resistivity (Ωcm), R is the resistance (Ω), L is the distance (cm), A is the cross-section area (cm^2), V is the applied voltage (V), and I_n is the electrical current (A).

Three samples have been fabricated and characterized under the same conditions. Each sample was dispensed ten times with the same dimensions (4.5 mm by 1 mm).

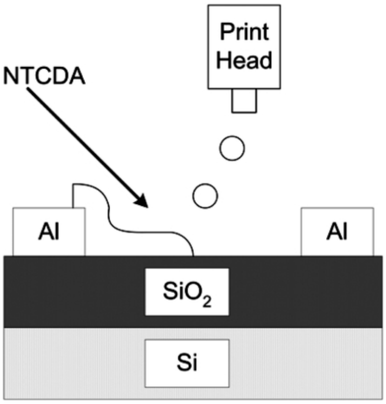

Fig. 2. Schematic of the device structure.

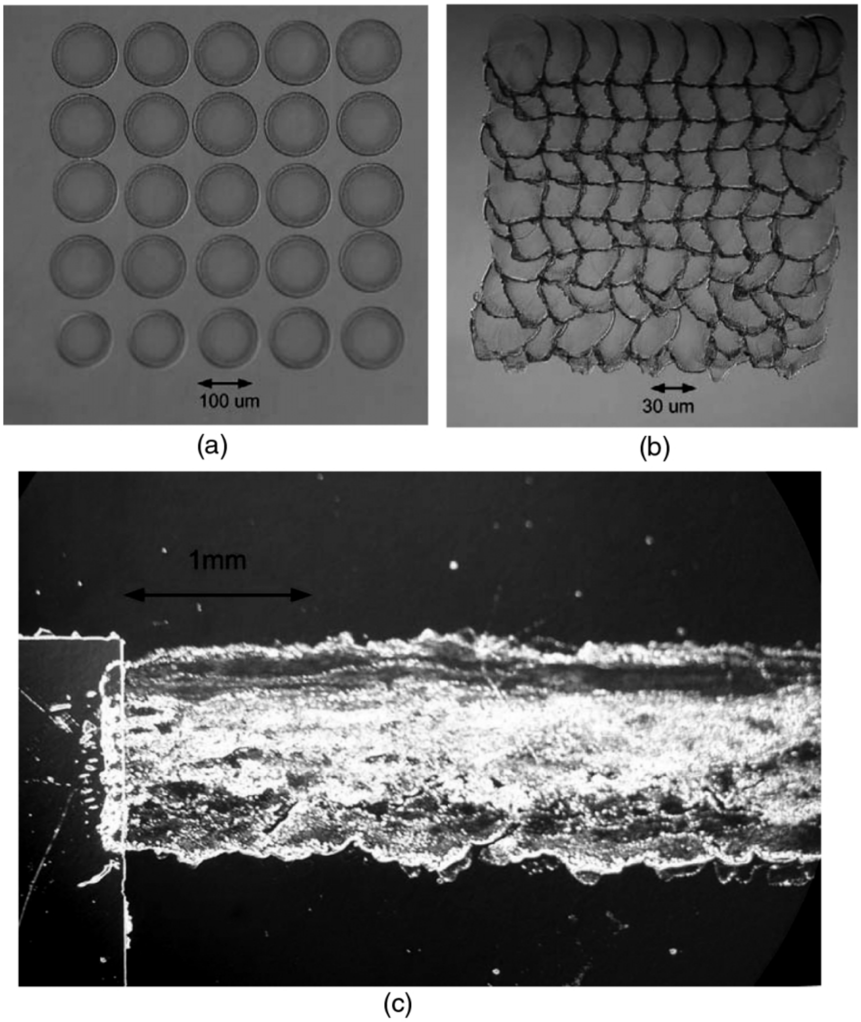

Fig. 3. Printed NTCDA dots and thin film: (a) NTCDA dots, (b) NTCDA thin film (single layer), (c) NTCDA thin film (10 layers).

After the film was deposited, the conductivity of the sample was measured without annealing. The measurement was done three times continuously, and no distinct variance could be observed. Next, the sample was annealed at 300 °C for 2 h, and characterized right after annealing, after 3 days, and after 6 days, respectively. The measurements were undertaken with direct contact between the probe and the NTCDA film. The average conductivity right after annealing for these three samples is 3.38×10^{-4} S/cm with error of 2.45×10^{-6} S/cm.

The typical IV characteristic of the NTCDA thin film is shown in Fig. 4. The results indicate that the NTCDA conductivity was enhanced by approximately two orders of magnitude after thermal annealing. The annealing process may play a role of not only eliminating the residual solvent (DMF), but also leading to re-flow and re-crystallization of NTCDA. After the NTCDA thin film was stored in an ambient atmosphere for 3 and 6 days, an obvious decrease of conductivity was observed, as shown in Fig. 4. This has been reported as the effect of moisture and oxidation [14]. Re-annealing of the thin film in an ambient atmosphere did not show noticeable improvement of conductivity. In addition, the degraded sample was soaked in DMF, and annealed again under the same conditions. The low conductivity still remained the same, and no increase of conductivity can be observed. This means that the influence of moisture and oxidation is irreversible, and that the re-annealing of the thin film cannot improve the conductivity again.

The highest conductivity, approximately 10^{-4} S/cm, could be obtained after thermal annealing. This result is much higher than the reported NTCDA film conductivity of 10^{-7}–10^{-8} S/cm [15]. Based on the reported free electron density of 10^{13}–10^{17} cm^{-3}, the mobility of NTCDA film can be obtained as high as 10^{-1}–10^{-2} cm^2/Vs. This mobility result needs to be verified by further investigation.

4. Conclusions

For the first time, the n-type organic semiconductor, NTCDA, was successfully deposited based on solution

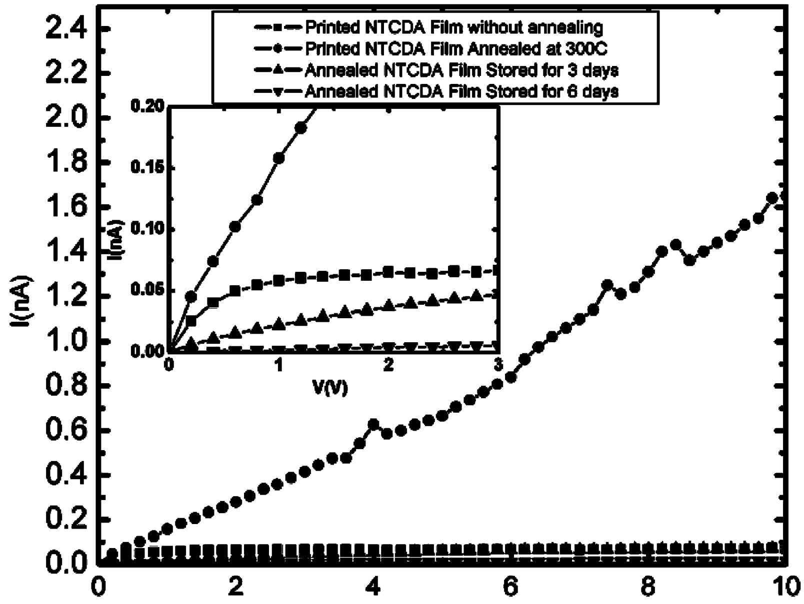

Fig. 4. *I–V* characteristics of printed NTCDA thin film.

processing by ink-jet printing technique. The conductivity of the NTCDA film was enhanced by approximately two orders of magnitude by thermal annealing at 300 °C. The highest conductivity was approximately 10^{-4}–10^{-5} S/cm, which is much higher than the reported NTCDA deposited by vacuum sublimation. This provides an efficient and simple approach to deposit the n-type polymer semiconductors to fabricate microelectronic and optoelectronic devices. The conductivity degradation was also observed after exposure to an ambient atmosphere.

Further investigation will address the mobility verification, the optimization of annealing parameters, the droplet sizes suitable for flat panel displays, the use of plastic substrates, and the applications to the fabrication of microelectronic devices.

Acknowledgments

This work is partially supported by the DARPA DAAD19-02-1-0338 grant and the CEnIT seed grant at Louisiana Tech University.

References

[1] C.W. Tang, S.A. Van Slyke, Organic electroluminescent diodes, Appl. Phys. Lett. 51 (1987) 913–915.

[2] J.H. Burrougher, D.D. Bradley, A.R. Brown, R.N. Marks, K. Mackey, R.H. Friend, P.L. Burns, A.B. Holmes, Light emitting diodes based on conjugated polymers, Nature 347 (1990) 539–541.

[3] G. Yu, G. Srdanov, H. Wang, Y. Cao, A. Heeger, Photovoltaic cells and photodetectors made with semiconductor polymers: recent progress, Proc. SPIE 3929 (2000) 118–125.

[4] L. Torsi, N. Cioffi, C. Di Franco, L. Sabbatini, P.G. Zambonin, T. Bleve-Zacheo, Organic thin film transistors: from active materials to novel applications, Solid State Electron. 45 (2001) 1479–1485.

[5] C.J. Drury, C.M.J. Mutsaers, C.M. Hart, M. Matters, D.M. de Leeuw, Low-cost all-polymer integrated circuits, Appl. Phys. Lett. 73 (1998) 108–110.

[6] J.Y. Kim, J.H. Jung, D.E. Lee, J. Joo, Enhancement of electrical conductivity of poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) by a change of solvents, Synthetic Met. 126 (2002) 311–316.

[7] H.E. Katz, A.J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y.-Y. Lin, A. Dodabalapur, A soluble and air-stable organic semiconductor with high electron mobility, Nature 404 (2000) 478–480.

[8] S.P. Speakman, G.G. Rozenberg, K.J. Clay, W.I. Milne, A. Ille, I.A. Gardner, E. Bresler, J.H.G. Steinke, High performance organic semiconducting thin films: ink jet printed polythiphene [rr-P3HT], Org. Electron. 2 (2001) 65–73.

[9] Y. Yang, S.-C. Chang, J. Bharathan, J. Liu, Organic/polymeric electroluminescent devices processed by hybrid ink-jet printing, J. Mater. Sci.: Mater. Electron. (2000) 89–96.

[10] T. Kawase, H. Sirringhaus, R.H. Friend, T. Shimoda, All-polymer thin film transistors fabricated by high-resolution ink-jet printing, 2000 IEEE International Electron Devices Meeting, 10–13 December, 2000, pp. 623–626.

[11] S.B. Fuller, E.J. Wilhelm, J.M. Jacobson, Ink-jet printed nanoparticle microelectromechanical systems, J. Microelectromech. Syst. 11 (2002) 54–60.

[12] S. Biehl, R. Danzebrink, P. Oliveira, M.A. Aeferter, Refractive microlens fabrication by ink-jet process, J. Sol–Gel Sci. Technol. 13 (1998) 177–182.

[13] E.S. Yang, Microelectronic Devices, McGraw-Hill Book Company, 1988.

[14] L. Torsi, A. Dodabalapur, L. Sabbatini, P.G. Zambonin, Multi-parameter gas sensors based on organic thin-film transistors, Sensors Actuators B 67 (2000) 312–316.

[15] A. Nollau, M. Pfeiffer, T. Fritz, K. Leo, Controlled n-type doping of a molecular orgnanic semiconductor: naphthalene-tetracarboxylic dianhydride (NTCDA) doped with bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), J. Appl. Phys. 87 (2000) 4340–4343.