

## Quasi Two Dimensional Deposited Silver Nanowires for Nano Scale Circuitry in an Ultrathin Layer System

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**Abstract.** We fabricate nearly straight silver nanowires with different width by electrochemical deposition, which is possibly applied on nano- scale circuitry in future. The silver adheres to the underlay of the cover glass, with an ultrathin thickness and slick surface, which indicates that the silver deposits by a kind of quasi 2 dimensional way. The silver wires widen from several tens to hundreds of nanometers deposits with a few branches, controlled by adding different electrical signals at a special temperature. The silver wire spreading is possibly induced by both electrical signals and the temperature, which is potentially used to control the number of branches of silver nanowires, as well as lengths of the nanowires. Deposited in a constant current mode, the silver wires performance a unidirectional character, different from silver wires grown in voltage mode. The characters of growth directing indicates an stirring prospect that it is possible to obtain straight lines and right angles composed of silver wire which is needed in circuits by adding appropriate signals in the electrochemical deposition system.

### Introduction

Based on the current requirement by micro electric circuits, people become interested in small scale and low dimension materials for electric circuits, especially silver and copper, etc. . Silver has abundant characteristics: high electric and heat conductivity, chemical stability, easy processing etc., which makes it become one of the most preferable materials applied in circuits. Electrochemical deposited silver can adhere to the underlay, with a thin thickness and slick surface [1].

Two dimensional electrochemical deposition system provides abundant morphologies, affected by many physical and chemical factors [2] [3]. The appearances of growth behaviors is so various that a strong interest raises up [3] [4].

In this paper, a system of ultra thin electrolyte deposition is applied to grow silver nanowires. silver ions from AgNO<sub>3</sub> solution deposits in ultra thin liquid layer, which branch from a prepared central silver square, by adding electric signal between two parallel linear electrodes. It is discovered that the width, length, angle, etc. of silver nanowires can be influenced by changing the electric signals and temperature in different growing mode.

## Design of the Silver Deposition Mechanics

The electrolytic process happens in an ultra thin liquid film. For  $\text{AgNO}_3$  solution, the separation coefficient  $k_0 < 1$ . According to the theory of crystal growth [1],  $\text{AgNO}_3$  solution will release  $\text{AgNO}_3$  solvend on the interface between liquid and solid. Consequently the concentration increases while the freezing point of solution decreases. Applying an accurate temperature controlling system, temperature can be decreased very slowly, resulting a uniform concretion process. With our special experimental system, we can monitor the freezing process of solution. By controlling the freezing process of  $\text{AgNO}_3$  solution, monocrystal is produced to gradually take up the most space of liquid film, which results in the decreasing thickness of the liquid film.

Deionized water was used as electrolyte instead of  $\text{AgNO}_3$  solution, but the highest voltage we can get cannot drive the deposition process. Based on this limitation we can conclude that the supplier of silver ions is not only the silver square adhered in the centre of substrate but also the  $\text{AgNO}_3$  solution.

According to the fractional condensing effect, the concentration of  $\text{AgNO}_3$  solution in the liquid film will raise up by the ice layer is thickening, but will not exceed the saturated concentration at the same temperature. The concentration is high enough that the solution shows a high conductivity, which is necessary for electrochemical deposition. In this condition, silver will separate out from the  $\text{AgNO}_3$  solution as long as some electric signals added on the electrodes, such as current or voltage with enough intensity. Limited by the ultra thin liquid film, silver will deposit in the film by a quasi two dimensional way.

We modify the substrate by sputtering a silver square in the centre of substrate. The uniform electric field between two electrodes polarizes the silver square [1] [5] [6]. The electric charges assemble near the pointed end of the square. According to the polarizing orientating, cathode or anode reaction will happen as follows, respectively:

a) near the platinum line anode side, silver ions get electrons and deposit to silver wires:



b) near the platinum line cathode side, silver atoms of the central silver square lose electrons, transforming to silver ions into the electrolyte:

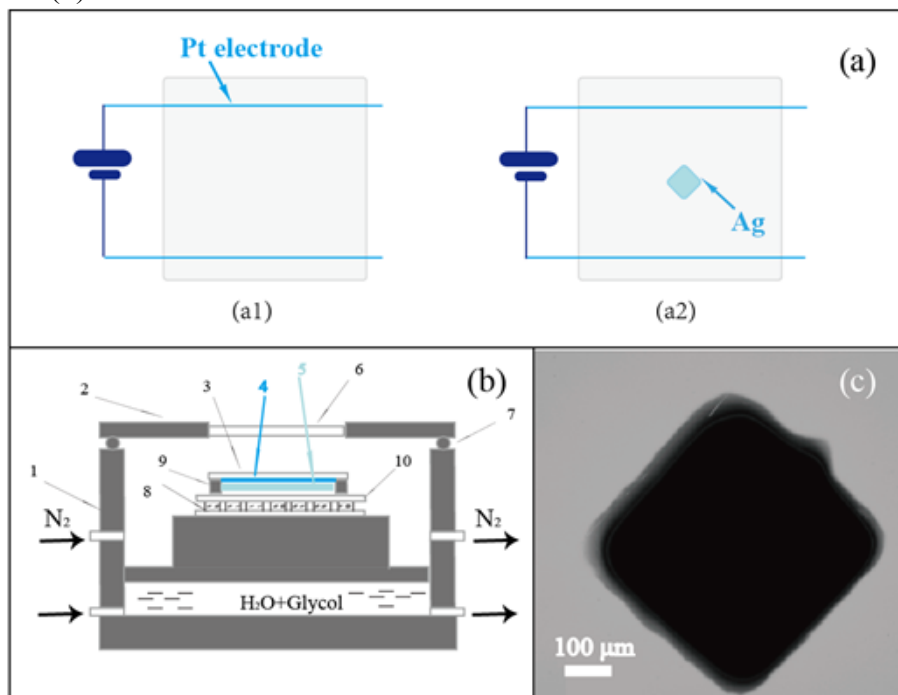


There is a problem that whether the ionized silver atoms from the polarized square is the only origin of deposited silver. The best way to explore this problem is to monitor the concentration of  $\text{AgNO}_3$  solution, but it is unpractical because of the experimental system is sealed. Instead, the patterns of silver square before and after experimental process is observed to clarify the origin of silver atoms of deposited wires. By explore different patterns of deposited silver wires in different environments, better methods to control the growth of silver wires are possibly discovered to get high quality nano scaled wires used in nano circuits, which will improve the manufacture level of micro to nano electronics industry.

## Design of the Experimental Instrument

Before we deposit silver wires, we clean the substrate, which is a cover glass with a side length 18mm. We immerse the cover glass in boiled acid solution, which is composed of potassium dichromate and sulphuric acid, wipe it with ethanol and then rinse it with deionized water, dry it with nitrogen. In order to observe effects of depositions in different environment, we modify a cover glass with a sputtered square silver plating in the centre of cover glass, with a side length of  $500 \mu\text{m}$  and a thickness of 100 nm, as figure 1(a2) illustrates. The optical photo is shown in figure 1(c). In contrast, figure 1(a1) shows a blank cover glass without modified silver pattern. Before the substrate is covered with the deposition face down to the clean bottom glass, a drop of 0.001mol/L  $\text{AgNO}_3$  solution with an approximate pH value 4.5 is dropped on the bottom glass, between two linear electrodes. In the end of this process, any air bubble cannot exist. In the result, an even

electrolyte liquid film forms. In this thin liquid film, silver is electrochemically deposited on the underlay of cover glasses. The cover-bottom glasses with  $\text{AgNO}_3$  solution combination is fixed on a system like figure 1(b).



(a) cover glass without (a1), with (a2) silver square (b) the electrochemical deposition system: 1. thermostatic chamber(copper) 2. heat preservation cover 3. cover glass 4. ultra thin liquid film 5. monitor window 6. ice layer 7. rubber ring 8. Peltier element 9. platinum electrodes 10. bottom glass (c) prepared silver square adhering the cover glass

Fig.1. The experimental instrument

As figure 1(b) shows, we construct a thermostatic chamber controlled by water bath. The key part of instrument is a electrolytic cell, consisted of electrodes, the cover glass substrate,  $\text{AgNO}_3$  solution and bottom glass. In our experiment, both anode and cathode are produced by platinum line with a diameter of 0.2 mm. The Pt electrodes laid on a clean cover glass are 10 mm away from each other. In order to decrease the thickness of solution layer, the solution becomes gradually frozen from room temperature to  $-1\sim-6$  °C very slowly. To freeze the electrolyte, the electrolytic cell is fixed in the thermostatic chamber as figure 1(b) shows. A Peltier element, which is used to control the temperature, is fixed tightly under the electrolytic cell. When the current through Peltier element changes, the temperature changes consequently, which helps control the temperature field in liquid film rapidly. The cooling water system on the bottom of chamber connects to a water bath system outside. In the result, When the water bath system starts, the required temperature in chamber is obtained.

By adjusting the temperature, most of water becomes ice, only an ultra thin layer left at last. After maintaining the temperature in the chamber near the freezing point for a while that the liquid-solid film has achieved to thermal equilibrium, we strengthen the cooling to freeze  $\text{AgNO}_3$  solution rapidly. By adjusting the currency in the Peltier element the  $\text{AgNO}_3$  solution is heated and cooled repeatedly, until some special thermal equilibrium is achieved that only one ice nucleus exists in the liquid film. Thus, at a tiny super-cooled temperature, the single ice nucleus grows up very slowly, keeping a smooth boundary, which is usually a nearly circle. Finally the nearly monocrystalline ice forms and the liquid film becomes ultra thin. Every steps of the crystallizing process above can be observed through the transparent top of the chamber by an optical microscopy.

By changing the temperature, the voltage between Pt electrodes and the depositing time, silver deposits in the ultra thin liquid film of  $\text{AgNO}_3$  solution, between the cover glass and interface of the nearly monocrystalline. Silver can be deposited with as less influence as possible from the interface effect of ice if the ice is nearly monocrystalline, because thus there are less crystal defects.

## Test results

The samples are observed with optic microscope Nikon Microscope Eclipse 80i as well as scanning electron microscope LEO-1530VP.

Without silver square in the centre of cover glass, as shown in figure 1(a1), we cannot observe visible silver wires in both optic and electron microscope, under the voltage added between two electrodes varies from 2V to 20V. It is inferred that the electric field is not big enough to polarize the  $\text{AgNO}_3$  solution with a concentration of 0.001 mol/L. Only with a silver square plated on the cover glass, we can observe the silver wires spread from the pointed end of square near to the anode side, which are shown in figure 2 and 3 as follows.

We have got various patterns of silver wires shown in figure 2, each deposited for 20 minutes by a constant voltage mode. Indicated in figure 2(a), there appear several silver branches, responsible to the constant voltage of 8V at a temperature of  $-4.5^\circ\text{C}$ . The silver branches from the central silver square are very slim and spread wider and wider in the depositing process. In add, different parts of silver branches show different brightness, which suggests different thicknesses of the silver branches.

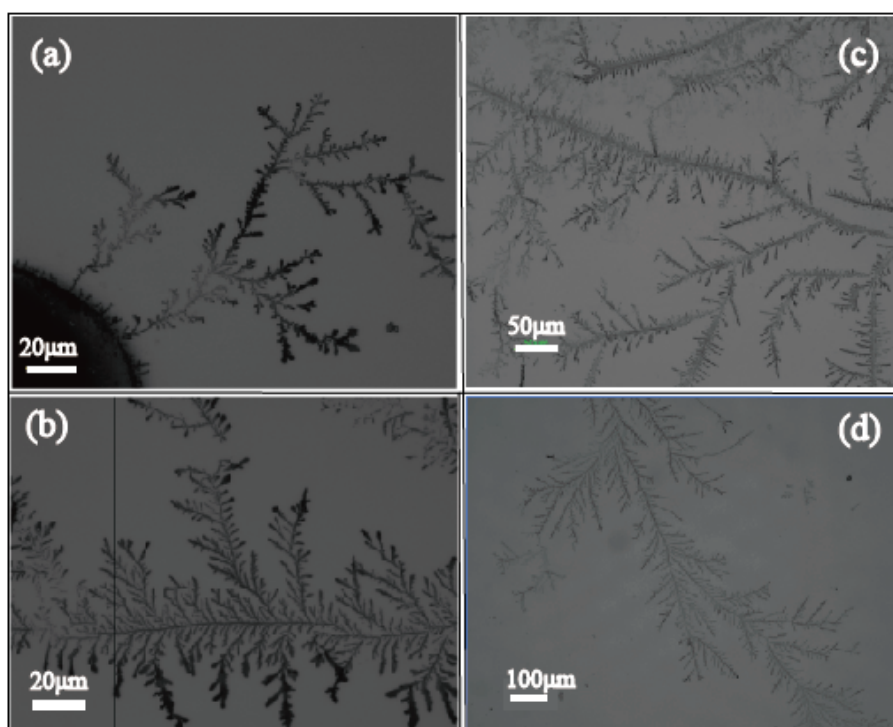


Fig.2. Silver wires deposited under the constant voltage of (a) 8, (b) 8, (c) 6, (d) 4 V. The temperature is kept at (a)  $-4.5$ , (b)  $-5.5$ , (c)  $-4.5$ , (d)  $-4.5^\circ\text{C}$ .

To explore the electrical signal influence to the silver patterns, we change the mode of signal, as well as the signal intensity and the temperature. Other optical photos of silver wires deposited in constant voltage mode are displayed in figure 2(b), (c) and (d). Responsible to figure 2(b), (c) and (d), the voltages are respectively 8V, 6V and 4V. The temperature are maintained at  $-4.5^\circ\text{C}$  except sample in figure 2(b), which the temperature is adjusted to  $-5.5^\circ\text{C}$ . Compare the photos from figure 2(a) to (d), it is found that the pattern of silver wires varies along with both the voltage and temperature changing. As shown in figure 2(b), the silver wires appear darker than other photos, which suggest the possibility that lower temperature leads to thicker deposition. It means that lower temperature is favorable to approach two dimensional deposition instead of three dimensional deposition. And the silver wires spread less branches than figure 2(a), which implies that lower temperature can restrain the silver branching. The silver wires also appear more straight in figure 2(b) than in (a), meaning a further proof that branching is limited at lower temperature.

At the same temperature  $-4.5^\circ\text{C}$ , silver wires look lighter in optical photos by the voltages decreasing, as figure 2(c), (d) indicates, compared to silver wires in figure 2 (a). In figure 2 (c), the quantity of branches is smaller than that in figure 2 (a), while it is bigger than that in figure 2 (d).

Also it is clear that wires in figure 2 (d) look lighter, which means thinner in thickness. Infer from his comparison, we can conclude that smaller voltage helps better performance on quasi two dimensional electrochemical deposition of silver.

Figure 3 (a) to (d) indicate silver patterns depositing with constant currencies through the  $\text{AgNO}_3$  solution, respectively. Similar to constant voltage mode, silver patterns are different under different currency and temperature. The temperature is maintain at  $-3^\circ\text{C}$ , and the responsible depositing currency varies from 1 mA in figure 3(a), 0.5 mA in figure 3(c) to 0.2 mA in figure 3(d). Responsible to sample in figure 3 (b), the temperature is kept at  $-4^\circ\text{C}$  and the currency is 1 mA. Observing the more and more spreading silver branches from figure 3 (a), (c) to (d), we can infer that smaller currency widens silver branching, similar to constant voltage mode. On the other hand, there is an important difference, that the silver wires are much more direct in the constant currency mode than deposited in voltage mode, and single branch is more slick and wider, which indicates nearer to two dimensional deposition. By comparison, silver wires in figure 3 (b) looks close to the wires shown in figure 2. This helps prove that lower temperature leads to less branches again, even if in currency mode.

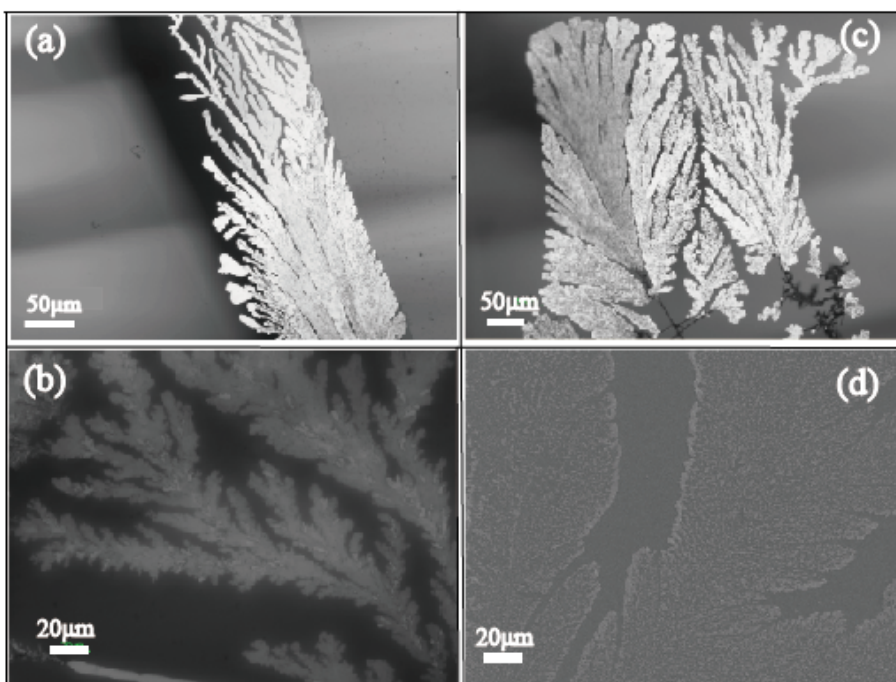


Fig.3. Silver wires deposited under the constant currency of (a) 1, (b) 1, (c) 0.5, (d) 0.2 mA. The temperature is kept at (a)  $-3$ , (b)  $-4$ , (c)  $-3$ , (d)  $-3^\circ\text{C}$ .

Figure 3(d) is a photograph obtained by scanning electronic microscopy, which indicates the fine structure of deposited silver. In this photo, silver cover most part of the substrate. In the branch it can be seen that silver adhere to the substrate like feather, , which the growing process can be define as two dimensional depositing. As a result, the series photos of figure 3 shows smaller currency and lower temperature more benefit to two dimensional electrochemical deposition.

The silver square is observed after the depositing process has been finished, by optic microscopy. The photo of the dissolved square is shown as figure 4 (a). The high resolution photo of the district circled in (a) is indicated in figure 4 (b). In figure 4 (b), colored edge with irregular figure show decreased thickness after electrochemical deposition, which means dissolving happens at the end point near the cathode when silver wires spread to the anode from the other side terminal of silver square.

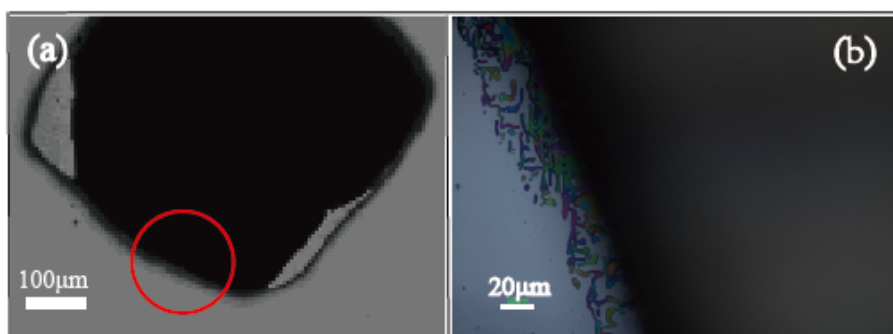


Fig.4. dissolved edge of silver square

## Conclusion

We succeed fabricated silver wires growing by quasi two dimensional way in an ultra thin liquid film system. Electrochemical deposited silver wires can be observed only when a silver square is prepared adhering to the substrate, which implies that silver atoms in the square are the origin of deposited silver wires. The dissolved pattern of the silver square helps us confirming this conclusion.

The pattern of silver wires deposited at a constant voltage can be controlled by changing voltage as well as depositing temperature. The lower temperature descends, the less branches are produced, and the more straight the wires grow. The lower depositing voltage has similar effect: lower voltage brings thinner thickness and less branches of silver wires.

Similar to voltage mode, depositing process at a constant current also indicates the positive factors to two dimensional electrochemical deposition. Different from the voltage mode, silver branches string tighter than deposited in voltage mode, and growth with nearly the same direction. The unidirectional performance of silver wires inspires us that it is possible to control the angle between two silver branches, by depositing silver in a constant current mode. Thus we can obtain straight lines and right angles composed of silver wire which is needed in circuits.

Next step we need to improve the controlling of temperature and electric signal added on the deposition system. The current mode is preferred based on better unidirectional performance, in order to get straight lines while the voltage mode is preferred when diversion branch is needed in the circuit. Our future efforts will help creating perfect wires used in nano scale circuits.

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