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FABRICATION OF METALLIC NANOWIRES BY TWO-PHOTON ABSORPTION♦

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Abstract: A chemical system consisting of a metallic salt, a water-soluble polymeric matrix and an iron(III) citrate complex, acting as the photosensitive specie absorbing at two-photon, has been used to produce metal deposition upon exposure to a femtosecond laser. The fabrication of continuous and uniform gold nanowires has been optimized. Their dimensions vary from a few hundred nanometers to one micron for their widths, and range from a few to several hundred microns for their lengths.

Keywords: *two-photon absorption, photoreduction, metallic nanowires*

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INTRODUCTION

Many fabrication techniques of noble metal nanoparticles are being developed due to the numerous potential applications in nanophotonics, electronics, biology imaging, catalysts and material science [1, 2]. Recently, two-photon absorption lithography has been described for producing polymeric structures [3-5]. In this technique, the photochemical process occurs by two-photon absorption of the laser beam. Due to the nonlinear intensity dependence of the process, the light absorption is localized in a small volume near the focal region and a deep penetration is possible within the material. Thus, three-dimensional structures can be achieved by scanning the focal point in the three dimensions of the material. The development of such optical technology to obtain continuous metal features is only described by a few reports [6-9]. In this paper, we present experimental results on the fabrication of gold nanowires using a two-photon lithographic process inspired by the chemistry of silver photography.
During this process, the photoreduction of soluble metallic ions by Fe (II) complex leads to the precipitation of the insoluble metal. This is a two-steps photo-reduction approach, Fe (III) citrate complex being used as the photoinitiator specie. During the first step, the two-photon excitation of Fe (III) citrate complex by a femtosecond laser radiation generates Fe (II) specie at the laser focal point. Then, each reduced iron complex can react with its neighbour metallic (gold) ions to generate the localized metal. The complete redox scheme is:

$$\underset{\text{soluble in water}}{\text{Metal (ionic species)}} + \text{Fe (II) citrate} \longrightarrow \underset{\text{insoluble}}{\text{Metal (reduced state)}} + \text{Fe (III) citrate}$$

In a practical way, to obtain continuous metal features, the Fe (III) citrate, and the metallic cation are dispersed in a soluble polystyrene matrix. The process can be performed with various metallic cations such as Cu^{2+}, Ag^{+}, Ni^{2+} and $AuCl_4^-$. According to the ion-exchange properties of poly(styrenesulfonate), a homogeneous dispersion of the salts is obtained, avoiding phase separation in the solid state. The fabrication of gold nanowires is performed in micrometer-thin active layers that are spin-coated on microscope glass plates. At the end of the process, the unreacted active material and the polymer matrix are removed by immersion in alcohol. In this paper, we mainly discuss the influence of the laser power on the characteristics (size and shape) of gold nanowires.

EXPERIMENTAL

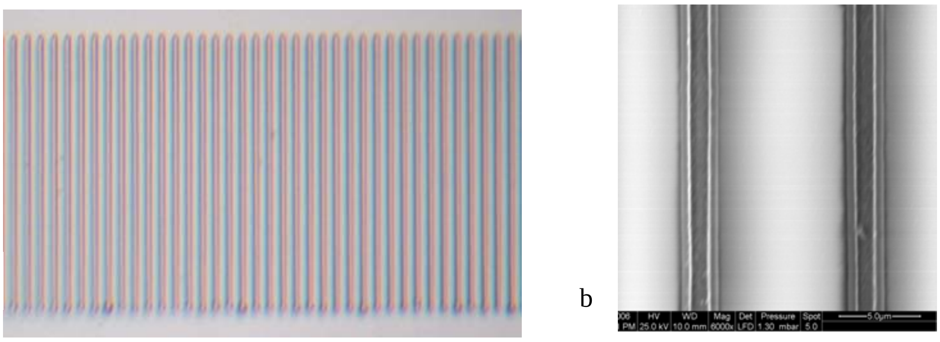
Chemicals such as $AgNO_3$, $HAuCl_4$ (99%) were purchased from Aldrich and used as received. When needed, a polyimide underlayer was prepared as previously described [10]. Thin solid films were prepared by spin-coating (3500 rpm) on microscope glass plates (25 x 25 mm) from an aqueous solution containing the active products. This solution was freshly prepared before use, mixing equal parts of two stable solutions denoted A and B. Solution A was prepared by dissolving 0.1 mmol of $HAuCl_4$ in 1 mL of poly(4-styrenesulfonic acid) 18% wt H_2O, denoted PSS. Solution B was prepared by dissolving 0.1 mMol of Ammonium ferric citrate green in 1 mL of PSS solution.

The films were then placed on a three-axis microscope stage allowing their translation relative to the laser focal point. All two-photon metal deposition experiments were performed using a femtosecond laser at 740 nm. The Ti : Sapphire laser produces pulses with duration of 100 fs and a repetition rate of 82 MHz. The laser beam was focused on the sample through an x100 oil objective lens with a numerical aperture (NA) of 1.25, using a Zeiss Axiovert 200 microscope. The sample was washed in isopropanol for 30 minutes and then rinsed in ethanol to remove the PSS.
The SEM images were recorded using a Quanta 200 field-emission scanning electron microscope (15-20kV) from FEI. AFM measurements were performed on a Veeco 3100 scanning probe microscope with a Si_2N_4 tip, using the "tapping mode".

RESULTS AND DISCUSSION

This two-photon metallic photo-precipitation process allows the formation of three-dimensional structures with a sub-micron resolution. In this work, we have studied the fabrication of metallic wires with dimensions varying from a few hundred nanometres to one micron for their widths, and ranging from a few to several hundred microns for their lengths (see Figure 1a).
Typical laser powers are in the tens of milliwatts, measured at the laser output. The deposition is performed at the active layer│substrate interface in order to recover the metallic deposit at the substrate surface after removing the unreacted matrix. Under our experimental conditions, no lines were observed for laser powers below 15 mW. Higher laser powers, ranging from 30 to 40 mW, are required to initiate the process for other metals such as silver, copper or nickel. This can be attributed to a higher reactivity of gold (III) (oxidative power) when compared to others metallic ions.

a



b

Figure 1. *a) optical image of a metallic wire array ; the wires lenght is 200 μm, b) SEM image-enlargement of two double wires*

Surprisingly, when "writing" a metallic line by moving the laser spot at the active layer/substrate interface we have always obtained a "double" wire pattern centered around the area of engraving as shown on Figure 1b (magnification image). The metal deposition does not occur at the centre of the laser beam, but on its outer diameter. This confirms the same behaviour that has been reported recently for the fabrication of silver wires [9].

Due to the weak interaction forces between glass and gold, a partial or complete detachment of wires on the untreated glass surface was often observed upon washing. On Figure 2, one sees double lines that are rolled-up or freely moving. These images clearly indicate that continuous wires are generated. The wires adherence can strongly be increased by using a thin polyimide underlayer (800 nm) deposited on top of the glass substrate. In this case, the wires always remain uniform and straight after the washing step. We assume, as expected, that polyimide establishes strong coordinative gold-nitrogen bonds with gold wires.

a

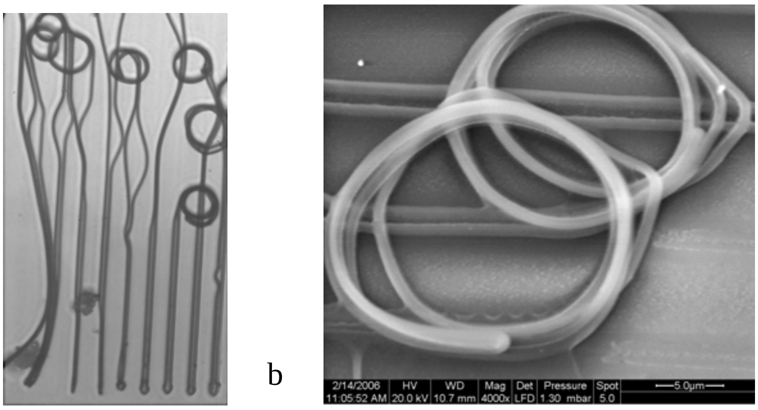


Figure 2. *a) optical image of gold wires array on an untreated glass support, after washing, b) SEM image-double wires disconnected from the substrate*

A typical AFM (Atomic Force Microscopy) profile of a double line is shown on Figure 3. As shown by the cross-section plotted across the double line, both wires are almost identical exhibiting a squared cross-section, and vertical walls. The 3D view confirms that we are able to fabricate regular and homogeneous wires.

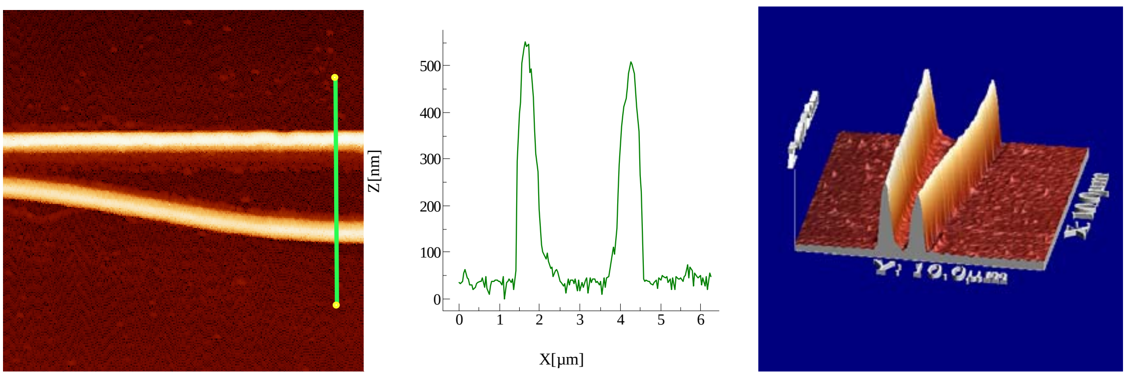


Figure 3. *AFM measurements of typical gold wires : cross section and 3D view*

To explain the double-wire phenomenon we assume that gold nanoparticles are generated, as expected, at the focal point, and then they are pushed by an optical tweezing effect at the beam border. Nanoparticules generated on the left and right sides of the beam axis aggregate on the beam border to make the left and the right lines, respectively. This optical tweezing effect is expected to be proportional to the laser power, which is in good agreement with our experimental results (Figure 4).

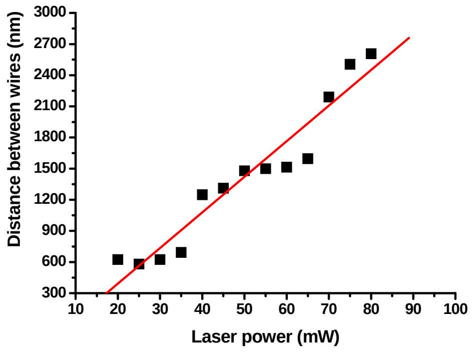


Figure 4. *Influence of the laser power on the distance between the wires*

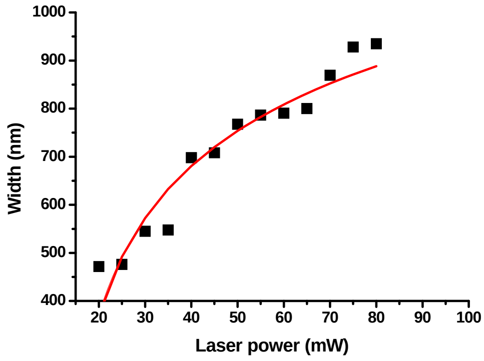


Figure 5. *Influence of the laser power on the width of wires*

In addition, increasing the laser power leads to an increase of the wire width as shown on Figure 5. In the followings, we investigate this dependency using a very simplified model that defines the wire width as the beam radius of threshold laser intensity necessary for the metal deposition. We neglect any diffusion process of active species (photosensitizer and gold ions), and suppose that gold nanoparticules are uniformly generated in the beam volume defined by the threshold intensity. We consider that the optical tweezing effect pushes the same number of particles in the right and left directions, and that the two lines obtained after aggregation have a total width comparable to the initial threshold beam diameter.
In this model, the width of a single line is given by:

$$W = w_0\,(½ \ln I_0/Is)^{1/2} = w_0\,(½ \ln P_0/Ps)^{1/2} \qquad (1)$$

where the Gaussian beam intensity I on the thin sample surface is given by $I = I_0 \exp(-2r^2 / w_0^2)$, the beam waist is w_0, the beam radius is r, and the threshold intensity is. P_0 and P_S are the incident and threshold laser powers, respectively.
This model is very simplified, but the fitting parameters: w_0 = 970 nm and Ps = 15mW are in good agreement with the experiment. In particular no line has been recovered for laser power less than 15 mW. However, a complete removal of the deposit during the washing step cannot be totally excluded. This threshold power could originate from the difficulty to transfer the charge between iron (II) and gold in the solid state. Further experiments are currently under investigation to confirm this model.

CONCLUSIONS

Poly(styrenesulfonate) containing a metal salt and an iron photoactive dye is an efficient system for direct writing of metallic micro/nanostructures. The fabrication of continuous and uniform gold nanowires has been carried out by two-photon reduction at the focal point of a femtosecond laser. The use of an additional polyimide underlayer permits a strong adherence as well as a regular shape of the wires. The principal advantage of the process relates to the spatial control of the localized photo-induced reduction of the gold salt. Fabrication of wire arrays with wire dimensions varying from some few hundred nanometres to one micron for the width and ranging from a few to several hundred microns for the length have been demonstrated. A better understanding of the physical process is needed to optimize the fabrication of 3D devices. This two-photon photoreduction technique is a new and versatile approach to the patterning of metals. It may have interesting applications in the fabrication of new types of structures for applications in optics, electronics, and biological sensors.

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