8-27-2012

Direct writing of Au nanoneedles array on glass by confined laser spinning

Yingling Yang
Purdue University, yang219@purdue.edu

Dong Lin
Purdue University

Gary J. Cheng
Birck Nanotechnology Center, Purdue University, gjcheng@purdue.edu

Yang, Yingling; Lin, Dong; and Cheng, Gary J., "Direct writing of Au nanoneedles array on glass by confined laser spinning" (2012). *Birck and NCN Publications.* Paper 1145.
http://dx.doi.org/10.1063/1.4746427

AIP | Applied Physics Letters

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Citation: Appl. Phys. Lett. **101**, 091911 (2012); doi: 10.1063/1.4746427
View online: http://dx.doi.org/10.1063/1.4746427
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v101/i9
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Direct writing of Au nanoneedles array on glass by confined laser spinning

Yingling Yang, Dong Lin, and Gary J. Cheng
Birck Nanotechnology Center and School of Industrial Engineering, Purdue University, West Lafayette, Indiana 47906, USA

(Received 15 June 2012; accepted 2 August 2012; published online 30 August 2012)

Generation of gold nanoneedles on glass by confined laser spinning was explored by using a nanosecond pulsed laser. When the coated Au thin film was irradiated under the confinement of glass, gold nanoneedles were formed by spreading the molten liquid of gold under high pressure. The mechanism of the confined laser spinning process is studied. The maximum velocity and instability of molten liquid during confined laser spinning were estimated. The diameter of nanoneedles can be controlled by changing the thickness of coated gold thin film. Large scale of gold nanoneedles can be formed by this direct writing method and collected by confined glass. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4746427]

Due to their high-aspect ratio, tunable nanoscale geometry and unique mechanical, electrical, and optical properties, needle-like metal nanostructures are of considerable interests to revolutionize applications such as probing and manipulating biological processes in living cells, precise control over the color and directionality of ultra small optical emitters.[1,2] Currently these nanoneedle structures are typically produced by atomic scale methods which build up the continuous one-dimensional structures one atomic layer at a time.[2] From a technical and economic perspective, these methods are slow, complex, and expensive to meet the needs. Laser is an efficient and versatile tool to fabricate nanoscale nanostructures.[3] The production of ultra long ceramic nanofibers has recently been reported by laser spinning,[4] which combines laser with a supersonic nozzle and a high pressure. Herein, we introduce a laser based fabrication technique, confined laser spinning, directly writing gold nanoneedles on glass under ambient conditions.[5] Compared to laser spinning, confined laser spinning is more compact, simpler, and easier to control, collect and align laser formed nanoneedles.

Confined laser spinning uses spatially confined configuration to generate gold nanoneedles. In order to directly produce long metal needles from melted droplets, the temperature needs to be quickly increased above melting point, and the pressure needs to be high enough to initiate spinning process. The utilization of pulsed lasers can produce molten metal drops at very high temperatures during short periods,[6] which ensures that the metal remains fluid with a low viscosity during elongation. The spatially confined configuration provides an ultrahigh pressure shock because of confined laser ablation, which rapidly elongates the melted metal droplets before cooling.[3] To produce the metal needles with nanoscale diameter, the diameter of the initial drop before elongation should be as small as possible. Thus, we chose metal thin film deposited on glass as the beginning materials, which restricts the sizes of molten drops. Finally, the extreme requirements for nanoneedle formation were all satisfied by confined laser spinning.

The concept of confined laser spinning is illustrated in Figure 1. The spinning process can be simply described as follows: the melting and then evaporation of metallic thin film, high-pressure pulse generation and lateral propagation, and formation of nanoneedles. During the operation, the laser beam was passing through a focus lens directly for controlling the final beam size and laser fluence. The intensity of laser spot satisfied Gauss distribution; thus, the laser intensity was the highest at the spot center and was the lowest at the spot edge. When the laser transmitted through the transparent glass and arrived at the metal film, the metal material absorbed the laser energy and then vaporized and ionized instantly inside the laser spot, where laser intensity was above the evaporation threshold. At the same time, the metal material melt and formed liquid droplets at the edge of the laser spot, where laser intensity was above melting point, but is lower than evaporation threshold. The vapor exploded violently at the middle spot in the limited space and continued absorbing the remaining laser energy. As a result, a high-pressure pulse formed inside the spot during the laser heating and condensing of the vapor. The high-pressure pulse laterally expelled the molten droplets at the spot edge to the spot exterior, because the pressure was not counterbalanced in the outside directions. Metal nanoneedles were drawn from these molten droplets and finally resolidified fast on the glass surface.

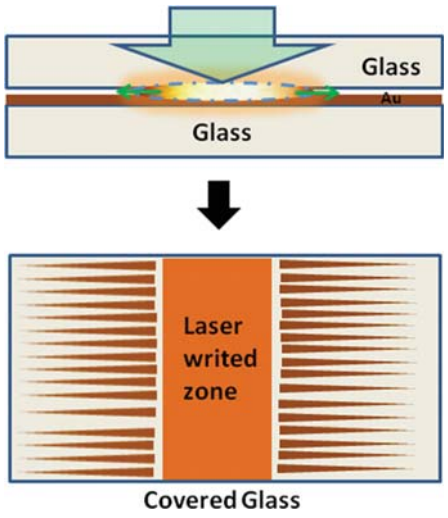

FIG. 1. Schematically illustration of gold nanoneedle generation by confined laser spinning.

A short pulse Q-switched Nd-YAG laser in TEM_{00} mode (Continuum® SureliteTM III) was used as laser source. The laser pulse width was 5 ns, and the laser pulse energy was measured by an optical power meter (Newport, type: 1916c). The beam diameter was calibrated by a photosensitive paper (Kodak Linagraph, type: 1895) and it was fixed at 2 mm in all experiments. ITO glass was used as the needle collector and the transparent confinement to increase laser induced pressure. Au thin film with a thickness of 30 nm was deposited on glass with SPI Module-T Sputter/Carbon Coaters. The morphology of laser produced nanoneedle was characterized by using a Hitachi S-4800 field emission scanning electron microscopy (SEM). ITO glass was used as covered collector because of its high electrical conductivity, which was propitious to observe sample morphologies by SEM.

Figure 2 shows the typical morphology of gold nanoneedles formed on ITO glass surface by confined laser spinning processing. Here, the laser fluence was about 7.52 mJ/cm^2. The SEM pictures show that these nanoneedles lie along the same direction which is perpendicular to the laser spot edge. The packing density of these separated nanoneedles is varying with the processing conditions. The average diameter of these parallel nanoneedles is about 40 nm. The picture in Figure 2(b) with higher magnification reveals that these nanoneedles have well-defined needlelike morphology with diameter decreasing along nanoneedles, smooth surface, and high aspect ratio. The tips of these needles are very sharp, with diameter as small as about 5 nm. The side of nanoneedles with bigger diameter is away from the center of laser irradiated region.

According to the model of Fabbro *et al.*,[7] the peak value of local shock pressure P_p can be evaluated under the confined configuration. It is proportional to the square root of laser intensityI_0:

$$P_p(\mathrm{GPa}) = 0.01\left(\frac{\alpha}{2\alpha+3}\right)^{0.5} Z^{0.5}(\mathrm{g/cm^2 s}) \times I_0^{0.5}(\mathrm{GW/cm^2}), \tag{1}$$

where α is the fraction of absorbed energy (normally between 0.2 and 0.5), and Z is reduced acoustic impedance, calculated by

$$\frac{2}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2}, \tag{2}$$

where Z_1 and Z_2 are the impedances of the confining media (ITO glass) and the target material (gold), respectively. The Z value can be estimated by $Z = \rho D$, where D is the shock velocity.[8] The estimated values of Z_1 and Z_2 are 3.52×10^6 and $9.554 \times 10^6 \mathrm{g/(cm^2 s)}$, respectively. The maximum velocity of molten liquid u at the spot border can be evaluated from Bernoulli's law[9,10]:

$$u = \left(\frac{2P_a}{\rho}\right)^{0.5} \approx \left(\frac{2P_p}{\rho}\right)^{0.5}, \tag{3}$$

where ρ is the density of irradiated material (gold: 19.3 g/cm^3), and P_a is the mean pressure value averaged over the pressure pulse duration. Using Newton's second law for the droplet elongation motion and neglecting friction between liquid and glass, the maximum length of nanoneedle ($l_{\max}$) is obtained when the liquid velocity drops to 0 (Ref. 10):

$$l_{\max} = l_0 u\left(\frac{\rho r}{2\sigma}\right)^{0.5}, \tag{4}$$

where σ is the surface tension coefficient, the value of Au liquid is in the range of 1.1 N/m, r is a constant across length radius of nanofiber (40 nm), and l_0 is the initial length of liquid (29 μm). The evolution time of this needle formation process is[10]

$$t_{\max} = \frac{l_0 u \rho r}{2\sigma}. \tag{5}$$

The instability of the liquid cylinder could be another factor limiting the maximum length of final nanoneedle. The characteristic time of the instability development is estimated approximately as[10,11]

$$t_{in} = \frac{8v\rho r}{\sigma}, \tag{6}$$

where v is the kinematic viscosity of the metal liquid. The measured value of kinematic viscosity of liquid gold is 3.58 Pa s.[12] The instability could be effective and induce the breakup of the viscous fluid thread, if $t_{in} < t_{\max}$. According to Eq. (6), the length of broken piece is proportional to its radius, and it does not affect by the elongation velocity of liquid cylinder. This phenomenon is demonstrated by SEM picture (Figures 3(a) and 3(b)). Figure 3(a) shows that the gold nanoscale beads are connected together (in the black dotted circle) due to instability. It is a transition status between forming nanoneedles (Figure 2) and nanoscale beads (Figure 3(b)). Figure 3 was observed from the transition zone, which is between the nanoneedle forming zone and laser written zone. It is noted that the instability of liquid cylinder provides a simple method to fabricate well separated nanoscale beads aligned along the direction of pressure difference. Such metal nanostructures are considered is useful for transfer light by coupling.

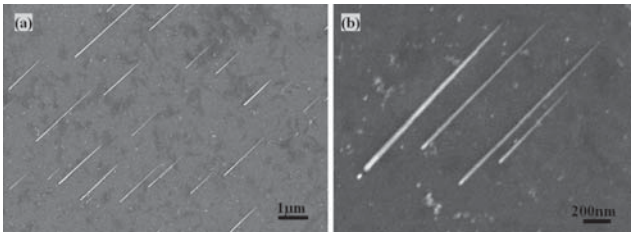

FIG. 2. High density of gold nanoneedles formed on ITO glass: (a) large scale and (b) higher magnification of nanoneedles.

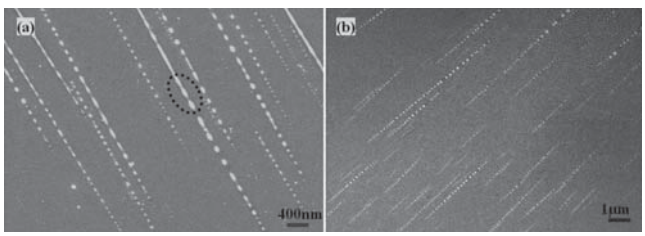

FIG. 3. (a) Status between forming nanoneedle and nanobeads, and (b) nanobeads formed by instability of gold liquid under high pressure.

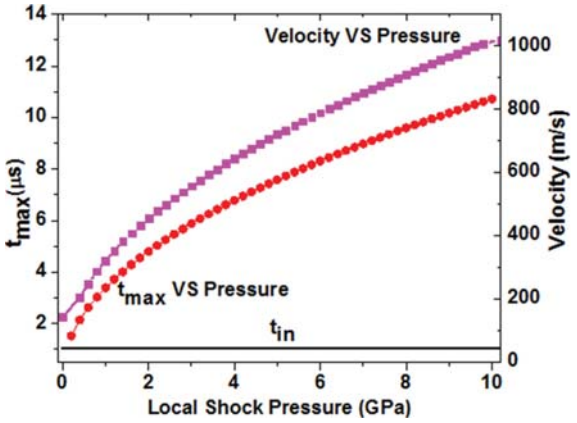

FIG. 4. t_{max} and maximum velocity of molten liquid at different local shock pressure.

Figure 4 shows the t_{max} and maximum velocity of molten liquid under different local shock pressure. It is noted that the maximum velocities of molten liquid increase with increasing the local shock pressure. The nanoneedles were formed under high shock pressure; however, high pressure would cause instability of liquid cylinder. Higher local shock pressure would also result in longer t_{max}. From the Figure 4, the t_{max} at any local shock pressure is longer than t_{in}, which explains the existence of transition zone. The higher velocity of molten gold causes the instability for the generation of aligned nanobeads. After passing the transition zone, the velocity of nanobeads decreases to form nanoneedles.

To summarize, this work demonstrates formation of gold nanoneedle by confined laser spinning. The formation mechanism of the nanoneedles is investigated. During the laser ablation, higher pressure was generated on the center of the laser spot and lower pressure on the edge of the spot. The high pressure expelled the molten droplet on the edge towards the outside of the laser spot. The instability happened when the evolution time of molten liquid was higher than the critical value. After the velocity of molten liquid reduces, gold nanoneedles were formed. This method provides a fast and simpler technique to form large scale gold nanoneedles by laser direct writing.

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