

Two-photon laser deposition of gold nanowires

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We report on the fabrication of gold nanostructures by direct laser writing. Such metallic structures are obtained by reduction and precipitation of the corresponding metallic ions we have included in the polymer host. The reduction is initiated by two-photon absorption of the femtosecond laser. In this paper we show that the chemical composition of the active mixture as well as the laser power has a strong influence on the fabricated structure. We show that optimized conditions permit the fabrication of very regular structures whose dimension can vary from several microns to a few hundreds of nanometers. A model is proposed which predicts variation laws in good agreement with experiments.

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1. Introduction

In the last decade, two-photon absorption (TPA) processes have been intensively studied and improved for three-dimensional (3D) micro- and nanostructures fabrication. The main difference between this procedure and those classical one (electrochemical, photochemical, lithographical) is that the chemical photoreduction reaction is spatially confined in a small volume at the laser focal point.

The two-photon absorption has been especially applied for the fabrication of structures by photo-induced polymerisation of resins [1-3], but also for other kind of materials. Metal nano-particles generation, mainly gold and silver, has recorded significantly progresses due to their interest in optics, electronics, and biology [4, 5]. For instance, Kaneko reported the TPA-induced photo reduction of gold ions in a polyvinyl alcohol (PVA) film [6]. He obtained gold gratings but formed by nanoparticles rather than a solid film. Baldacchini used multiphoton processes to directly fabricate two-dimensional silver structures inside of 1 μm thick polyvinylpyrrolidone (PVP) film [7]. Marder and co-workers reported on the laser- and electron-beam-induced photo-reductive growth of 2D and 3D electrically conductive metal structures inside of a solid matrix or on surface [8]. Another group, Tanaka and co-workers, demonstrated two-photon-induced direct metal-ion reduction within aqueous silver and gold salts solutions [9]. He obtained three-dimensional electrically conductive silver, and two-dimensional (2D) gold structures, respectively. It is beyond the scope of this paper to present a fully exclusive review of existing works. However, the above-cited examples give a good overview of existing works. We see that if authors focussed essentially on gold and silver, the host in which metallic

ions are included can be very different and is found to play an important role.

In our case we concentrate on a polymer host in which TPA photoreduction of metallic salts (gold, silver, cooper, nickel) is obtained under ambient conditions [10]. The main interest of our process is that it is easy to prepare and "low cost" because it is based on commercial products. In addition it allows the preparation of very stable Au(III) solution. The consequence is that it is relatively simple to vary the chemical composition as well as physical parameters such as the viscosity which plays an important role in the thin-film spin coating process.

In previous studies, we succeeded in obtaining continuous and regular metallic nanostructures (1D and 2D), instead of isolated metal nanoparticles, the kind of structures which are obtained when using a photochemical process drawn from the well-known silver photographic one [11]. In this work we optimized the composition of the mixture, which consists of ammonium iron(III) citrate, a TPA photosensitive specie, and a soluble gold salt, uniformly dispersed in a polymeric matrix in order to fabricate small 1D and 2D gold nanostructures.

2. Experimental conditions

To fabricate gold nanostructures an aqueous solution containing the active products was used. This solution was freshly prepared before use, mixing equal parts of two stable solutions denoted A and B. Solution A was prepared by dissolving various amounts of HAuCl_4 in 1 mL of poly (4-styrenesulfonic acid) 18wt % 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 concentration of tetrachloroauric acid (HAuCl_4) in the final solution is varied from $0.625 \times 10^{-5} \text{M}$ to $5 \times 10^{-5} \text{M}$.

Before the metal fabrication, the glass slides were heated in isopropanol for 30 minutes and then dried under a nitrogen flow. After cleaning, the surface of the glass slide was covered with a thin layer of polyimide of thickness 900 nm, to improve the fixing of the structures onto the substrate surface [12].

Thin films (from the aqueous solutions) were prepared by spin coating (2500 rpm, 60 s) on a microscope glass plate, with a thickness layer of 1 to 2 μm approximately. The sample was then placed on a motorized microscope stage which is controlled by a computer. All the two-photon deposition experiments were performed using as a Ti:Sapphire femtosecond laser system, at the wavelength of 740 nm. This laser emits pulses of duration 100 fs, at a repetition rate of 82 MHz. The laser beam is focused on the sample through an 100 $\times$ Ph3 oil-immersion objective lens with a numerical aperture of 1.25, using a Zeiss Axiovert 200 inverted microscope. After «writing» the gold structures, the unreacted polymer matrix is removed by washing with ethanol and distilled water, leaving us with the 1D and 2D nano-objects attached on the polyimide layer and surrounded by air.

3. Results

The TPA photoprecipitation process in thin films allows us to fabricate any kind of structures from nanodots and nanowires to 3D objects. However in this paper we will concentrate on the characterisation of planar structures dots and lines. One of the most important characteristic of this technique in thin film is that a double nanowire line is always obtained.

Fig. 1 shows typical Atomic Force Microscopy (AFM) images of two gold double nanowire deposited on a polyimide coated glass substrate. These lines have been fabricated at a laser averaged power $I=60$ mW and the concentration of gold ions in solution is here $2.5 \times 10^{-5}\text{M}$. Let us precise that the actual transmission of the optical microscope set-up between the laser output and the focal point is 43%. This means that a given 60mW output laser power corresponds to 26 mW sent at the focused laser spot in the material. The diameter of the laser spot at the focal point is evaluated to 700 nm.

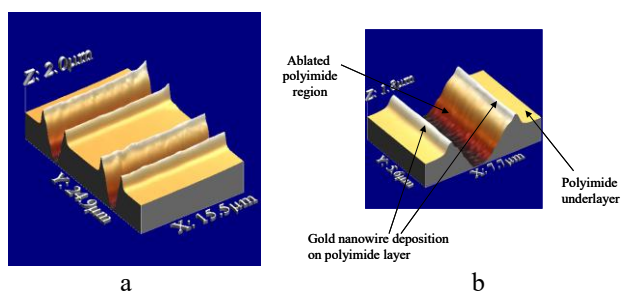


Fig. 1. AFM measurements of a typical double line.

The 3D AFM images (Fig. 1a and Fig. 1b) reveal continuous and regular gold deposition. This has to be emphasized: after optimizing the process, we succeeded in obtaining reproducible lines with a very good surface quality.

First of all we would like to point out the existence of a deep hole at the centre of the fabricated structure. As we can see on Fig. 1a and Fig. 1b, this hole is exactly located at the centre of the path of the laser beam. We notice that it goes deeper than the initial surface of the polyimide. Indeed the level of this polyimide surface is given by the flat surface which is clearly seen at the borders of the lines, on Fig. 1b, or between the two lines, on Fig. 1a. This flat surface corresponds to parts which have not been illuminated by the laser. This proves that the polyimide layer has been attacked.

A cross-section of line is given on Fig. 1. On this figure we define the geometrical parameters which are used to describe the characteristics of the deposited gold wires:

- D_p is the depth of the hole made in the polyimide
- H is the height of metallic wire
- W is the width measured at half height of this line
- D is the distance between wires measured at pics

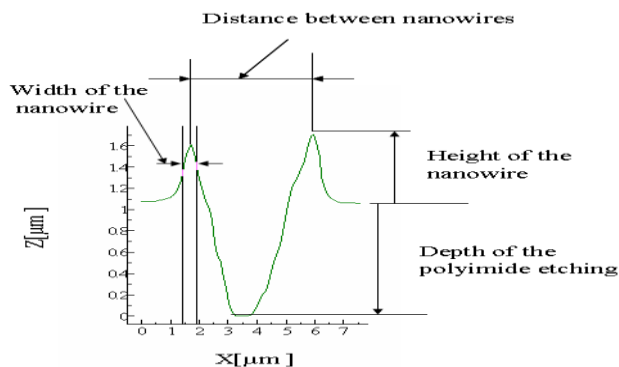


Fig. 2. AFM profile of the fabricated line.

One important question is to wonder what happened to the polyimide. Looking at Fig. 1a and Fig. 1b one can imagine that the polyimide has been pushed laterally by the laser and gave rise to the two lines at the borders. In this paper we show that it is not the case. We observe that the polyimide has been removed. In addition we observe that the two thin lines at the borders of the hole come from the PSS metallic solution and are thus mainly constituted by the precipitated gold metal.

A first argument is that we observe similar lines on glass substrate as shown on Fig. 3. On Fig. 3a an optical microscope view, we see that the lines are not strongly stuck to the glass surface. Fig. 3b shows a view of what happens during the separation: one of the lines slipped on the surface. The section of a typical narrow line is given on Fig. 3c. We see that the profile is similar to the one of

Fig. 3. In particular, the heights and the widths are comparable.

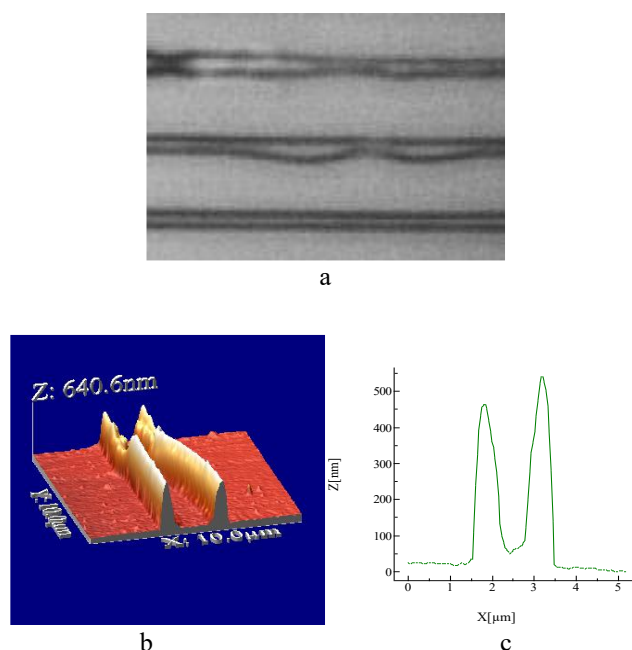


Fig. 3. Lines deposited on glass substrate. a) optical image b) AFM 3D view c) cross section of a typical line.

A second argument relies on the influence of gold concentration. The dependence is shown on Fig. 3. We observe that the height of the metallic layer is almost proportional to the gold concentration in PSS solution. As a result we observe that the height becomes very small when gold concentration is reduced. At the same time, D_p the depth of polyimide etching remains approximately unchanged around 900 nm, which is the polyimide layer thickness.

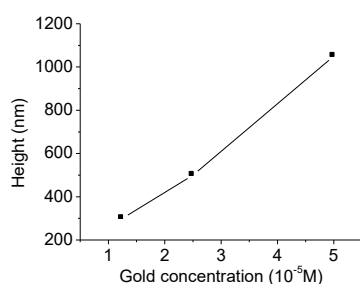


Fig. 4. Height of the metallic line as a function of gold concentration.

The fabricated line is very sensitive to the writing conditions. At low laser power the line quality becomes poor: rough granular structure, irregularities in height and width. On the contrary, at high power we obtain very regular lines but the polyimide layer is etched as already mentioned. The required power also depends on gold and iron citrate concentrations. Fortunately we found an

"optimum" composition which leads to good quality lines without etching (Fig. 5). It consists in the association of a laser power reduced to 20 mW together with a gold salt concentration increased to $5 \cdot 10^{-5} M$. The size of lines remains around 650 nm, but the distance between the two lines which constitutes the double wire is reduced. In addition, polyimide is not etched and we obtain a very nice line.

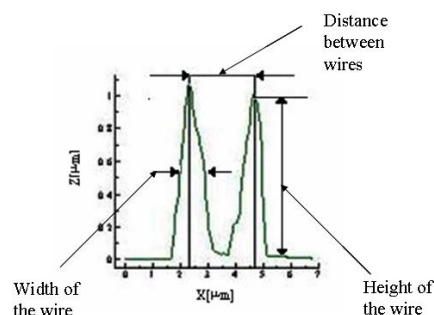
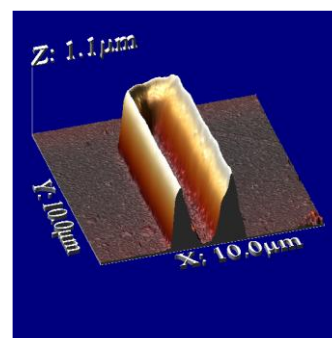


Fig. 5. AFM measurements of a gold double wire, recorded at 20 mW and $5 \cdot 10^{-5} M$ gold salt concentration.

These experimental observations gave us reasons to investigate the influence of the concentration in active species on the size and shape of the gold lines. Fig. 3 and Fig. 3 show the result of a very systematic study of the influence of both the laser power (P) and the gold ion concentration (cc). Fig. 3 is concerned with the distance between the two lines, here evaluated as the internal distance, i.e. $D-W$. Fig. 3 deals with the line width, W . For both figures the data have been plotted both as functions of P and cc in order to clearly exhibit the influence of these parameters.

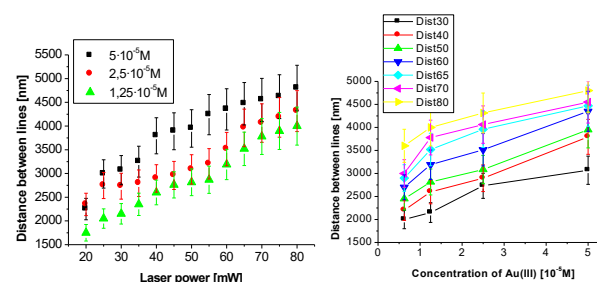


Fig. 6. Dependence of distance between lines on laser power and gold concentration.

From Fig. 3 we observe that the distance strongly increases with laser power and gold concentration from $1.75\ \mu\text{m}$ at 20 mW and $1.25 \times 10^{-5}\text{M}$ gold concentration to almost $5.0\ \mu\text{m}$ at 80 mW and $5 \times 10^{-5}\text{M}$ gold salt concentration, i.e. it is multiplied by a factor of 3.

A similar behaviour can be observed when looking at the width dependence, Fig. 3. The line width is varying from 500 nm, at 20 mW and $1.25 \times 10^{-5}\text{M}$ gold concentration, to $1.3\ \mu\text{m}$, at 80 mW and $5 \times 10^{-5}\text{M}$ gold concentration.

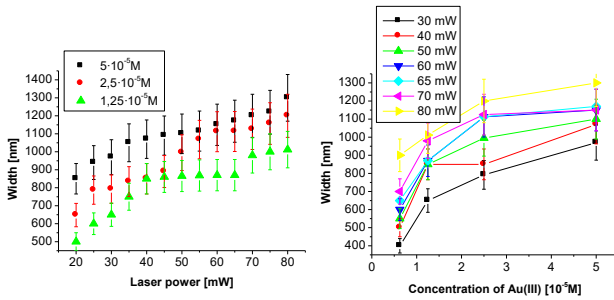


Fig. 7. Dependence of the width of the line on laser power and gold concentration.

Instead of lines it is possible to fabricate spots when the laser spot is not moved and remains at the same place.

Fig. 8 shows typical AFM measurements for a single nanodot, here with 350 nm diameter and 119 nm height. It has been fabricated at 25 mW laser power, with an exposure time of 5s and a gold salt concentration of $2.5 \times 10^{-5}\text{M}$. It is important to notice that no etching of the polyimide underlayer occurred. This shows that it is possible to fabricate really small nanostructures with this technique provided that the laser power and the composition of the solution are well adjusted.

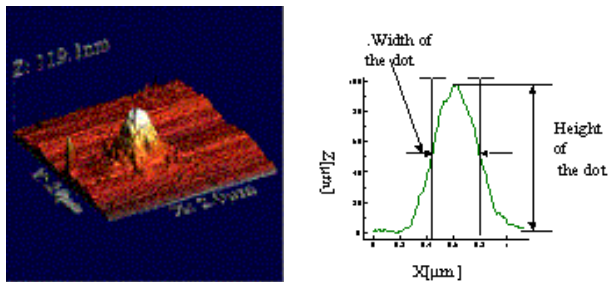


Fig. 8. A gold nanodot fabricated at low laser power and cc.

On the contrary, when increasing the concentration of gold salt at $5 \times 10^{-5}\text{M}$, a micro-ring is obtained instead of a nanodot. The morphology, investigated using AFM measurements, shows that the structure is similar to a double wire, except that it has a circular form instead of linear one because the laser spot is fixed.

The top-view and the 3D view of Fig. 3 show an internal and an external diameter of the micro-ring, as well as vertical walls. A cross-section measurement gives a width of 900 nm and a height of 500 nm. In addition, similarly to what occurred for the double lines, we observe a 900 nm deep hole, which is etched inside the polyimide at the centre of the ring.

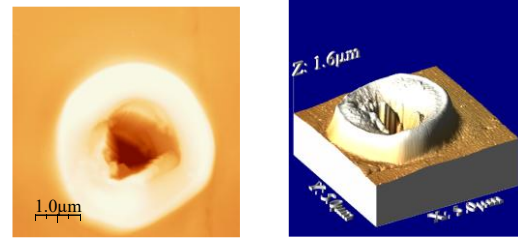


Fig. 9. Micro-ring fabricated at higher laser power and cc.

4. Discussion

In this paper we showed experimentally that there exist two phenomena in competition: a metallic fabrication process which is initiated by the two-photon absorption, and an ablation process which is destructive. As a matter of fact we established that the polyimide layer is destructed and ablated. Since this material is rather resistant it means that temperatures high enough to induce such degradations are reached, probably higher than $500\ ^\circ\text{C}$. Therefore we suggest the following two steps mechanism: after the gold nanoparticles are generated at the focal point, they strongly absorb the laser energy. This induces the etching of the polyimide underlayer, which is caused by the heating at the laser spot area.

We checked that no metal deposition occurs when the mode-locking of the femtodecond laser is turned off. This proves that the line fabrication is really initiated by TPA process which definitely appears as a required step.

According to these assumptions we propose a phenomenological model able to explain the results. The two above-discussed processes are included in the following expression of the height of the line:

$$H \propto \left(\frac{I^2}{1 + I^2/I_s^2} - \alpha I \right) T$$

where T is the laser duration and I the laser intensity. The first term describes the two-photon induced fabrication process including saturation when all gold ions have been reduced. It is quadratic at low powers as expected for a second order nonlinear process. The second term is destructive ($\alpha > 0$) and linear in I as expected for a thermal effect which is linear. Some numerical results are shown on Fig. 3 10. We assumed that the intensity distribution at the focal point is described by a Gaussian beam of waist w . On the left side we plotted the expected height. As observed experimentally, at low laser powers, only small etching is produced. When laser intensity is increased the material is etched at the centre and we are left with two

lines, one on each side. In agreement with experimental observations, we predict that the distance D between the two lines increases with power. This is plotted on the right-hand graph. The shape of the curve is in relatively good agreement with measurements. In particular, D increases with the laser power. In addition we see that D also increases with α , as is observed in experiments. Indeed linear absorption is produced by gold particles, and so α is expected to be proportional to the gold solution concentration.

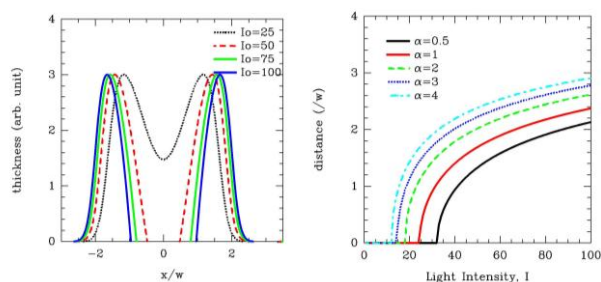


Fig. 10. Modelisation of double line characteristics.

5. Conclusions

In this work we showed how to fabricate micro and nano metallic structures with a good quality based on a metallic reduction induced by a femtosecond laser irradiation. The chemical composition of the active mixture as well as the laser power are found to have a strong influence on the fabricated structure. We showed that it is possible and important to adjust the fabrication conditions in order to control the fabricated structures.

We proposed a model which roughly explains the observed results. It is based on a combination of two mechanisms: a two-photon absorption process, and an additional ablation process caused by a temperature increase which is due to the laser absorption in previously fabricated gold particles.

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