An active microheater matrix using polymer semiconductor diodes for thermal patterning

S Mutlu and A O Sevim

Department of Electrical and Electronic Engineering, Bogazici University, Bebek, TR-34342, Istanbul, Turkey
E-mail: senol.mutlu@boun.edu.tr

Received 26 October 2009, in final form 24 December 2009
Published 15 February 2010

Abstract

A novel active microheater matrix employing polymer semiconductor diodes is presented. Polymer diodes are used as heat sources instead of resistive microheaters to eliminate current leakages through unselected heater cells. In a $4 \times 4$ resistive microheater matrix, 44% of the applied current passes through the desired resistor, whereas in a $64 \times 64$ matrix, only 3% passes. Active heater matrices have been fabricated using a complementary metal oxide semiconductor (CMOS) process discrete components or amorphous silicon on glass technology, but not using organic electronics. This approach offers low cost and simplicity with a possibility of using flexible substrates. The fabricated $16 \times 16$ polymer diode matrix has a structure of indium tin oxide (ITO)/poly(3-hexylthiophene-2,5-diyl) (P3HT)/aluminum. They have a turn-on voltage of around 3 V. Polymer diode performance improves with temperature. A $2.7 \mu A \, mm^{-2}$ current density at 5 V at room temperature improves to $12.2 \mu A \, mm^{-2}$ at 120 °C due to the thermal excitation of the trap states on the boundaries of the polymer grains. The temperature of the selected heater increases with the applied current density. A current density of 3 mA mm$^{-2}$ heats the surface of the heater to 110 °C. Thermal patterning is achieved on thermally sensitive paper. $800 \times 800 \mu m^2$ heater cells generate $930 \times 930 \mu m^2$ black patterns.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Many molecular biology and chemical analysis techniques require localized heating or heat gradients to test certain reactions or to generate certain byproducts [1, 2]. Localized heating is also used in thermal inkjet printing [3] and other thermal patterning applications [4]. Thin film microheaters are routinely used in these kinds of applications and can operate relatively fast compared to their macro counterparts due to their small thermal masses. They can also be fabricated easily using standard micro fabrication techniques.

In most of these applications either a single microheater or an array of microheaters is used. These include the single usage of microheaters in gas preconcentrators [5] and usage of microheater arrays in gas sensing [1]. Fingerprint sensing [6] and movement of water droplets using thermocapillary actuation [7] have also been demonstrated with microheater arrays. Their usages in cell [2], DNA [8] or other biochemical analysis are also possible. However, microheaters find more applications and become more effective when a matrix of microheaters is formed to generate localized heating on selected areas [1, 4, 9]. This kind of a system can do a two-dimensional thermal patterning. In such a system, chemical and biological reactions can be tested at different temperatures simultaneously. A thermal gradient pattern can be created on the surface for the investigation of its effect on biological or chemical interactions. Any thermally sensitive film or paper can be patterned this way. Furthermore, in most of these applications, maximum heating temperature of around 110 °C is sufficient, which can be supplied by polymer thin films.

However, a cost-effective way of realizing a matrix of microheaters has not been achieved for thermal patterning...
yet since a passive matrix of resistive microheaters could not create localized heating. An active matrix must be employed by integrating a diode or transistor for each heater, which increases fabrication complexity and cost. Realization of a heater matrix can be straightforward using discrete resistors and transistors on a printed circuit board (PCB) [9] or in CMOS fabrication [1] or using the amorphous silicon (a-Si) on glass technology used in liquid crystal and organic light-emitting diode (OLED) display fabrication [10]. Active selection of a single microheater can be achieved with the integrated transistors that these technologies allow. In fact, a 16 × 8 active microheater matrix forming a microfluidic platform for non-contact droplet actuation using Marangoni flow has been realized on a PCB using discrete resistor components [9]. There, each resistor pixel is controlled by a discrete DMOS transistor. This solution may not be practical for some applications since the number of heaters that can be put on a certain area is limited due to large package sizes of the components. The packages increase thermal masses, which increase thermal response time. Furthermore, biological or chemical thin films to be patterned cannot be deposited on top of the discrete components because of the step heights the components create on the surface.

In CMOS fabrication, the area of a matrix is limited to couple square millimeters due to prohibitive cost. Furthermore, since silicon is a good thermal conductor, a post-CMOS process is needed to thermally isolate microheaters, usually by etching the silicon underneath the heater to have suspended structures [1, 4]. Similarly, fabrication of the heater matrix on a large area using a-Si backplanes on glass substrates would not be cost-effective, especially for disposable biochemical reaction chips, because of the high cost of building and maintaining the infrastructure required for their fabrication. Furthermore, they cannot be made flexible, which can be desirable for roll-to-roll printing applications. Instead, conjugated polymers can be used to fabricate the active heater matrix on any hard or flexible and thermally non-conductive surfaces such as plastic and glass. Conjugated polymers are semiconductors commonly used in the fabrication of polymer diodes, light-emitting diodes [11], transistors [12], integrated circuits [13], photodetectors and solar cells [14]. They offer flexibility, simplicity, speed and lower cost in the fabrication of semiconductor devices. Furthermore, polymer-based systems are amenable to roll-to-roll production [15], which allow them to be fabricated in much larger areas than the wafer sizes of the current CMOS industry and a-Si backplanes of liquid crystal displays with lower cost per area. In this work, an active microheater matrix is fabricated using polymer semiconductor diodes and shown to generate thermal patterns for the first time.

In the next section of this work, analysis and simulation results are presented to show why a passive-resistive microheater matrix cannot work. This is followed by the discussion of how semiconductor polymer diodes can be used to make an active microheater matrix. Fabrication methods and results are given next. The characterization results of the fabricated polymer diodes done at elevated temperatures are given. The polymer diode heater matrix is shown to induce localized heating on selected areas using an infrared thermal imaging camera. Finally, a thermal patterning example of the heater matrix is shown to work on thermal paper.

2. Active matrix operation of microheaters

In an N × M matrix of microheaters, it is desirable to have the least number of row and column electrodes, ideally in total N+M electrodes, N for row and M for column electrodes. A representative 4 × 4 resistive microheater matrix is shown in figure 1(a). This matrix configuration cannot render a practical system with localized heating on selectable areas due to current leakages through the rest of the resistive microheaters. When current is applied to row electrode A and column electrode 1 to locally heat the area on the heater A1, it would be divided by the other resistive paths between pads A and 1. All of the alternative paths for the applied current are shown in figure 2 [16]. It shows that the leakage currents on the rest of the heaters cannot be neglected due to many alternative paths. Results of simulation program with integrated circuit emphasis (SPICE) show that only 44% of the applied current
The polymer diode is formed with a structure of anode electrode, cathode electrode and P3HT film in between. Analogous to conduction and valence bands, charge transport in polymer semiconductors depends on two energy levels: LUMO (lowest unoccupied molecular orbital), which is equivalent to valence band energy level. The anode material, and HOMO (highest occupied molecular orbital), which can be curved or bended. Therefore, polymer/organic electronics stands out as a novel solution to this problem. Polymer semiconductors can be employed as thin films to form diodes on any type of thermally insulated substrates. Many different semiconductor polymers have been used for this purpose. Pentacene from the acene family of organics is a commonly used small molecule semiconductor with the best mobility of around 4 cm² V⁻¹ s⁻¹ and high environmental stability [17]. However, since it requires high vacuum thermal evaporation for deposition, its usage increases fabrication complexity and cost. Other polymer semiconductors include polythiophene and poly(phenylene vinylene) (PPV) families, which are easier to process since they can be dissolved in solvents and be spin-coated [18]. Unfortunately, most of them are easily degraded by humidity and oxygen at ambient conditions [19] and they have lower mobilities compared to pentacene. Regioregular poly(3-hexylthiophene) (rr-P3HT) is one of the most environmentally stable conjugated polymers [20]. It provides relatively high mobility of around 0.01 cm² V⁻¹ s⁻¹ for the least complexity and cost in fabrication compared to other semiconductor polymers. This mobility can be further increased to around 0.1 cm² V⁻¹ s⁻¹ by optimizing deposition and synthesis of the polymer for higher degree of head-to-tail regioregularity in the film [18, 21, 22]. P3HT is chosen in the fabrication of polymer diodes used in this work because of these reasons.

The diode is made of ITO and the cathode is made of aluminum. Untreated ITO has a typical work function of 4.7 eV and sometimes even lower value such as 4.5 eV depending on deposition methods and conditions. This can be increased by plasma (typically to be around 5 eV and as high as 5.4 eV), ultraviolet, ozone or chemical treatments or even with the application of poly(3,4-ethylenedioxythiophene)/

A1 diode, and thus causes localized heating only on that area since the rest of the paths have at least one pair of back-to-back diodes, which prevents current conduction in the rest of the paths between A and 1. The only leakage currents are due to the reverse saturation currents of the diodes, which can be neglected very easily.

3. Semiconductor polymer diodes as heat sources

In this work, it is suggested that an active heater matrix can be built from a diode matrix. There are a limited number of solutions to build such a diode matrix. It is not really practical to build it using a CMOS or a-Si on glass backplanes or with discrete components on the PCB as discussed in the introduction, especially if disposable and cheap biological and chemical reaction involved applications are considered. In addition, some applications may require flexible substrates that can be curved or bended. Therefore, polymer/organic electronics stands out as a novel solution to this problem. Polymer semiconductors can be employed as thin films to form diodes on any type of thermally insulated substrates. Many different semiconductor polymers have been used for this purpose.
poly(styrenesulfonate) (PEDOT:PSS) thin film (typically to 5 eV) on it [23]. ITO used in this work is not characterized for its work function since its work function is close to the HOMO band of P3HT, which is reported to be in the region of 4.7 and 5.2 eV [24, 25]. Thus, the interface between these two materials is considered mostly ohmic in nature. However, since P3HT is a p-type semiconductor, the interface between P3HT and aluminum is mostly a Schottky contact. In a typical diode, holes injected from the anode electrode and electrons injected from the cathode electrode combine on the semiconductor polymer, thus allowing current to pass only in one direction. An aluminum cathode is reported to have a work function of 4.3 eV [26]. Since the work function of aluminum is not matched with the LUMO level of P3HT, which is reported to be between 2.6 and 3.0 eV [26], electrons are not injected efficiently from the aluminum side. This makes holes the main carriers in the conduction of the fabricated devices, lowering the efficiency of the diode. Metals with close work functions to the LUMO level of P3HT are alkaline metals such as calcium with a work function of 2.9 eV. Unidirectional conduction in the polymer diode with a multilayer cathode structure of ITO/P3HT/calcium/aluminum would ideally involve both electron and hole carriers. This structure would be more efficient since it would conduct more current for the same voltage applied to the diodes made with aluminum electrodes. More current would cause more self-heating of the diodes since electron–hole combination over the P3HT film causes mostly phonon (heat) generation not photon, which would make them better heat sources and hence better devices for the heater matrix. Unfortunately, alkaline metals are very reactive to oxygen and moisture in air, making these materials impractical for real life applications at the moment. Thus, calcium has not been used in this work.

The adaptation of a polymer diode as an actively addressable heating element requires certain deviations from an ideal diode structure. In an ideal polymer diode, the thickness of the active layer is made very thin, around 100 nm [11]. This is because the rectification happens at the vicinity of the electrode–polymer interface. The rest of the polymer thickness may be considered as the bulk of the polymer and it only adds a serial resistance to the rectifying diode. In an ideal diode, this bulk resistance must be minimized, and hence, the thickness of the polymer film. However, if the function of the polymer diode is to heat using a unidirectional current, this serial resistance of the bulk of the polymer is desirable since it increases the heating power, making the diode a better heating element. Thus, a thicker semiconductor polymer layer in this kind of application of polymer diodes must be used. Based on this fact, the thickness of the active polymer layer fabricated in this work is made around 5 μm as explained in the fabrication section, which means an increase of almost two orders in thickness compared to the previously reported polymer diodes. As a result the heating element, which is simply fabricated as a semiconductor polymer sandwiched between two electrodes, forms a diode in series with a resistor. The diode action at the polymer–electrode interface rectifies the current direction, thus allows active selection of heating elements. The resistance in series formed by the bulk of the polymer acts as a heater.

4. Fabrication

All the fabrication steps for polymer diodes are performed under standard room conditions, with a relative humidity level of 40–50% and a temperature of 21–26 °C. Diodes are fabricated on ITO-coated glass wafers with a sheet resistivity of 20 Ω/square, purchased from Precision Glass and Optics (Germany). They are cleaned in acetone, isopropyl alcohol and deionized water consecutively for 3 min using an ultrasonic cleaner. The process sequence of the fabrication is depicted in figure 4. ITO is patterned photo lithographically using a 2.8 μm thick positive photoresist and etched in a 1:1 HCl:H2O solution. Then, the photoresist mask is removed. A solution of semiconductor polymer, regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) purchased from Aldrich, is prepared by dissolving P3HT in chlorobenzene with a ratio of 5 mg mL−1. The solution is stirred at 65 °C on a hotplate for 1 h, and then in an ultrasonic cleaner at 65 °C for another hour to fully dissolve the polymer. After filtering the mixture with a 0.25 μm Teflon syringe filter, the P3HT solution is drop-cast on the glass substrate. The polymer solution is left to dry on the wafer at room conditions for 2 h. The wafer sits flat as the solution dries to make sure that the polymer solution stays on the surface. Afterwards the polymer film is baked on a hotplate at 90 °C for 1 h. This obtains a film thickness of approximately 5 μm. For the deposition of the aluminum electrodes, a shadow mask is prepared from a 50 μm thick stainless steel (SS301) sheet. A photoresist mask is patterned on a steel surface using lithography and then the steel is isotropically etched using electrochemical etching in a 1:7 HCl:DI water solution [27]. A vacuum chamber with a base pressure of 10⁻⁶ Torr is used to evaporate an 85 nm thick aluminum layer. The shadow mask is aligned perpendicular to the patterned ITO electrodes and evaporation forms orthogonal aluminum electrodes.

The fabricated 16 × 16 polymer diode matrix is composed of diodes with dimensions of 800 μm × 800 μm separated by a 200 μm gap between ITO electrodes and 600 μm gap between...
aluminum electrodes. The bigger gap of 600 μm is due to our technical limitation in shadow masking. The fabricated shadow mask has less resolution than the lithographically patterned ITO electrodes since an isotropic etching through a 50 μm thick stainless steel is involved. Furthermore, the alignment error of the shadow mask to the substrate in our setup is around 100 μm. In addition, a 100 μm gap is kept between the substrate and the shadow mask during evaporation in order to not damage the polymer film on the surface. Because of these non-idealities in the formation of aluminum electrodes, a safe final gap of around 600 μm is left in the design such that accumulative errors in the patterning would not cause any short circuits between neighboring aluminum electrodes. After the fabrication of the matrix, electrical contacts with the pads of the aluminum cathodes and ITO anodes are made by bonding copper wires to the pads using conductive silver epoxy. The fabricated device is shown in figure 5.

5. Characterization

After the fabrication of the heater matrix, dc current–voltage characteristics of the diode heater cells are made using a semiconductor parameter analyzer (Keithley SCS 4200). The devices are tested under an argon environment on top of a hotplate. The measurements are taken at different temperatures that are set by the hotplate. Since the diodes would be used as heat sources, it is crucial to monitor their characteristics at elevated temperatures. The argon environment makes sure that the polymer is not degraded while being operated or heated. Otherwise, at normal atmospheric conditions, the diode characteristics change as the polymer is doped by the oxygen or water vapor in the air and becomes more conductive. 16 neighboring polymer diodes forming a 4 × 4 configuration on the matrix are randomly selected and operated in parallel. Their current–voltage curves are measured 10 min after the hotplate temperature is set to the test temperature to make sure that the whole device reaches the same temperature uniformly. Instead of testing an individual diode, 16 diodes are selected in parallel to eliminate the effects of diode-to-diode variations and measure their average performances. The measurement results are shown in figure 6. The current density is found by dividing the applied current to the total area of 16 diodes. The results reveal that as the temperature of the polymer diodes increases, their performances improve. The turn-on voltage of the diodes, which is around 3 V, decreases. The diodes start to conduct more current for the same voltage value compared to the values achieved at lower temperatures. An example is the improvement of 2.7 μA mm⁻² current density at 5 V at room temperature to 12.2 μA mm⁻² at 120 °C. The improvement due to temperature increase is not permanent but it is repeatable. If the temperature of the devices is reduced to room temperature, the current–voltage graph at the beginning is obtained. Increasing the temperature again improves the diode characteristics again. This shows that the improvement is not due to thermal annealing of the polymer film. The reason for the observed performance improvement is due to the thermal excitation of the trap states on the grain boundaries of the thin polymer film, which is a well-documented phenomenon in polymer thin films [17, 18]. In this mechanism, the boundaries between the joining grains within the thin film act as trap states. These trap states are like deep pits that are required to be filled with charges before other charges can cross them. Increasing the electric field on the thin film or elevated temperatures causes these pits to become shallower. Hence, the required amount of charge and energy that is needed to cross the boundary is lowered. This increases the charge mobility, which in turn increases the forward current of the diode [17].

The current–voltage measurements of the diodes are performed from room temperature to 120 °C. The diodes did not fail at these temperatures. After the temperature tests, when the devices are at room temperature, the applied current densities are increased from 0 to 3 mA mm⁻² by increasing the applied voltages. The diodes did not fail at these elevated current densities, either. These tests show that polymer diodes can be self-heated to the temperatures tested in these experiments by applying current and be used as heat sources.
Figure 7. Thermal pictures of the 16 × 16 heater matrix taken by an infrared thermal imaging camera. An area consisting of 4 × 4 heaters are selected and current densities of (a) 0, (b) 1, (c) 2 and (d) 3 mA mm\(^{-2}\) are applied.

6. Result and discussion

After showing successful diode operation of the polymer diodes at elevated temperatures and current densities, the microheater matrix is tested using an infrared thermal imaging camera (TI25 from Fluke). A 16 × 16 heater matrix is placed flat, 15 cm away from the thermal camera. An area consisting of 4 × 4 cells is selected by applying current to four consecutive column electrodes and four consecutive row electrodes. Instead of testing 1 cell, 16 cells in a 4 × 4 configuration are preferred for testing since it is easier to see and measure a larger area on the thermal camera. The current is recorded and increased, while the thermal images are taken by the camera. Some examples of the taken pictures are shown in figure 7. As the current density applied to the cells increased from 0 to 3 mA mm\(^{-2}\), the selected 4 × 4 area shows increased temperature on the images. These pictures show that the fabricated polymer diode matrix can locally heat the selected area. The graph of maximum surface temperatures on the selected area of the matrix acquired from the thermal pictures and the applied current density is plotted in figure 8. A maximum temperature of around 110 °C is achieved on the polymer diode surface with an applied current density of 3 mA mm\(^{-2}\). The surface temperature increases with the increasing current density.

After showing successful operation of the heater matrix with a thermal camera, a thermal patterning test is made using thermal paper. Thermal paper (fax paper) is a commonly used paper in fax machines. One side of this white paper is coated with a thermally sensitive dye that turns black at temperatures above 90 °C. A piece of this paper is cut and put on the thermal matrix. A 1 mm thick, same size glass piece is also put on top of it to ensure a good intimate contact between the thermal paper and the matrix. After making sure that the paper is flat and uniformly touches the matrix, individual heater cells are selected by applying current to row and column electrodes for 30 s. The cells are activated randomly and manually since there was not an available electronic driver board for this matrix. The resulting thermal patterns on the thermal paper after this simple test are shown in figure 9. Around 930 × 930 μm\(^2\) black square shapes are formed on the paper where selected heater cells (800 × 800 μm\(^2\)) are. These results also show the pixel size of the thermal patterning. It is clear from these results that the fabricated heater matrix can generate
any thermal pattern or gradient on the surface with a proper electronic driving circuit.

7. Conclusion

A novel active microheater matrix has been implemented using semiconductor polymer diodes for thermal patterning for the first time in this work. In this system, a current applied to the row and column electrodes of the selected heater cell caused localized heating on that area. It was shown with SPICE analysis that a passive resistive microheater matrix was dysfunctional for this purpose because of the high leakage currents over the unselected resistors. In a 4 × 4 resistive heater matrix simulations, 44% of the applied current passed at 5 V at room temperature improved to 12.2 μA over the unselected resistors. In a 4 × 4 matrix on a thermally sensitive paper was also achieved. By applying current to the selected 800 × 800 μm² diodes, 930 × 930 μm² black squares were patterned on the thermal paper. The fabricated polymer diode matrix working as active microheater matrix can be used in thermal patterning of thermally sensitive materials. It can create local areas with different temperatures and thermal gradients that may be required in biological or chemical analysis.

Acknowledgments

This work is sponsored by the Scientific and Technological Research Council of Turkey (TÜBİTAK, project code 106E013) and by Bogazici University Research Fund under project number 09A201P.

References