

Supporting Information

New metallization method of modified tannic acid photoresist pattern

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Experimental section

Chemicals

Tannic acid (TA, 98 wt%) was supplied by Zhangjiajie Jiurui Biotechnology Co., Ltd. Methacryloyl chloride (MA, 98 wt%), 4-Dimethylaminopyridine (DMAP, 98 wt%), Triethyl amine (99 wt%), Di-tert-butyl decarbonate (t-Boc, 98 wt%), Pentaerythritol triacrylate (PETA, 98 wt%), Butylated hydroxytoluene (98 wt%), 2-Acetoxy-1-methoxypropane (PGMEA, 98 wt%), Tetramethylammonium hydroxide (TMAH) aqueous solution (2.38 wt%) were purchased from Shanghai Macklin Biotechnology Co., Ltd. Silver nitrate, Ammonia water (13.8 mol/L), Dimethyl formamide (DMF, 98 wt%), Acetone (98 wt%), and Trisodium citrate dihydrate (98 wt%) were provided by Shanghai Chemical Reagent Co., Ltd. 2-Methyl- α -[2-[[propylsulfonyl]oxy]imino]-3(2H)-thienylidene]benzene acetonitrile (PAG103) and 2-(4-Methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (3D) were purchased from Beijing Technology Co., Ltd. All chemicals were analytical grade and were used without further purification.

Synthesis of modified tannic acid (TA-Boc-MA)

TA-Boc-MA samples were prepared by reaction of tannic acid with t-Boc and MA in a mixture of acetone and DMF. Briefly, Di-tert-butyl decarbonate (t-Boc) (10.0 g) was dropped into acetone and DMF solution (4:1, volume ratio) of tannic acid (170 g/L, 50 mL) with stirring in N₂ atmosphere at room temperature (25 °C), followed by the addition of the DMF solution of DMAP (0.02 g/L, 10 mL) in 10 minutes and then the reaction mixture was continued for 12 h. Then, 7.0 g triethylamine and 7.3 g methacryloyl chloride were successively dropped into the solution within 15 minutes after the resultant solution was cooled down below 5 °C. After 15 minutes of reaction, the solution was raised to room temperature naturally and the reaction was maintained for 9 h. Next, the resulting solution was dropwise added into ultrapure water to precipitate the product. The product was filtrated and washed with ultrapure water for three times. Finally, the solid powder was dried in vacuum at 40 °C for 24 h.

Blending of photoresist

The photoresists were blended by mixing TA-Boc-Ma, PAG103 and 3D, PETA with PGMEA with stirring continuously above 6 h. The detailed ratio of components was shown in Table S1.

Table S1 The detailed ratio of photoresist components

Components	PGMEA	TA-Boc-Ma	3D	PAG103	PETA
Mass fraction	80.0%	17.0%	0.5%	0.5%	2.0%

The formation of lithographic pattern based on modified tannic acid

The photoresists were filtrated through a 0.22 μm filter and then spin-coated onto silicon wafers (or Polyethylene terephthalate film, Polyimide film, flexible ITO and so on) at 1200 rpm for 30 s, followed by soft baking at 90 $^{\circ}\text{C}$ for 90 s. Subsequently, the film was first exposed for 4 minutes with a mask by 365 nm UV light (14 mw/cm^2), baked at 110 $^{\circ}\text{C}$ for 90 s, developed in an TMAH aqueous solution for 1 min and washed with ultrapure water at room temperature. After that, a second blanket exposure was applied to the patterned substrate for 1 min, followed by baking at 120 $^{\circ}\text{C}$ for 2 minutes.

Formation of Ag Pattern

Ag pattern was fabricated by a simple electroless plating process. Firstly, 1.0 g of silver nitrate was dissolved in 100 mL of water, followed by dripping ammonia water (25 wt%) to form a white precipitate and then continue to drip until the white precipitate disappears for preparing the solution of tollens' reagent. Afterwards, 1.0 g of trisodium citrate dihydrate and 1.0 g of polyvinylpyrrolidone (K30) was mixed with tollens reagent by stirring for 15 minutes, followed by adjusting the pH to about 8.5 with acetic acid. And then lithographic patterned substrate from the previous step was immersed into the solution at 60 $^{\circ}\text{C}$ for certain time and was taken out for washing with ultrapure water and drying with compressed air. At this point, the fabrication of Ag pattern had been finished. Finally, Ag pattern was annealed on a hot plate at 200 $^{\circ}\text{C}$ for 10 min.

Preparation of Ag Film

The method for preparation of Ag film was similar to the fabrication of Ag pattern. The Si substrate coated with the photoresist directly underwent the second exposure mentioned above without first exposure and other treatments were the same.

Etching of Ag film

The etching of Ag film was conducted by XPS spectra (Thermo Scientific ESCALAB 250Xi spectrometer). Etching energy was 1 keV and etching time was 1500 s and etching rate is 40 nm/min.

Characterization

Fourier transform infrared spectrum (FTIR) test was performed on a TensorII FTIR spectrometer at room temperature. ^1H spectra were set down on Bruker 400 MHz Spectrometer in DMSO-d₆ with TMS as a standard at room temperature. SEM imaging and elemental mapping was obtained by an SU8018 electron microscope with an Oxford energy-dispersive X-ray (EDX) analysis system. XRD patterns were obtained by a Smart Lab Se diffractometer equipped with Cu K α radiation. XPS spectra were obtained by a Thermo Scientific ESCALAB 250Xi spectrometer. The UV-visible

absorption spectra were carried out with TU-1901 double beam UV–vis spectrophotometer. Square resistance test was performed by a resistance tester with four-point probe. The measurement of flexible electronic device was performed by an electrochemical workstation.

The calculation method of graft ratio of t-Boc and MA:

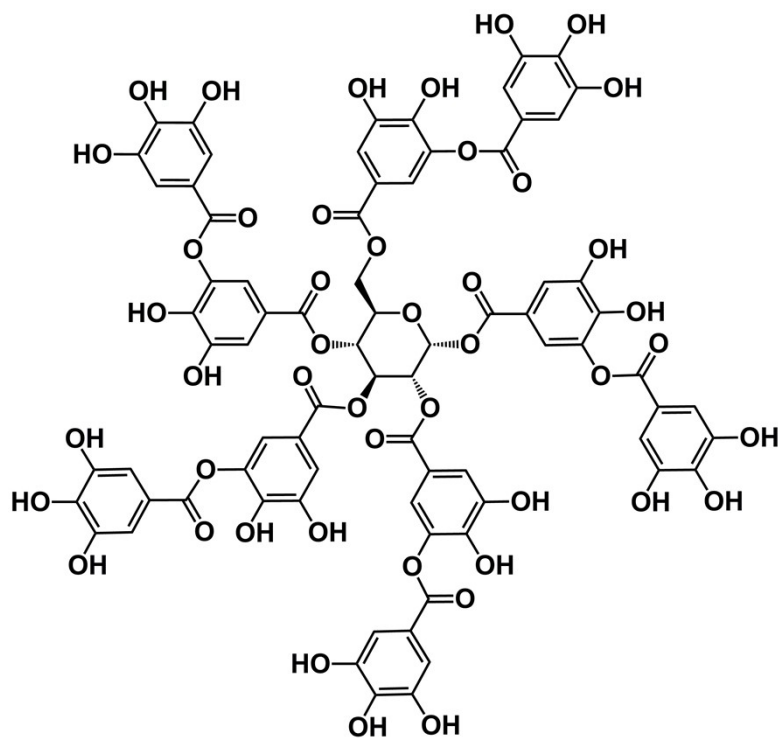
The grafting molar ratios of t-Boc and MA on the phenolic group of tannic acid were calculated by the numbers of phenolic group on tannic acid, hydrogen on the phenyl ring, methyl in the tertiary butyl and vinyl. 1 mol of tannic acid, t-Boc and MA has 20 mol hydrogen of phenyl ring, 9 mol of methyl hydrogen on tert butyl and 2 mol of hydrogen on vinyl, respectively. And 1 mol of tannic acid has 25 mol of phenolic group. The calculation formulas are as follows:

$$GR(t - Boc) = \frac{n(\text{hydrogen of tert butyl})}{n(\text{hydrogen of phenyl ring})} \times \frac{20}{9 \times 25} \times 100\%$$

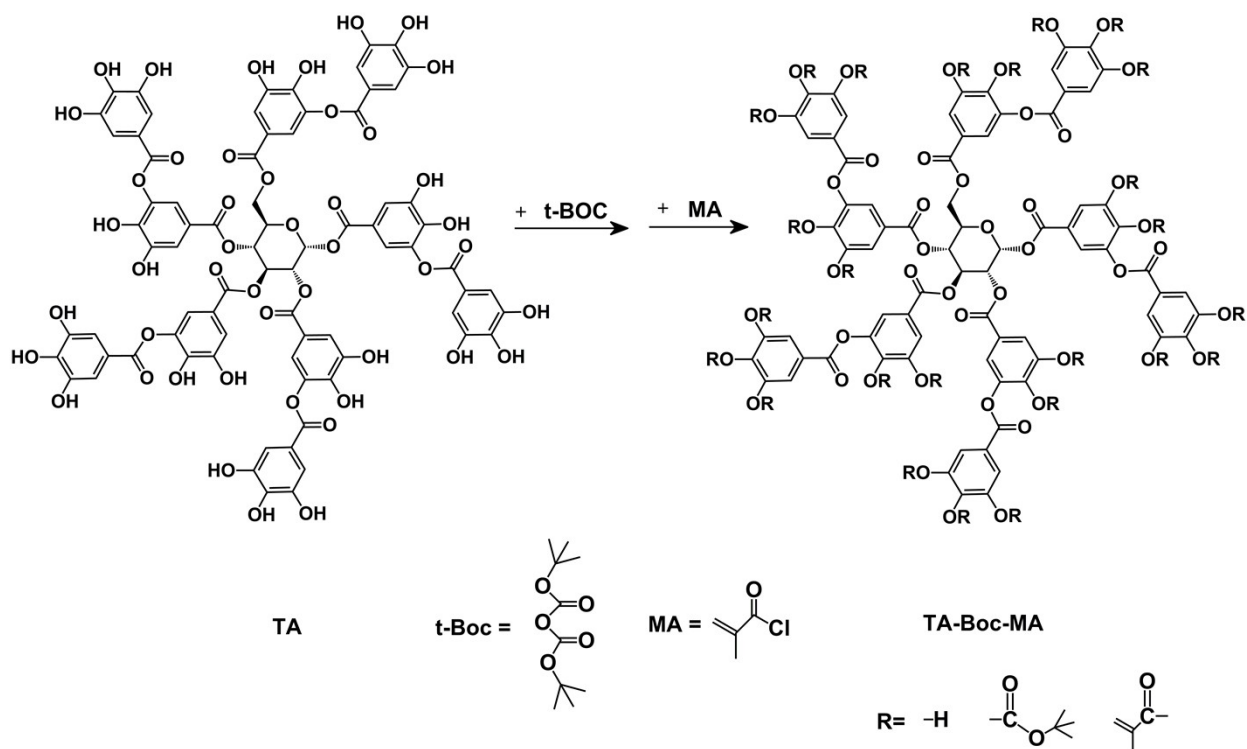
$$GR(MA) = \frac{n(\text{hydrogen of vinyl})}{n(\text{hydrogen of phenyl ring})} \times \frac{20}{2 \times 25} \times 100\%$$

GR: grafting ratio; n: the number of hydrogens integrals according to ¹HNMR spectra

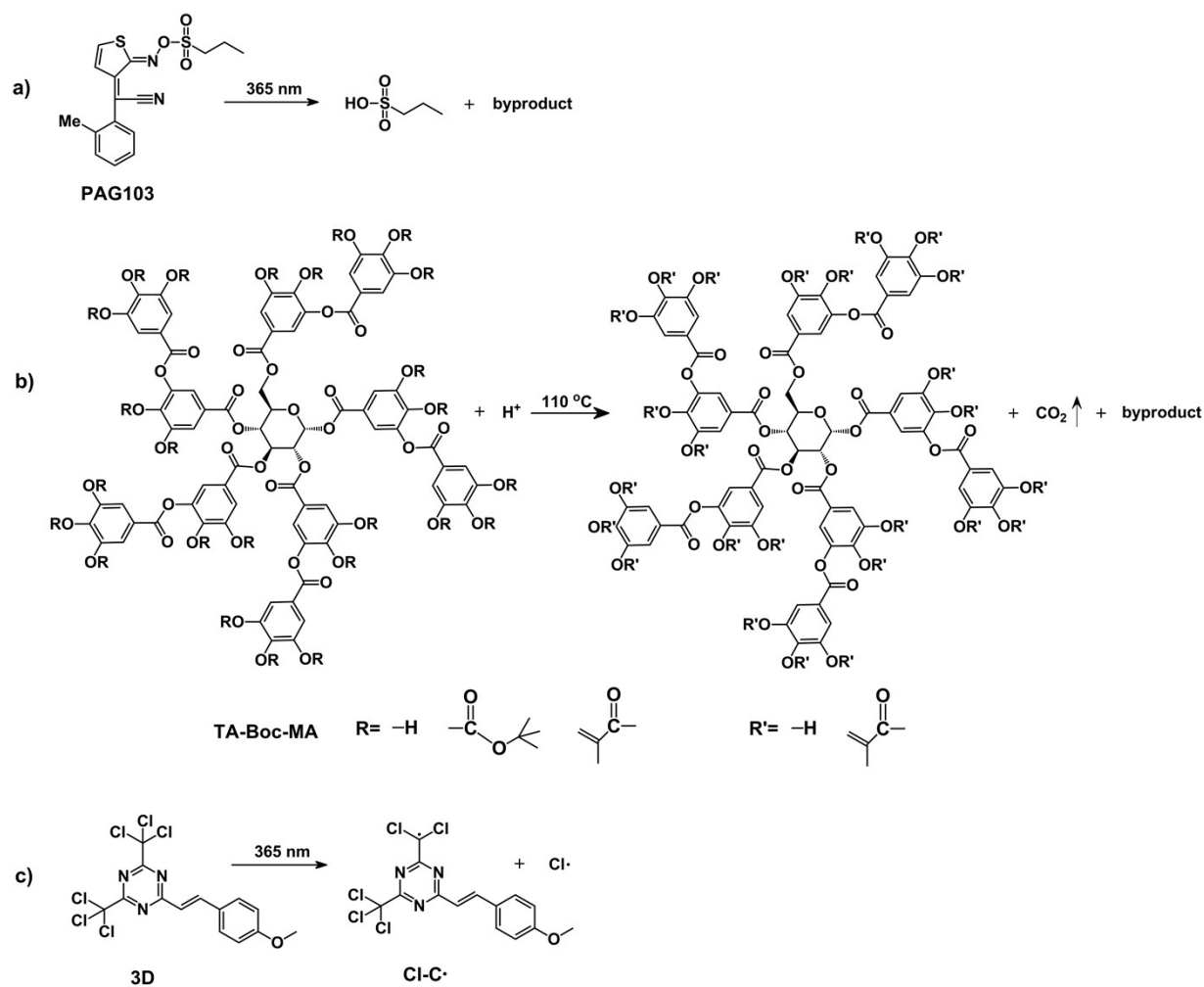
According to ¹HNMR results, the calculated grafting ratio of t-Boc and MA are 56% and 21%, respectively.”



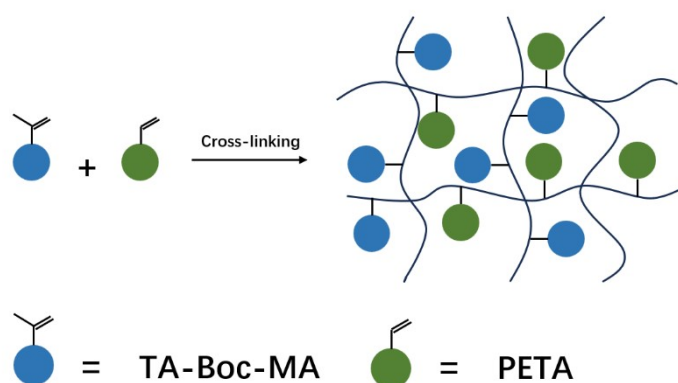
Scheme S1 The structure of tannic acid (TA).



Scheme S2 The reaction of TA with t-Boc and MA



Scheme S3 The reaction equation of PAG 103 for H⁺ production (a), deprotection of Boc groups (b) and 3D for radical (b).



Scheme S4 The schematic diagram of cross-linking between TA-Boc-MA molecules or between TA-Boc-MA and PETA.

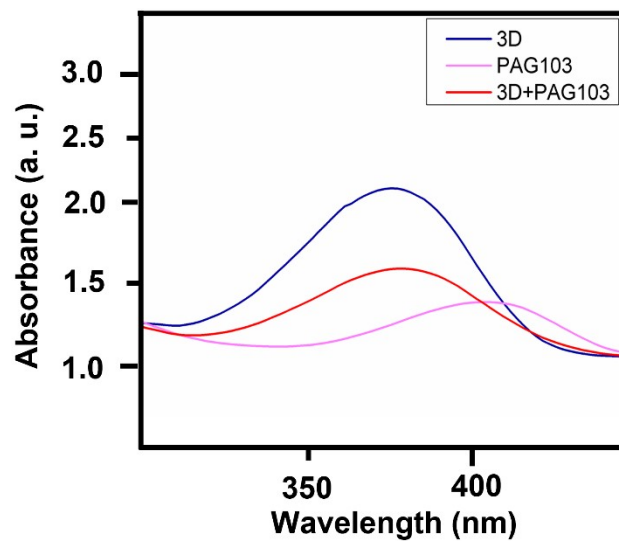


Figure S1 UV-vis absorption spectra of 3D, PAG103, and their mixtures (1:1, mass ratio).

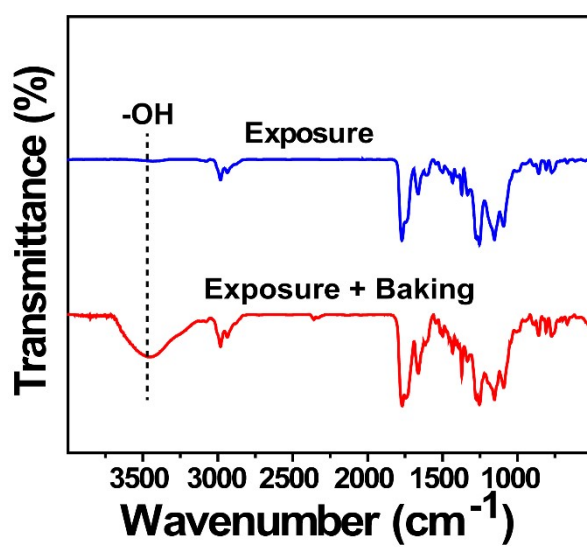


Figure S2 The FTIR of photoresist before and after baking.

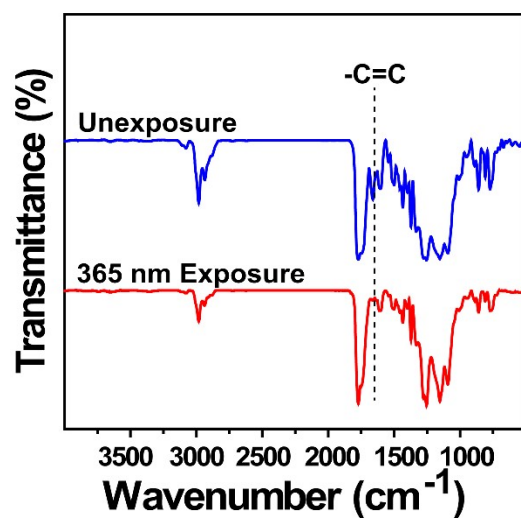


Figure S3 The FTIR of photoresist before and after exposure by 365 nm UV light.

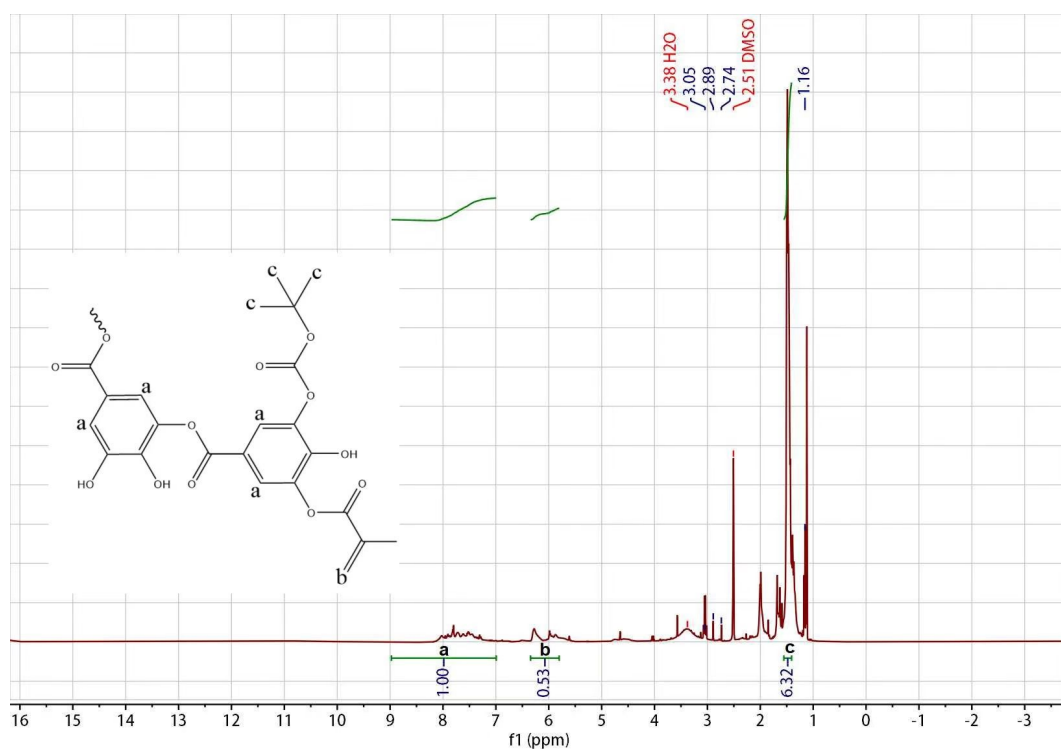


Figure S4 The ^1H NMR spectra of TA-Boc-MA resin in DMSO- d_6 . a: hydrogen of phenyl ring; b: hydrogen of vinyl; c: hydrogen of methyl in the tertiary butyl. δ : 3.38 (H_2O), 2.51 (DMSO), 2.89 and 2.74 ($-\text{CH}_3$ of DMF) and 3.05 ($-\text{CH}_2$ of triethylamine).

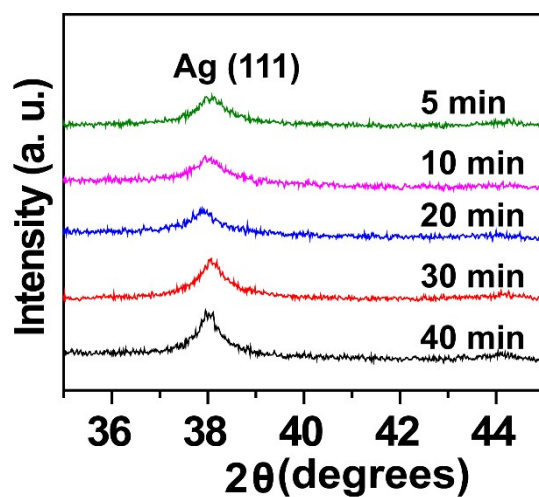


Figure S5 The XRD patterns of Ag pattern at different electroless deposition time.

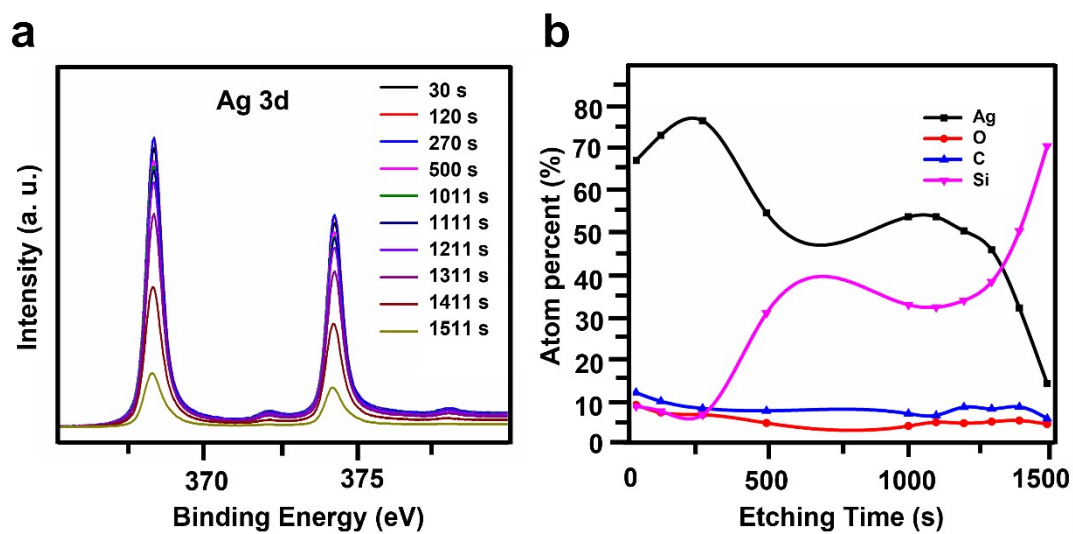


Figure S6 High-resolution of Ag 3d spectra (a) and atom percent of Ag, O, C and Si (b) of Ag pattern at different etching time. Electroless deposition time of the Ag pattern in the Figure 4 is 40 minutes.

Table S2 The square resistance of Ag film at different deposition time before and after annealing at 200 °C.

Time of electroless deposition (min)	10	20	30	40
Square resistance ($\Omega \text{ sq}^{-1}$)	810	400	322	10
Square resistance after annealing ($\Omega \text{ sq}^{-1}$)	58.1	28.5	12.6	0.7