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Synthetic Metals 115 (2000) 5–11

SYNTHETIC METALS

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Printing, molding, and near-field photolithographic methods for patterning organic lasers, smart pixels and simple circuits

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Abstract

This paper describes several 'soft lithographic' techniques that use rubber stamps, molds, and conformable photomasks for micro and nanofabrication. It illustrates how these methods provide low cost routes to patterning for applications in organic electronics and integrated optics. It summarizes some of our recent work in (i) roller printing of organic transistors and related circuitry for transistors, organic 'smart pixels' and complementary inverters that have critical dimensions as small as 1 μm, (ii) nanomolding of first and third order distributed feedback, distributed Bragg reflector and photonic crystal resonators for plastic lasers that have narrow emission profiles in the visible range, and (iii) fabrication of low voltage organic transistors and inverter circuits with 0.1 μm channels formed using low cost near-field photolithographic methods.

Keywords: Printing; Microcontact printing; Molding; Lasers; Organic electronics; Soft lithography

1. Introduction

Existing methods for lithography (photolithography, electron-beam lithography, etc.) work exceedingly well for patterning in conventional inorganic microelectronics, the task for which they were principally designed. For other applications, such as those in organic electronics, fiber optics or integrated optical systems that use polymers or sol–gel glasses, these methods have disadvantages: they often require resists, solvents and developers that are incompatible with the materials that must be patterned, they are unable to take advantage of the easy processability of many organic materials, they cannot be used for single-step patterning of large areas, and they do not work well when applied to rough, uneven or curved substrates. Because of these and other limitations, opportunities may exist for patterning techniques that use contact printing [1], imprinting [2], molding [3–5], low cost forms of near field photolithography [6,7], and for methods based on screen printing [8,9], or ink jet printing [10–13].

This paper describes some of our recent efforts to explore soft lithographic techniques [14–16] for applications in organic electronics and integrated optics. Recent work by Whitesides and co-workers [17,18] and Nuzzo and co-workers [19,20] demonstrates some applications in the area of conventional inorganic electronics. We begin by outlining the fabrication of elastomeric stamps, molds and conformable photomasks that are critical to these techniques. We then describe the use of the stamps in patterning for organic electronics by summarizing steps for printing arrays of thin film transistors (TFTs) and simple complementary inverter circuits [21,22]. Some of the capabilities of the elastomeric molding techniques are demonstrated through the fabrication of a variety of sol–gel glass and polymeric distributed laser resonators and of monolithically integrated organic transistors and organic light emitting diodes (LEDs) [23–27]. We also illustrate the use of a simple form of near field photolithography that relies on a conformable phase mask for producing low voltage organic transistors and inverters with 0.1 μm features [28]. In a concluding section, we highlight areas for future development.

2. Fabricating elastomeric stamps, molds and conformable photomasks

Elastomeric elements with features of relief as small as 20 nm can be fabricated by casting and curing an elastomeric prepolymer (polydimethylsiloxane, PDMS) against a

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0379-6779/00/$ – see front matter
PII: S0379-6779(00)00292-7

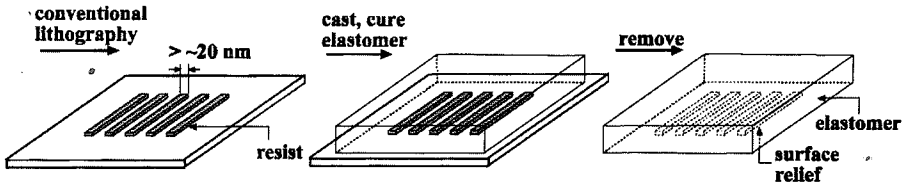

Fig. 1. Casting and curing an elastomer against a structure of surface relief forms elastomeric elements that can be used as stamps, molds or conformable photomasks.

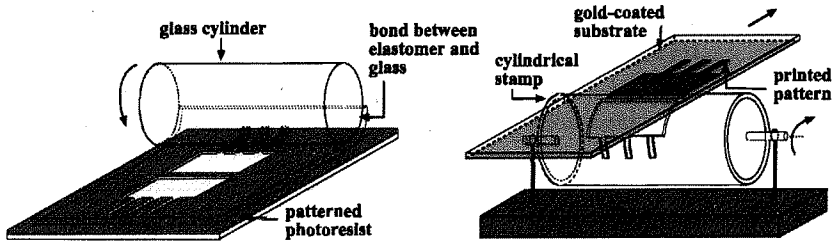

Fig. 2. Rolling a glass cylinder over the surface of a thin film of PDMS that has been exposed to an oxygen plasma leads to the formation of a strong bond between the elastomer and the glass, and causes the film to peel away from the patterned photoresist. The frame on the right shows how cylindrical stamps can be used for a type of continuous printing that is compatible with reel-to-reel processing.

'master' structure with relief on its surface [1,3,5]. Fig. 1 summarizes the fabrication of these elements. Many elements can be produced from a single master, and each element is reusable. This approach provides a convenient, low cost route to elastomeric stamps, molds and conformable photomasks. Although planar stamps are useful for many applications, thin (<1 mm) stamps bonded to rigid cylindrical substrates are better suited for printing over large areas; they also minimize distortions in printed patterns that arise from slight mechanical deformations of the stamp. Fig. 2 illustrates the fabrication of such a cylindrical stamp and suggests its use for continuous reel-to-reel printing. The design combines ideas described in [29,30]. The fabrication relies on the strong bond that forms when a glass surface is brought into contact with a surface of PDMS that has been treated with oxygen plasma [31,32].

3. Printing procedures for organic electronics

The elastomeric elements described in the preceding section can be used as high resolution stamps to transfer patterns of inks to planar and non-planar surfaces. This technique, known as microcontact printing [1,14–16], has the highest resolution (~30 nm features are possible [33]) when inks of alkanethiols are printed onto thin films of gold or silver. In this case, wet chemical etching removes unprinted regions of the gold and leaves a pattern with the geometry of the stamp. Although printed circuits of gold are generally not useful for conventional microelectronics, they are well suited for applications in organic electronics because gold is chemically inert and, following removal of the inks, it forms good ohmic contacts with a wide variety of common organic semiconductors. Fig. 3

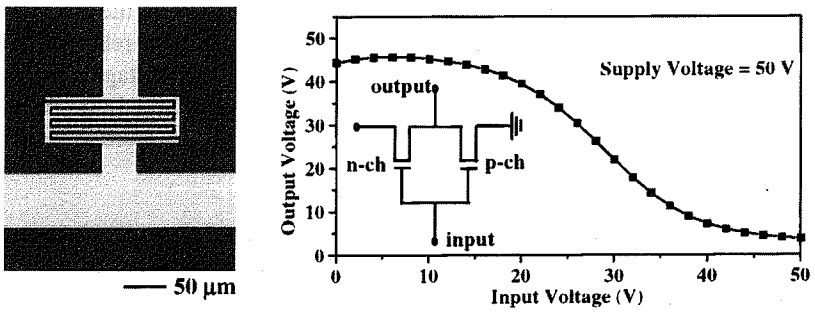

Fig. 3. The frame on the left shows interdigitated source/drain electrodes (separation ~2 µm) of gold printed using a cylindrical stamp. The frame on the right shows the transfer characteristics of an organic complementary inverter circuit formed with printed electrodes and appropriate interconnections. The performance of this device comparable to that of similar structures formed with photolithography.

shows optical micrographs and transfer characteristics of a simple organic complementary inverter circuit printed using a cylindrical stamp similar to the one shown in Fig. 2. This inverter uses a flexible plastic substrate of poly(ethylene terephthalate) (PET), a gate electrode of indium tin oxide (ITO), a solution-cast film of polyimide (thickness ~1 μm) as a gate dielectric, printed gold (thickness ~20 nm) source/drain electrodes with appropriate interconnections (resolution ~1 μm), and shadow-mask patterned layers of α-sexithiophene (α-6T) [34] and copper hexadecafluorophthalocyanine (F_{16}CuPc) [35] as p and n-type semiconductors, respectively. Details of the fabrication, the electrical characteristics and the materials are given in [21,22]. Attractive routes to fabrication of useful organic circuits may involve the combined use of emerging high resolution (<2 μm) techniques, such as microcontact printing, for defining critical features (separations between source/drain electrodes) and more established low resolution (>30 μm) methods, such as screen printing or ink jet printing, for patterning other elements (dielectrics, gates, electroluminescent materials, etc.).

4. Molding approaches for laser resonators and smart pixels

Molding approaches that use elastomeric elements [3,5] to produce features of surface relief in polymers and sol–gel glasses have potential applications in integrated optics where surface relief gratings, photonic crystals and other periodic arrays of sub-micron features are used as laser resonators, reflectors, attenuators, couplers, etc. Fig. 4 illustrates, for example, how a mold that has two levels of surface relief can be used to form a ridge waveguide distributed feedback laser resonator. In this sequence, and in similar ones for simple single-level structures [25], ultraviolet light that passes through a transparent mold cures a liquid prepolymer. With elastomeric molds, fragile nanostructures can flex and bend during removal of the mold from the solid molded part. This feature and the non-stick surface of the PDMS minimize damage to the mold and to the molded part during release, and enable repeated use of the mold. We have used these procedures to produce functional laser resonators with features as small as 0.1 mm (see Fig. 5). Details of the fabrication of these structures and of their use for first order distributed feedback plastic lasers will be described in a future publication.

Fig. 6 shows scanning electron micrographs of a molded, sol–gel derived organically modified silicate (ORMOSIL) photonic crystal resonator it also displays the emission spectrum from a laser formed with this resonator. In this case, casting a sol of glycidoxypropyltrimethyloxysilane and tetramethoxysilane against a suitable elastomeric mold, produces the resonator. Sublimation of a ~200 nm film of tris(8-hydroxyquinoline) aluminum (Alq) doped with 0.5–5.0 wt.% of the laser dye DCMII onto these resonators defines a single-mode planar waveguide and completes the fabrication. When photopumped with the output of a

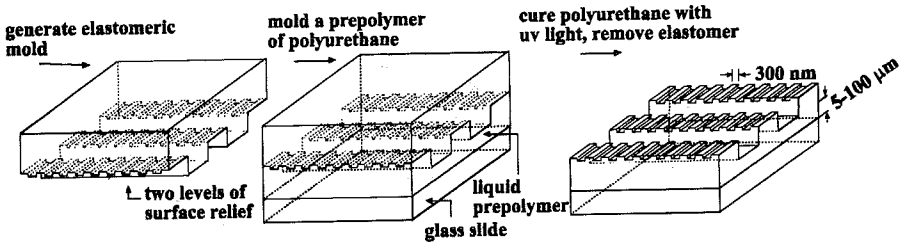

Fig. 4. Steps for fabricating a plastic distributed feedback ridge waveguide resonator by molding. Curing a liquid prepolymer by exposing it to ultraviolet light while in contact with an elastomeric mold produces a solid structure in a shape defined by the mold.

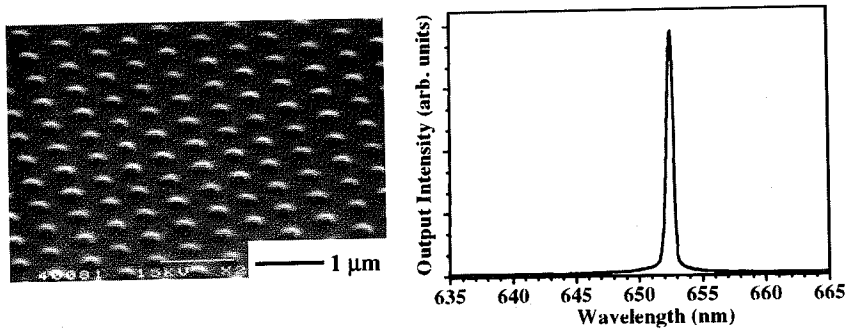

Fig. 5. Scanning electron micrographs of first order distributed feedback gratings defined by electron beam lithography in oxide (left frame) and by molding in an epoxy-novolac polymer (right frame). The structure on the right was produced with a mold that was generated by casting against the structure shown on the left. Note the small sizes of the features (~0.1 μm) and the correspondence between the defects in the 'master' structure and in the polymer replica.

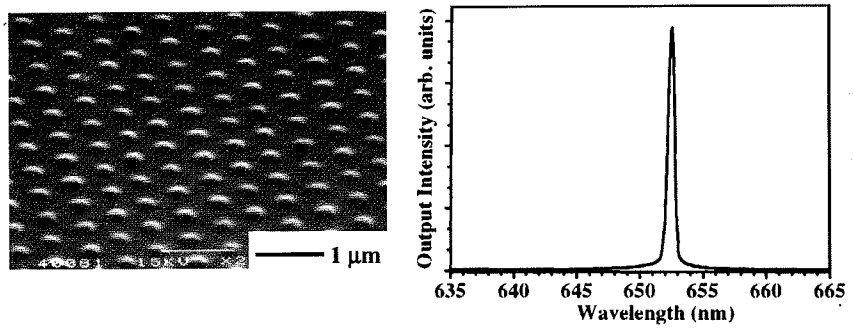

Fig. 6. The frame on the left shows a molded ORMOSIL photonic crystal laser resonator. The frame on the right shows the emission spectrum of a laser formed by photopumping a thin layer of organic gain material deposited onto this resonator.

pulsed nitrogen laser (337 nm, ~2 ns, ~10 kW/cm^2), these lasers emit red light [27]. The operating characteristics (lasing threshold, emission power and linewidth, spatial uniformity, etc.) are comparable to similar devices fabricated with photolithography. The good performance of these lasers and of ones that use printed and molded resonators in oxide and polymers [25,26] suggest the potential utility of molding and printing techniques for fabrication in the field of integrated optics. More generally, the results indicate that these methods can be applied to construction of certain types of devices that require single level nanostructures with relatively low distortions over macroscopic areas. These techniques may, in fact, be preferred for some applications because they are low cost, they can be applied to a range of materials that cannot otherwise be manipulated easily, and they can pattern structures that do not have even surfaces.

Fig. 7 illustrates, for example, the formation of a distributed feedback ridge waveguide laser by contact molding a thin film of organic gain material deposited onto the waveguides. Fig. 8 shows optical micrographs and emission spectra of lasers similar to those illustrated in Figs. 4 and 7. Fabricating this type of laser with conventional photolithographic methods would be difficult or impossible.

In addition to producing features of surface relief, a type of molding known as micromolding in capillaries [4] can be used, like microcontact printing, to define circuit elements for organic electronics. In this technique, the conformal sealing of an elastomeric element with features of surface relief against a flat, solid substrate defines capillary channels that can be filled with a variety of inks. When the ink consists of conducting carbon particles dispersed in ethanol, evaporation of the ethanol (PDMS is slightly permeable to ethanol

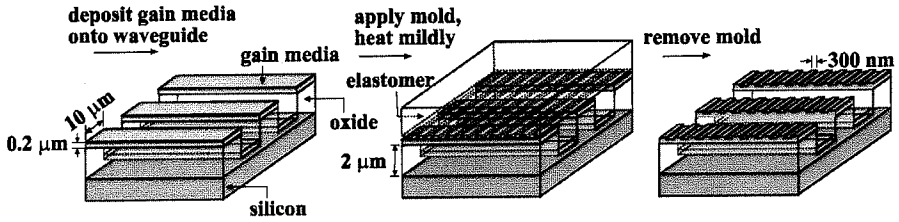

Fig. 7. Steps for fabricating a distributed feedback ridge waveguide laser that uses molded organic gain materials. A laser with this design would be difficult or impossible to fabricate using conventional photolithographic techniques.

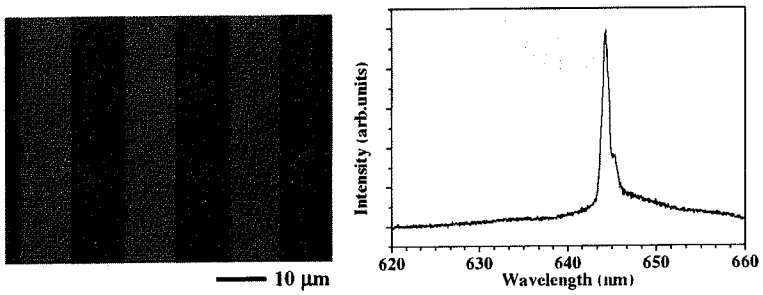

Fig. 8. The frame on the left shows an optical micrograph of a printed distributed feedback ridge waveguide laser; molded structures look similar. The frame on the right shows a typical emission spectrum from this type of laser.

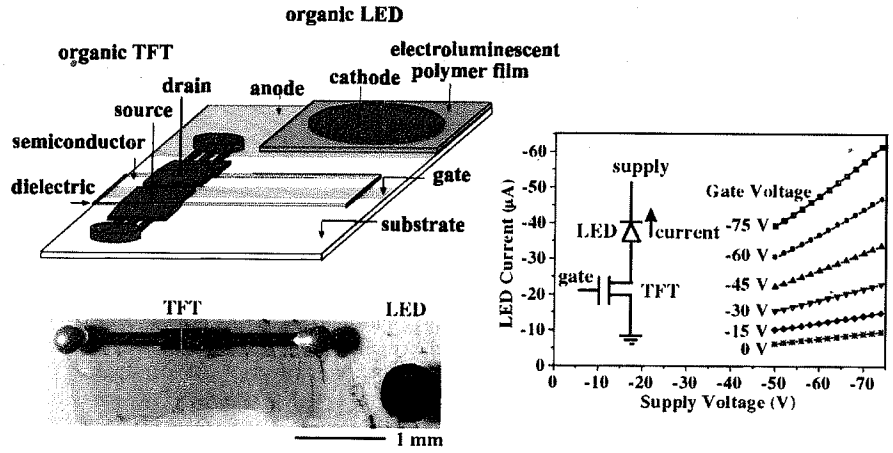

Fig. 9. The frames on the left show a schematic illustration and an optical micrograph of a non-photolithographically fabricated smart pixel. The dielectric, substrate, semiconductor and electroluminescent materials are all organic polymers. The frame on the right shows the electrical characteristics; the output intensity of the LED is proportional to the current.

vapor) produces solid carbon microstructures in the geometry of the channels [24]. Removal of the elastomeric mold leaves wires and electrodes of conducting carbon. We recently used this technique to form arrays of organic transistors and smart pixels with feature sizes as small as ~2 microns and with performance comparable to devices formed with photolithography [21,22,24]. Fig. 9 shows an illustration and measured characteristics of a micromolded smart pixel. These devices, which are similar to ones that we recently formed with microcontact printing [21,22], use PET substrates, ITO gates and anodes, solution-cast pre-imidized polyimide dielectrics, regioregular poly(3-hexylthiophene) [36] semiconductors, and a modified polyphenylene vinylene electroluminescent polymer [37]. Shadow evaporation of aluminum defined the cathodes for the LEDs. The performance of these smart pixels is similar to that of devices fabricated with photolithography on rigid inorganic substrates [38,39].

5. Near field photolithographic techniques for 0.1 mm organic transistors and inverter circuits

Elastomeric molds and stamps can serve as conformable photomasks for a type of near field photolithography [6,7]. In this technique, elastomeric photomasks are allowed to 'wet', or come into conformal contact with, the flat surface of a spin cast film of photoresist. Passing ultraviolet light through the elastomeric mask, while in contact with a layer of photoresist exposes the resist to the distribution of intensity that exists at the surface of the mask. The surface relief on stamps and molds like those illustrated in Fig. 1 modulates the phase of light that passes through them; these elements are, therefore, simple phase masks. If the depth of relief is chosen such that it causes a shift of the phase of the transmitted light by π, then nulls in the intensity appear at each step edge in the relief. The widths of these nulls are of the order of ~0.1 μm, when ~365 nm light from a conven-

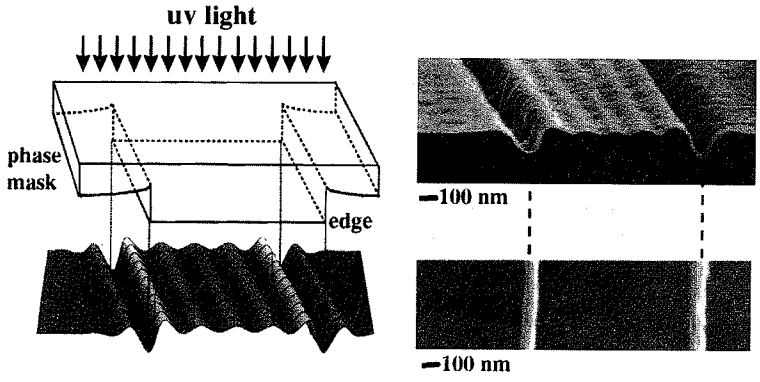

Fig. 10. Passing ultraviolet (UV) light through a transparent mask with surface relief produces nulls in the transmitted intensity at the step edges when the phase of the light is modulated by an odd multiple of π. The lower frame on the left illustrates the calculated distribution of intensity near the surface of such a phase mask. The frames on the right show patterns in image reversal and positive photoresist that result (after development) from near field exposure while in contact with an elastomeric phase mask.

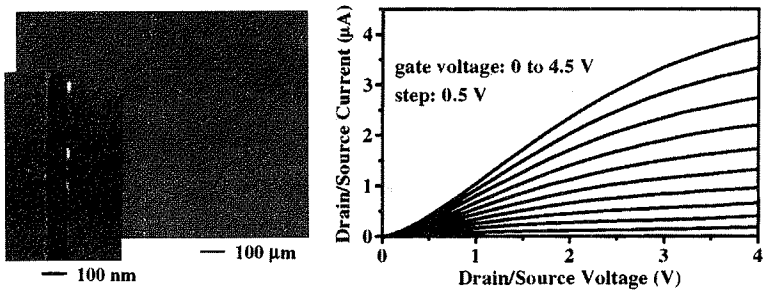

Fig. 11. The frame on the left shows low and high resolution scanning electron micrographs of slits in gold defined by a near field photolithographic technique that uses an elastomeric phase mask. The frame on the right shows the current/voltage characteristics of an n-channel organic transistor that uses source/drain electrodes fabricated with printing and near field lithography.

tional mercury lamp is used. These nulls produce, after exposure and development, ~0.1 μm lines in positive photoresist. Fig. 10 provides an illustration.

Depositing a uniform thin layer of metal onto resist patterned in this manner and then removing the resist with acetone produces slits in the metal film. For applications in organic electronics, 0.1 μm slits in gold are useful for defining narrow separations between source and drain electrodes whose other dimensions are patterned using microcontact printing, for example. Fig. 11 shows a slit in a film of gold and presents the electrical characteristics of an n-channel transistor formed using this structure and a sublimated layer of $F_{16}CuPc$ as the semiconductor. The low voltage operation of the device derives from its extremely small dimensions. Other characteristics of these devices and of complementary inverters that are formed with them will be presented elsewhere [28].

6. Conclusions

Our recent work with printing, molding and near field lithographic techniques that use elastomeric elements (soft lithographic techniques), provides some evidence that these methods may be attractive for certain applications that are not well suited to conventional patterning techniques. Although laboratory prototypes of a variety of simple devices show encouraging results, most realistic applications will require more complex structures whose fabrication may be most easily accomplished by integrating the techniques described here with other methods that have complementary capabilities. This integration and the development of simple approaches for performing registration and multilevel fabrication are subjects of current work.

References

[1] A. Kumar, G.M. Whitesides, Appl. Phys. Lett. 63 (1993) 2002.
[2] S.Y. Chou, P.R. Krauss, P.J. Renstrom, Appl. Phys. Lett. 67 (1995) 3114.
[3] G.D. Aumiller, E.A. Chandross, W.J. Thomlinson, H.P. Weber, J. Appl. Phys. 45 (1974) 4557.
[4] E. Kim, Y. Xia, G.M. Whitesides, Nature 376 (1995) 581.
[5] Y. Xia, J.J. McClelland, R. Gupta, D. Qin, X.-M. Zhao, L.L. Sohn, R.J. Celotta, G.M. Whitesides, Adv. Mater. 9 (1997) 147.
[6] J.A. Rogers, K.E. Paul, R.J. Jackman, G.M. Whitesides, Appl. Phys. Lett. 70 (1997) 2658.
[7] J.A. Rogers, K.E. Paul, R.J. Jackman, G.M. Whitesides, J. Vac. Sci. Technol. B 16 (1998) 59.
[8] F. Garnier, R. Hajlaoui, A. Yassar, Science 265 (1994) 1684.
[9] Z. Bao, Y. Feng, A. Dodabalapur, V.R. Raju, A. Lovinger, Chem. Mater. 9 (1997) 1299.
[10] J. Bharathan, Y. Yang, Appl. Phys. Lett. 72 (1998) 2660.
[11] T.R. Hebner, C.C. Wu, D. Marcy, M.H. Lu, J.C. Sturm, Appl. Phys. Lett. 72 (1998) 519.
[12] A. Atkinson, J. Doorbar, A. Hudd, D.L. Segal, P.J. White, J. Sol–Gel Technol. 8 (1997) 1093.
[13] S.J. Kim, D.E. McKean, J. Mater. Sci. Lett. 17 (1998) 141.
[14] Y. Xia, J.A. Rogers, K.E. Paul, G.M. Whitesides, Chem. Rev. 99 (1999) 1823.
[15] D. Qin, Y. Xia, J.A. Rogers, R.J. Jackman, X.-M. Zhao, G.M. Whitesides, in: A. Manz, H. Becker (Eds.), Topics in Current Chemistry, Springer, Berlin, 1998, pp. 1–20.
[16] Y. Xia, G.M. Whitesides, Angew. Chem. Int. Ed. 37 (1998) 550.
[17] J. Hu, R.G. Beck, T. Deng, R.M. Westervelt, G.M. Whitesides, Adv. Mater 10 (1998) 574.
[18] J. Hu, R.G. Beck, T. Deng, R.M. Westervelt, K.D.G. Maranowski, G.M. Whitesides, Appl. Phys. Lett. 71 (1997) 2020.
[19] N.L. Jeon, J. Hu, G.M. Whitesides, M.K. Erhardt, R.G. Nuzzo, Adv. Mater. 10 (1998) 1466.
[20] N.L. Jeon, P. Clem, D.Y. Jung, W. Lin, G.S. Girolami, D.A. Payne, R.G. Nuzzo, Adv. Mater. 9 (1997) 891.
[21] J.A. Rogers, Z. Bao, A. Makhija, Adv. Mater. 11 (1999) 741.
[22] J.A. Rogers, Z. Bao, A. Dodabalapur, A. Makhija, IEEE Electron Dev. Lett. 21 (2000) 100.
[23] J.A. Rogers, Z. Bao, L. Dhar, Appl. Phys. Lett. 73 (1998) 294.
[24] J.A. Rogers, Z. Bao, R.V. Raju, Appl. Phys. Lett. 72 (1998) 2716.
[25] J.A. Rogers, M. Meier, A. Dodabalapur, Appl. Phys. Lett. 73 (1998) 1766.
[26] J.A. Rogers, M. Meier, A. Dodabalapur, Appl. Phys. Lett. 74 (1999) 3257.
[27] O.J.A. Schueller, G.M. Whitesides, J.A. Rogers, M. Meier, A. Dodabalapur, Appl. Opt. 38 (1999) 5799.
[28] J.A. Rogers, A. Dodabalapur, Z. Bao, H.E. Katz, Appl. Phys. Lett. 75 (1999) 1010.
[29] Y. Xia, D. Qin, G.M. Whitesides, Adv. Mater. 8 (1996) 1015.
[30] J.A. Rogers, K.E. Paul, G.M. Whitesides, JVST B 16 (1998) 88.
[31] O.J.A. Schueller, D.C. Duffy, J.A. Rogers, S.T. Brittain, G.M. Whitesides, Sensors & Actuators A, 2000, in press.
[32] D.C. Duffy, J.C. McDonald, O.J.A. Schueller, G.M. Whitesides, Anal. Chem. 70 (1998) 4974.

[33] H.A. Biebuyck, N.B. Larsen, E. Delamarche, B. Michel, IBM J. Res. Develop. 41 (1997) 159.
[34] A. Dodabalapur, L. Torsi, H.E. Katz, Science 268 (1995) 270.
[35] Z. Bao, A.J. Lovinger, J. Brown, J. Am. Chem. Soc. 45 (1998) 11331.
[36] Z. Bao, A. Dodabalapur, A.J. Lovinger, Appl. Phys. Lett. 69 (1996) 4108.
[37] Z. Bao, Z. Peng, M.E. Galvin, Chem. Mater. 10 (1998) 1201.
[38] A. Dodabalapur, Z. Bao, A. Makhija, J.G. Laquindanum, V.R. Raju, Y. Feng, H.E. Katz, J.A. Rogers, Appl. Phys. Lett. 73 (1998) 142.
[39] H. Sirringhaus, N. Tessler, R.H. Friend, Science 280 (1998) 1741.