Fabrication of a 256-bits organic memory by soft x-ray lithography*

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This paper reports a procedure of soft x-ray lithography for the fabrication of an organic crossbar structure. Electron beam lithography is employed to fabricate the mask for soft x-ray lithography, with direct writing technology to the lithograph positive resist and polymethyl methacrylate on the polyimide film. Then Au is electroplated on the polyimide film. Hard contact mode exposure is used in x-ray lithography to transfer the graph from the mask to the wafer. The 256-bits organic memory is achieved with the critical dimension of 250 nm.

Keywords: molecular memory, crossbar array, soft x-ray lithography, electron beam lithography
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1. Introduction

Organic electronics have attracted considerable attention due to their low cost, easy-fabrication, flexibility and printing capability. There has been a significant amount of research focused on organic field-effect transistors,[1−3] organic light-emitting diodes,[4−6] memories,[7] photovoltaic cells,[8] and sensors.[9] Among them, much attention is paid to organic memory devices.[10] Molecular electronics with the architecture of crossbar-arrays has a promising future for both memory and logic applications. Although it offers the tantalizing prospect of eventually building circuits with critical dimensions of a few nanometers, the density of the circuits with molecular components is still limited by the lithography used in the fabrication of electrodes and interconnections. Previous nanoscale molecular devices have been fabricated by using electron beam lithography (EBL).[11,12] But EBL is impractical for commercial applications because of the low writing speed. High-energy electron beams can also damage the active molecule layer in the circuit. Nowadays, nano-imprinting lithography (NIL) is often used in the lithography of the crossbar structure.[13−15] A super-lattice nanowire pattern transfer method is also reported in Ref. [16], by which the nanowires containing up to 1400 nanowires at a pitch as small as 15 nm are fabricated. Soft x-ray lithography is an efficient lithography method in comparison with EBL,[17] because of its high lithography speed and low energy damage to the active molecule layer. At the same time, soft x-ray lithography causes less mechanical damage to the active molecule layer than NIL.

In this paper, we report a procedure for soft x-ray lithography for the fabrication of 256-bits molecular crossbar memory devices. The critical dimension is down to 250 nm. The bistable characteristics of the device are demonstrated by the current–voltage testing and the mechanism of the switching behaviour is discussed.

2. Device fabrication

2.1. Fabrication of the soft x-ray lithography mask

The mask of the 256-bits crossbar-array for the soft x-ray lithography is fabricated by EBL on polyimide (PI) free-standing membrane as shown in Fig. 1. Gold is the preferred absorber material practically,

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mainly because of its high absorption values and well-known subsequent processing steps. i) The 3.5 μm PI is spin-coated on the surface of silicon substrate, and baked on a hotplate (Fig. 1(a)). After being cooled in air, it is put into a clamp apparatus designed and backside etched by a hydrofluoric, nitric, and acetic acids system (Fig. 1(b)). ii) The 5 nm chromium and 10 nm gold are respectively evaporated as an electroplating seed layer by Johnsen U1 travas 92 EVAP electron beam evaporator at 4×10^{-4} Pa pressure (Fig. 1(c)). iii) Then, 500 nm thick polymethyl methacrylate (PMMA) is spin-coated on the substrate (Fig. 1(d)). The resist is exposed by using a JOEL5000LS electron beam writer at 50 keV accelerating voltage, then developed in methyl-iso-butyl-ketonc (MIBK): isopropyl alcohol (IPA) and rinsed in IPA (Fig. 1(e)). iv) Electroplating is carried out in gold sulfite $[Au(SO_3)_2]Na_3$ solution (Fig. 1(f)), then PMMA is removed by acetone (Fig. 1(g)), and the Cr/Au plating seed layer is removed by using induced coupled argon plasma (Fig. 1(h)). Then the mask of the 256-bits crossbar-array for the soft x-ray lithography replication is obtained, as shown in Fig. 2.

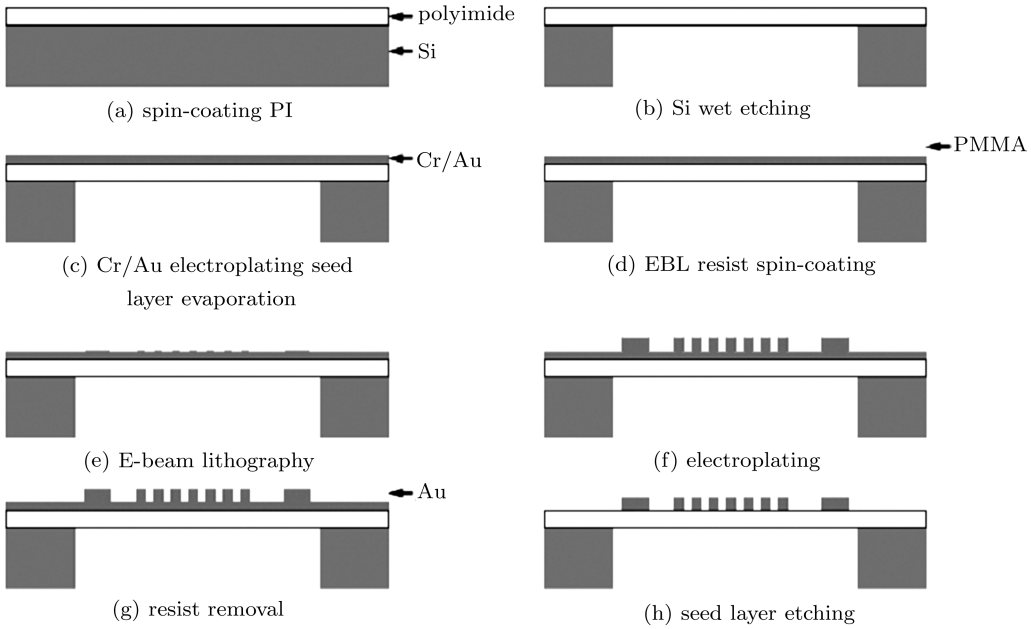


Fig. 1. Schematic illustration of the mask fabrication for the soft x-ray lithography.

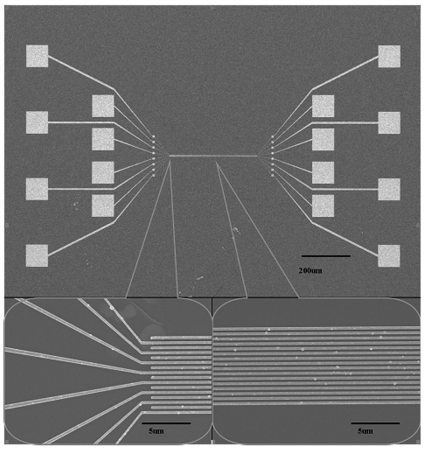


Fig. 2. The SEM image of the soft x-ray lithography mask fabricated by EBL and electroplating.

2.2. Fabrication of the devices

The soft x-ray lithography is introduced to the fabrication of the bottom metal electrodes of the 256-bits crossbar-array. First, 300 nm PMMA is spin-coated on the surface of an isolated substrate, which is formed by depositing 250 nm SiO_2 on silicon by using plasma enhanced chemical vapour deposition. Then, the resist is exposed in the soft x-ray lithography beamline and end-station at the National Synchrotron Radiation Laboratory and Beijing Synchrotron Radiation Facility, developed in MIBK: IPA and rinsed in IPA correspondingly. After the resist residue etching, 20 nm Ti and 80 nm Pt are respectively evaporated by the same electron beam evaporator above. The un-

wanted metal on the resist is removed in acetone by the lift-off processing and the bottom metal electrodes of the 256-bits crossbar-array are achieved.

The structure of eicosanoic acid (EA) used in this work and the schematic diagram of the device are shown in Fig. 3. A molecular monolayer of EA film is deposited over the entire device substrate, including bottom metal electrodes, using the Langmuir–Blodgett (LB) method.[18] During LB film deposition the surface force of the liquid maintains 30 Nm. The hydrophilic stopper of the EA is combined to the bottom metal electrodes, because of the hydrophilicity of the latter.

A 20 nm Ti protective layer is evaporated on the molecular layer before the fabrication of the top electrodes. The Ti layer is very reactive with the top functional group of the molecules to form a direct electric to the molecules. It also blocks the further metal penetration into the LB monolayer, and minimizes subsequent damage to the molecules, including further organic resist and solvent processing.

Top metal electrodes of 20 nm Ti and then 80 nm Au are next fabricated with the same soft x-ray lithography process just described, using the same mask. For the top electrodes, the mask is oriented perpendicular to the bottom electrodes and aligned to ensure that the top and bottom nanowires crossed. Finally, reactive ion etch (RIE) with CHF_3 (40 sccm) and O_2 (10 sccm) gases and a power of 400 W is used to remove the blanket Ti protective layer anisotropically down to the SiO_2 layer, but selectively leave the Pt electrodes intact. The molecules and Ti layer under the Pt top electrode are protected. After RIE, an array of devices with the molecular monolayer sandwiched between two metal nanowires is remained. The 256-bits crossbar-array and the details are shown in Fig. 4. The nanowires are about 250 nm width.

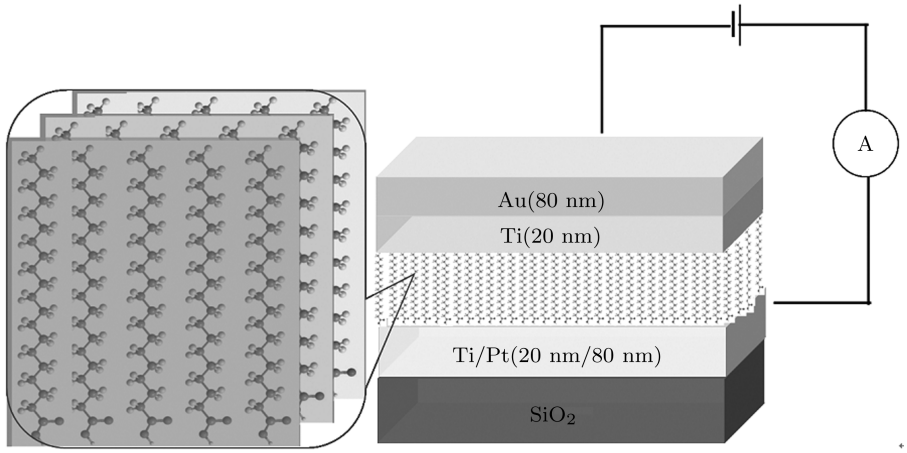


Fig. 3. Molecular structure of the EA ($C_{20}H_{40}O_2$) used to form LB monolayers, and schematic illustration of the structure of Ti/Pt/EA/Ti/Au crossbar.

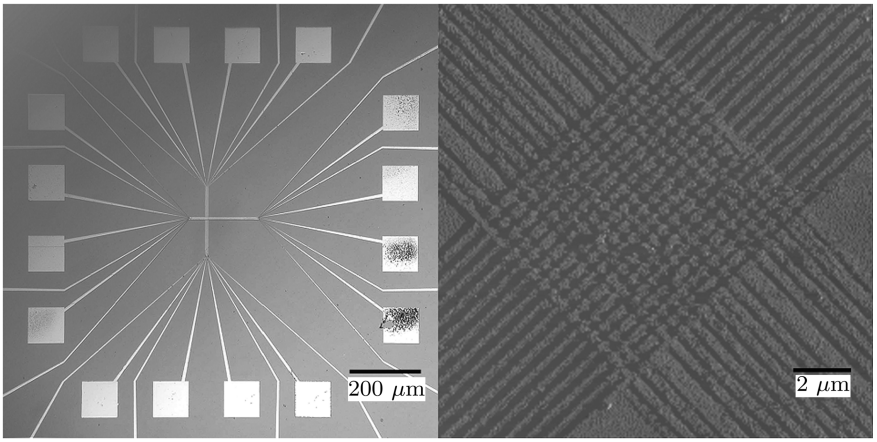


Fig. 4. An optical micrograph (a) and an AFM photo (b) of the 256-bits crossbar-array.

3. Results and discussion

The x-ray photoelectron spectroscopy (XPS) measurements are performed on the substrate to verify the formation after EA film deposition. Figures 5(a) and 5(b) show the XPS spectrum of the substrate after the EA film deposition. These figures show the presence of C (binding energy: 284 eV) and O (binding energy: 532 eV) on the sample surface. To confirm the formation of EA film on the Pt surface, wetting property testing is employed on the surface of Pt before and after the deposition. The surface changes from hydrophilic surface (water-contact angle 53.4°, Fig. 5(c)) to hydrophobic surface (water-contact angle 85.1°, Fig. 5(d)) after the EA film deposition. This change of wetting property confirms the formation of the EA film.

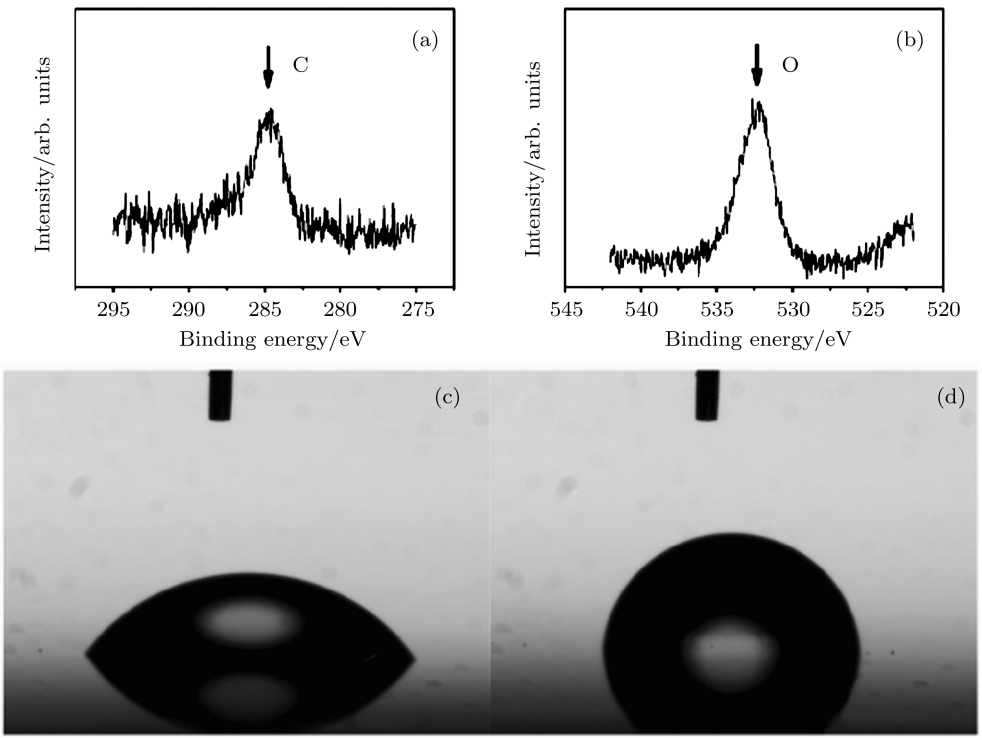


Fig. 5. The XPS spectrum of the substrate after the EA film deposition (a and b), water contact angle on Pt surface (c) and EA film surface (d).

Current–voltage characteristics of crosspoints in the 256-bits crossbar-array are obtained by applying a test voltage ($V_{\rm T}$) to the cross point between the bottom electrodes and the top electrodes using Keithley 4200 semiconductor characterization system and Cascade RF-1 probe station. Typical current–voltage characteristics are presented on a semi-logarithmic scale in Fig. 6(a). The inset shows the same data of the positive voltage on a double logarithmic scale. A positive voltage bias cycle from 0 V to 5 V is applied to the cross point under test of the 256-bits crossbar-array. It keeps high resistance state with $R_{\rm T} = 163.8$ MΩ (at 0.5 V), when $V_{\rm T}$ is swept from 0 V to 5 V (Fig. 6(a) I). A turning point at about 4.9 V is observed, at which the resistance of device drops from 5.1 MΩ to 253 kΩ, and the $R_{\rm T}$ measured at 0.5 V drops to 407.4 kΩ when the voltage falls down to 0 V from 5 V (Fig. 6(a) II). After the positive cycle added to the cross point under test, a similar negative cycle is swept from 0 V to –5 V. In this cycle, the turning point occurs at –3.6 V, at which the resistance of device rises from 346 kΩ to 1.81 MΩ (Fig. 6(a)III). Finally, the voltage rises from –5 V to 0 V to complete the cycle (Fig. 6(a) IV). When we choose 0.5 V as the reading voltage, the resistance of the OFF state is 163.8 MΩ, while the resistance of the ON state is 407.4 kΩ. The ON/OFF ratio is up to 4×10^2.

The on/off switching events are repeatable, as shown in Fig. 6(b). However, the ON/OFF ratio of $R_{\rm T}$ for this device decreases gradually after about 20 switch cycles, and the device breaks down to high resistance state. Much works are needed to improve the reproducibility of the memory device.

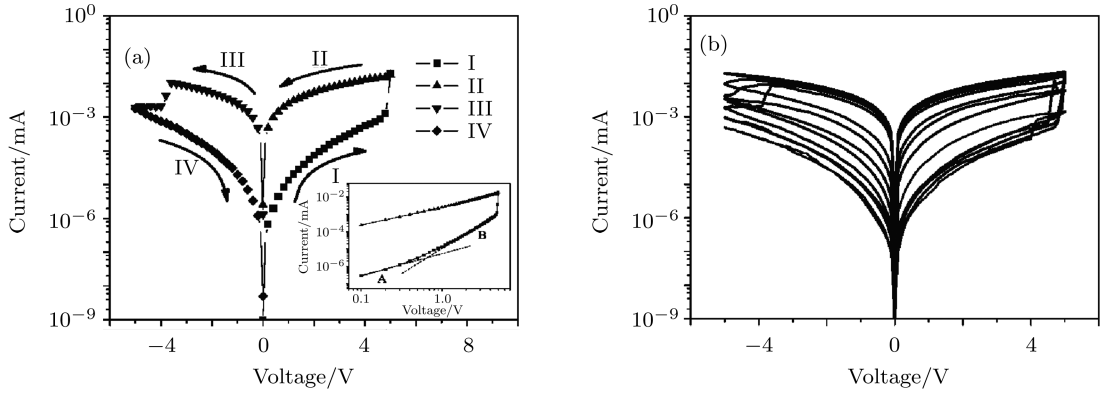


Fig. 6. Electronic characteristics of a typical molecular device. The current–voltage curves show complete off-on-off device switching cycle (a), and the repetition of a typical divice (b).

As shown in the inset of Fig. 6(a), with the increase of positive voltage in step I, the current increases linearly with applied voltage at low biases at the beginning, and the slope changes from 1 to 2 with increasing bias. This slope change indicates a transition from ohmic to space charge limited current transport.[19] In step II, the slope keeps 1 with the decreasing bias, which means an ohmic current transport. The mechanism of the switching behaviour is thought to be a strong function of the molecules and the electrodes and their interfacial interactions.[20]

4. Conclusions

In this paper, we show the 256-bits crossbar-array of EA fabricated by soft x-ray lithography and lift-off processing. The critical dimension is down to 250 nm at a laboratory environment. The electronic characteristics of the 256-bits crossbar-array with the bistable EA are similar to the structures using nano imprinting or UV lithography, which means soft x-ray with the energy about 500 eV does not have deathful damage to the electronic characteristics of the organic molecules. The mechanism of the switching behaviour might be a strong function of the molecules and the electrodes and their interfacial interactions.

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References

[1] Dodabalapur A, Torsi L and Katz H E 1995 *Science* **268** 270
[2] Sun Y, Liu Y and Zhu D 2005 *J. Mater. Chem.* **15** 53
[3] Tao C, Zhang X, Dong M, Liu Y, Sun S, Ou G, Zhang F and Zhang H 2008 *Chin. Phys.* B **17** 0281
[4] Burroughes J H, Bradley D D C, Brown A R, Marks R N, Mackay K, Friend R H, Burn P L and Holmes A B 1990 *Nature* (London) **347** 539
[5] Du P, Zhang X, Sun X, Yao Z and Wang Y 2006 *Chin. Phys.* **15** 1370
[6] Zhang L, Hua Y, Wu X, Wang Y and Yin S 2008 *Chin. Phys.* B **17** 3097
[7] Cavallini M, Biscarini F, Leon S, Zerbetto F, Bottari G and Leigh D A 2003 *Science* **299** 531
[8] Ma W, Yang C, Gong X, Lee K and Heeger A J 2005 *Adv. Funct. Mater.* **15** 1617
[9] Street R A, Mulato M, Lau R, Ho J, Graham J, Popovic Z and Hor J 2001 *Appl. Phys. Lett.* **78** 4193
[10] Tu D, Shang L, Liu M and Wang C 2007 *Appl. Phys. Lett.* **90** 052111
[11] Chen J, Reed M A, Rawlett A M and Tour J M 1999 *Science* **286** 1550
[12] Luo Y, Collier C P, Jeppesen J O, Nielsen K A, DeIonno E, Ho G, Perkins J, Tseng H, Yamamoto T, Stoddart J F and Heath J R 2002 *Chem. Phys. Chem.* **3** 519

[13] Chen Y, Ohlberg D A A, Li X, Stewart D R, Williams R S, Jeppesen J O, Nielsen K A, Stoddart J F, Olynick D L and Anderson E 2003 *Appl. Phys. Lett.* **82** 1610

[14] Chen Y, Jung G Y, Ohlberg D A A, Li X, Stewart D R, Jeppesen J O, Nielsen K A, Stoddart J F and Williams R S 2003 *Nanotechnology* **14** 462

[15] Wu W, Jung G Y, Olynick D L, Straznicky J, Li Z, Li X, Ohlberg D A A, Chen Y, Wang S Y, Liddle J A, Tong W M and Williams R S 2005 *Appl. Phys.* A **80** 1173

[16] Melosh N A, Boukai A, Diana F, Gerardot B, Badolato A, Petroff P M and Heath J R 2003 *Science* **300** 112

[17] Yi F, Ye T, Peng L, Chen D, Zhang J and Han Y 2004 *Chin. Phys.* **13** 0731

[18] Corkery R W 1997 *Langmuir* **13** 3591

[19] Chechel O V and Nikolaev E N 1991 *Instruments and Experimental Techniques* **34** 750

[20] Stewart D R, Ohlberg D A A, Beck P A, Chen Y, Williams R S, Jeppesen J O, Nielsen K A and Stoddart J F 2004 *Nano Lett.* **4** 133