Appl Phys A (2011) 103: 421–426
DOI 10.1007/s00339-011-6356-6

Applied Physics A
Materials Science & Processing

Two-photon laser fabrication of three-dimensional silver microstructures with submicron scale linewidth

Naoto Tsutsumi · Kazuya Nagata · Wataru Sakai

Received: 6 October 2010 / Accepted: 22 January 2011 / Published online: 19 March 2011

Abstract We show three-dimensional silver microstructures with a submicron scale linewidth fabricated via two-photon photoreduction of silver ions in a poly(N-vinylpyrrolidone) (PVP) matrix. Femtosecond laser at 508 nm directly excites the carbonyl group of PVP via two-photon excitation to reduce silver ions. Lone pair electrons in PVP stabilized silver ions and lower molecular weight of PVP prevented silver clusters growing larger. The effect of molecular weight of PVP on linewidth of silver nanowire is investigated.

1 Introduction

During the last decade, two-photon and multi-photon induced microfabrication in a solution and in solid materials have been widely studied [1–8]. Glezer et al. investigated two-photon writing of bits in transparent glass materials and presented the possibility of three-dimensional optical data storage [1]. Using photopolymerization by two-photon excitation, Kawata et al. succeeded microfabrication of self-standing bull-shaped miniature with a micron scale [2]. Katayama et al. induced voids with a micron scale in polymeric materials using two-photon excitation and demonstrated their use for gratings [3]. They also demonstrated femtosecond laser pulse induced crystallization in an amorphous inorganic ($In_2O_3 + 1wt\%TiO_2$) film [4]. Kaneko et al. fabricated gold nanoparticle gratings using two-photon laser photoreduction of gold ions in a poly (vinyl alcohol) matrix [5]. Baldacchini et al. demonstrated two-dimensional silver structures in poly(N-vinylpyrrolidone) (PVP) films by a multi-photon laser direct writing method [6]. Tanaka et al. also fabricated three-dimensional electrically conductive silver microstructures using two-photon laser photoreduction of silver ions in an aqueous solution [7]. Ishikawa et al. fabricated the magnetic metamaterial composed of two-dimensional silver rod pairs with a micron scale using two-photon photoreduction [8]. Kawata et al. reported recently the morphology and the size dependence of silver microstructures in a fatty salts-assisted multi-photon photoreduction process and highest resolution of silver line with 285 nm upon laser irradiation of 800 nm [9].

In this article, we show three-dimensional silver microstructures with submicron scale linewidth fabricated via two-photon photoreduction of silver ions in PVP matrix. The effect of molecular weight of PVP on linewidth of silver nanowire is investigated.

2 Experimental

Femtosecond laser at 508 nm directly excites the carbonyl group of PVP via two-photon excitation to reduce silver ions. Lone pair electrons in PVP stabilized silver ions and lower molecular weight of PVP prevented to grow silver clusters larger. Femtosecond laser at 508 nm was derived from the sum frequency mixing of pumping beam of Ti:sapphire and the signal beam from optical parametric amplification (OPA). Compared with former studies a near infrared beam around 780 to 800 nm to excite sensitizer via a two-photon process to reduce silver ions, a shorter wavelength is preferred to enhance the lateral spatial resolution (LSR) of fabricated silver nanowire, i.e., to deduce the linewidth of nanowire.

N. Tsutsumi (✉) · K. Nagata · W. Sakai
Department of Macromolecular Science and Engineering,
Graduate School of Science and Technology, Kyoto Institute of
Technology, Matsugasaki, Sakyo, Kyoto 606-8585, Japan
e-mail: tsutsumi@kit.ac.jp
Fax: +81-75-724-7805

Table 1 List of sample films with a different concentration of $AgNO_3$ in the PVP matrix

Sample No.	1	2	3	4	5	6	7	8	9	10
Mw of PVP	40,000									
$AgNO_3$ (10^{-2} mol L^{-1})	3.1	1.0	0.61	0.44	0.31	0.25	0.20	0.18	0.15	0

Sample No.	11	12
Mw of PVP	10,000	360,000
$AgNO_3$ (10^{-2} mol L^{-1})	0.15	0.15

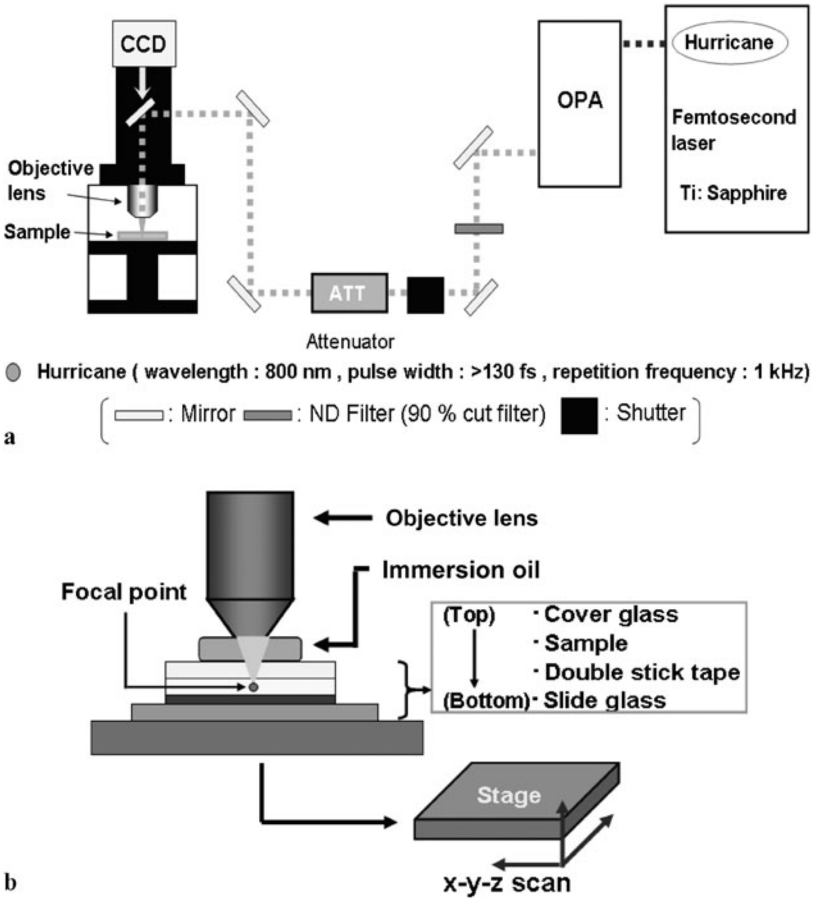


Fig. 1 (**a**) Schematic apparatus of laser irradiation system. (**b**) Detailed configuration of samples under microscope

Different molecular weight of PVP with Mw = 10,000, 40,000, and 360,000 (Nacalai Tesque, Japan) was used as the matrix. A 1.3 mol L^{-1} PVP aqueous solution was prepared. 1.2×10^{-3} mol L^{-1} silver nitrate ($AgNO_3$) (Nacalai Tesque, Japan) aqueous solution was prepared. With PVP of Mw = 40,000, ten samples including a different concentration of $AgNO_3$ was prepared from above solutions. Table 1 lists the samples with a different concentration of $AgNO_3$. Compared with the effect of the sample with a different molecular weight of PVP, the $AgNO_3$ concentration is fixed 0.15×10^{-2} mol L^{-1}. The sample film was cast from a solution at room temperature for two days under dark conditions.

A schematic apparatus of laser exposure system is shown in Fig. 1(a). The light source is a Ti:sapphire laser system (Spectra Physics Hurricane) with an operating wavelength of 800 nm, a repetition rate of 1 kHz, and a pulse width of 100 fs. Signal and idler beams are produced using an optical parametric amplification (OPA) system (Spectra Physics OPA-800C) pumped by the Ti:sapphire laser system. Sum frequency mixing light at 508 nm was produced in 0.2 mm thickness BBO nonlinear optical crystal with a pump beam of 800 nm and signal beam from an OPA system. Wavelength of signal and idler beams was controlled by adjusting the setting angle of BBO nonlinear optical crystal in OPA-800C. The wavelength of the light source was monitored using a spectrophotometer (Ocean Optics USB4000-UV-VIS spectrometer).

A detailed configuration of samples under the microscope is shown in Fig. 1(b). Femtosecond pulse light at 800 or 508 nm is introduced to a light microscope (Olympus BX51WI) and focused on a sample using an oil immersed objective lens (Olympus UPlan FLN, 100×, NA = 1.30). Microstructures of silver wire were fabricated in a sample film settled on a three-dimensional sample stage controlled by ALPS3861.

Scan speed of laser light on the sample is 2.0 $\mu m\,s^{-1}$ and the laser energy is controlled from 6 to 50 µW using an attenuator. Laser energy was monitored using a pyrometer (Ophir PD300-UV/Orion-PD pyrometer).

After laser illumination, the light source is switched from laser to white light, then fabricated structures are captured by a CCD camera and the linewidth of fabricated structures is measured. Two-dimensional and three-dimensional microstructures are measured using the same microscope equipped with a confocal unit (Olympus Fluoview FV300) having an argon laser at 488 nm, a He-Ne laser at 543 nm, and a He-Ne laser at 632.8 nm. Confocal images of silver microstructures are measured in the reflection mode using a He-Ne laser at 543 nm. All measurements of laser illumination, CCD capturing, and confocal imaging were carried out in one microscope with an object lens by switching the corresponding light path.

Absorption spectrum of the sample film is recorded in normal transmission mode on an ultraviolet and visible spectrophotometer (Shimadzu UV-2100PC, Japan). Infrared absorption spectrum of the sample film is also recorded in the normal transmission mode using a Fourier transform infrared spectrometer (Perkin Elmer Spectrum GX FT-IR spectrometer).

3 Results and discussion

Irrespective of the colorless solution prepared, cast films colored yellowish depending on the silver nitrate concentration. By decreasing the silver nitrate ($AgNO_3$) concentration, the yellowish color turned to pale. Figure 2 shows the absorption spectra of sample films after casting. Distinct absorption peak at 418 nm appeared for the sample from No. 1 to No. 9 and the absorption intensity decreases with decreasing the $AgNO_3$ content in a PVP matrix. These absorptions with a peak at 418 nm are due to that of surface Ag plasmon resonance. Huang et al. demonstrated that a silver nanoparticle with a size of 15 to 30 nm showed clear absorption peaks between 404 to 418 nm [10]. The spectral band characteristics for distinct silver cores is located at *ca* 280 (Ag_4^{2+} cluster), 295 (a-type cluster), 335 (b-type), 370 (c-type), or 380 nm (subcolloidal particles) [11]. Maillard et al. showed that surface Ag plasmon enhanced photoreduction of the Ag ion [12]. These results were reproduced in [13]. The FT-IR spectrum also showed the interaction between the silver nanoparticle and carbonyl group of the PVP matrix. The absorption peak due to a free carbonyl group at 1657 cm^{-1} is red-shifted by the presence of silver nitrate.

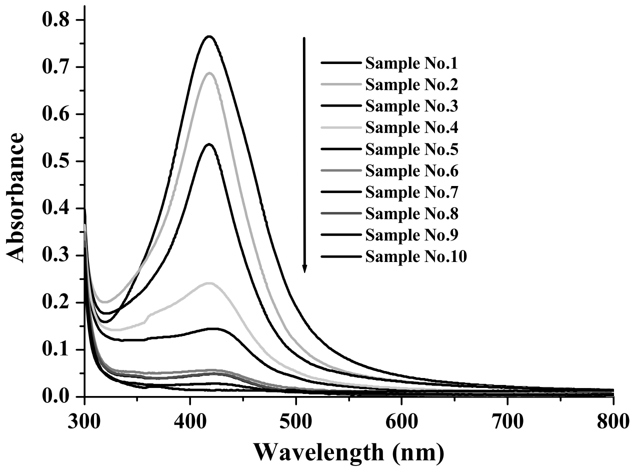
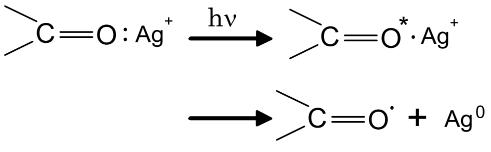
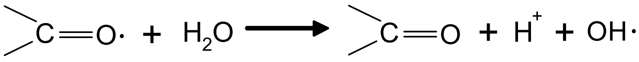


Fig. 2 Absorption spectra of cast film with various concentrations of silver nitrate

Femtosecond laser irradiation at 508 nm for the samples from No. 1 to No. 9 and Nos. 11 and 12 gave rise to the silver particle. The mechanism of reduction of the silver ion in the presence of PVP is as follows [13]. Since the carbonyl group in PVP has a strong absorption due to π–π^* transition at 254 nm, it can be excited through a two-photon process at 508 nm; as in (1), the carbonyl group excited through two photon excitation and reduces the neighboring silver ion to a silver atom. As shown in (2), reaction of a free radical of the carbonyl group with water gave rise to the original carbonyl group. Obtained silver atoms are gathered to form silver nanoparticle clusters in (3) or some silver atom is stabilized with the carbonyl group in (4).



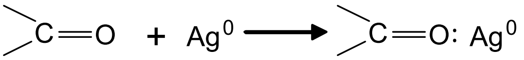
(1)



(2)

$$n\,Ag^0 \longrightarrow (Ag^0)_n \qquad (3)$$

or



(4)

In order to fabricate microstructures with a submicron scale linewidth using two-photon excitation, we need to determine the appropriate condition of laser irradiation and the appropriate concentrations of $AgNO_3$ in a PVP matrix. To fabricate microstructures with a smaller size, lower scanning speed is better. For the present multi-photon laser micromachining system, scanning speed of 1 $\mu m\,s^{-1}$ is the reliable lowest one. With consideration of total fabrication time, we chose the scanning speed of 2 $\mu m\,s^{-1}$. A single line with a length of 30 μm was first drawn for the various concentration of $AgNO_3$ ranging from 3.1×10^{-2} to 0.15×10^{-2} $mol\,L^{-1}$ in a PVP matrix shown in Table 1 with changing irradiation energy. Almost the same linewidth was drawn irrespective of the concentration of $AgNO_3$ in a PVP matrix. Thus, we chose the lowest concentration of 0.15×10^{-2} $mol\,L^{-1}$. Linewidth was estimated from the CCD image of the microscope after fabrication. The dependence of linewidth of silver clusters on irradiation energy is shown for the PVP samples with three different molecular weights in Fig. 3. With the laser energy between 12 to 40 μW, the linewidth was increased with some part of ablation, and above 40 μW clear ablation of the PVP matrix was observed. With the laser energy between 6 to 12 μW, narrow silver clusters with almost constant linewidth between 300 and 400 nm were fabricated. These apparent linewidths observed by the CCD image is limited by the diffraction limit of light, and thus almost a constant linewidth was measured irrespective of decreasing irradiation laser energy. The resolution limit for both fabrication and observation under an optical microscope is illustrated in the figure. Since these structures are formed inside the sample, the structures should be confirmed by, e.g., electron microscopy with a high resolution.

As investigated in an earlier study [10, 14], PVP protected the reduced silver atoms from the aggregation of themselves to form nanoparticle clusters. It is important to investigate how the molecular size of PVP affects the linewidth of silver nanoparticle clusters. Figure 3 shows that, comparing the linewidth of the sample with different molecular weight PVP prepared at the same irradiation energy, the higher molecular weight sample has a wider linewidth. In other words, PVP with a lower molecular weight maintains a narrower linewidth of silver nanoparticle clusters for higher irradiation energy. In a previous study [15], lower molecular weight of PVP protects smaller silver nanoparticle clusters (primary nanoparticle) keeps smaller coalescence of the primary nanoparticle (secondary nanoparticle). On the other hand, PVP with a higher molecular weight includes a larger amount of silver ions in the matrix. Larger silver clusters (primary nanoparticle) were produced to coalesce a larger secondary nanoparticle. This means that the longer molecular chain of higher molecular weight PVP assisted the effective energy concentration to the reactive site in which the larger clusters of silver are effectively formed. To fabricate a narrower linewidth of a silver line in the matrix, we deter-

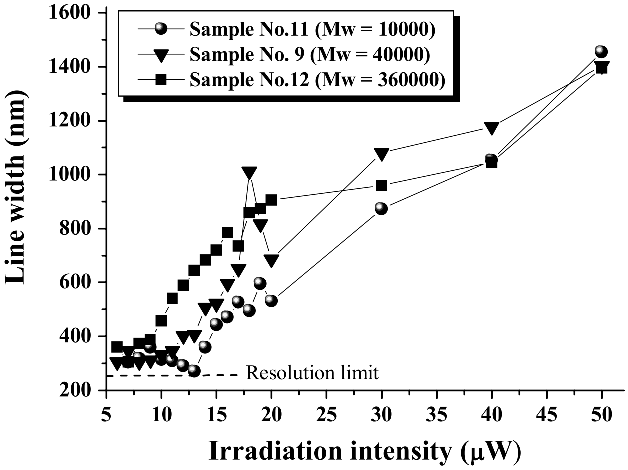


Fig. 3 Plots of linewidth of nanowire as a function of irradiation energy for different samples with various molecular weight of PVP

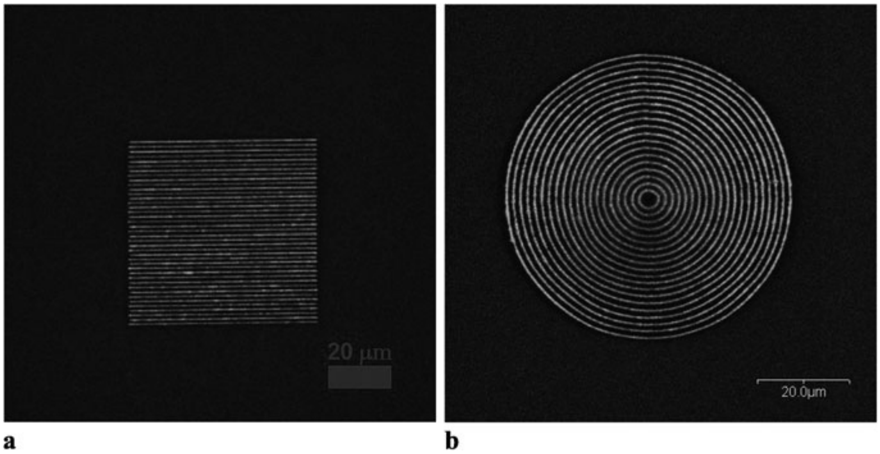


Fig. 4 CLSM images of two-dimensionally fabricated structures. (**a**) Parallel line structure and (**b**) circular structure

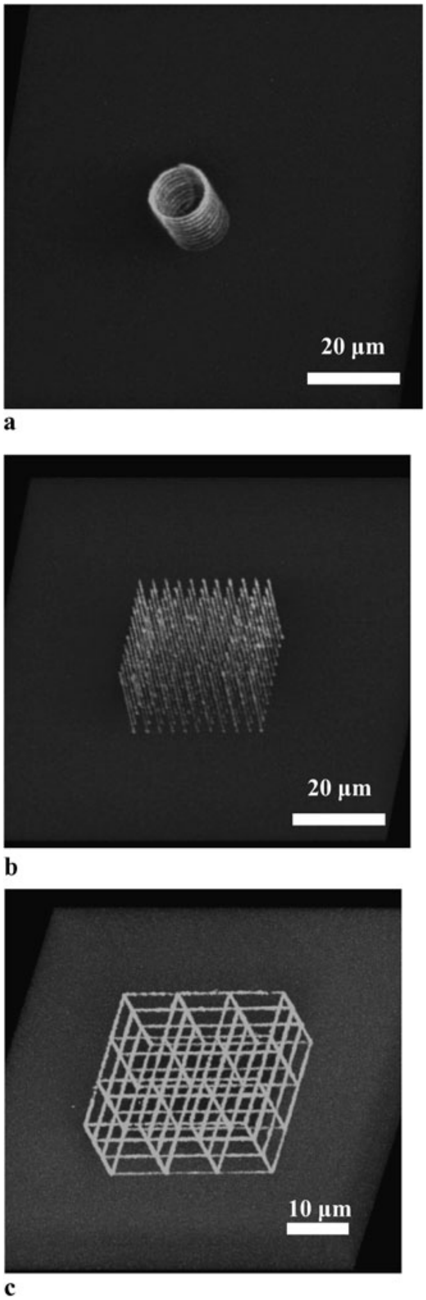


Fig. 5 CLSM images of three-dimensionally fabricated structures. (**a**) Coil structure, (**b**) pillar structure, and (**c**) rubic cube structure

mined PVP with a molecular weight of 10,000 as the host matrix and stabilizer of silver clusters; $0.15 \times 10^{-2}\ \mathrm{mol\,L^{-1}}$ of silver nitrate in a PVP matrix, and 10 µW of laser energy.

Using these appropriate conditions, two- and three-dimensional nanowire silver structures were fabricated in a PVP matrix by laser irradiation with an optical microscope. Parallel lines and concentric silver structures generated by computer-aided drawing software were fabricated in a PVP matrix using computer controlled three-dimensional submicron stages under laser irradiation using ALPS3861. After the structures are fabricated, they are imaged using a confocal laser scanning microscope (CLSM). CLSM images of these fabricated microstructures are shown in Fig. 4. Forty lines with a length of 60 µm and their interval of 1.5 µm were drawn and measured, and 20 circles with each radius interval of 1.5 µm with the smallest circle with a radius of 1.5 µm were drawn and measured.

Helix, pillar, and cubic silver microstructures were fabricated in a PVP matrix by laser illumination under an optical microscope. CLSM images of these fabricated microstructures are shown in Fig. 5. Ten coiled helixes with a radius of 5 µm, pitch interval of 2.74 µm and height of ca. 30 µm were fabricated. One hundred twenty-one pillars with a length of 30 µm and interval of 3 µm were also fabricated. Cubic with each edge of 10 µm were piled to form a rubic cube like structure in a PVP matrix.

4 Conclusions

In conclusions, we demonstrated two- and three-dimensional microstructures of silver particles fabricated by direct excitation of a carbonyl group of PVP matrix. Linewidth of fabricated silver nanowire is in the order of the submicron scale. Combination of these structures and polymeric waveguide including laser dye will give us new organic dye laser devices.

References

1. E.N. Glezer, M. Milosavljevic, L. Huang, R.J. Finlay, T.-H. Her, J.P. Callan, E. Mazur, Three-dimensional optical storage inside transparent materials. Opt. Lett. **21**(24), 2023–2025 (1996)
2. S. Kawata, H.-B. Sun, T. Tanaka, K. Takada, Nature **412**, 697 (2001)
3. S. Katayama, M. Horiike, K. Hirao, N. Tsutsumi, Diffraction measurement of grating structure induced by irradiation of femtosecond laser pulse in acrylate block copolymers. Jpn. J. Appl. Phys. **41**, 2155–2162 (2002)
4. S. Katayama, M. Horiike, T. Nakamura, K. Hirao, N. Tsutsumi, Femto-second laser induced crystallization and permanent relief grating structures in amorphous inorganic (In_2O_3 + 1wt%TiO_2) film. Appl. Phys. Lett. **81**(5), 832–834 (2002)
5. K. Kaneko, H.B. Sun, X.M. Duan, S. Kawata, Two-photon photoreduction of metallic nanoparticle gratings in a polymer matrix. Appl. Phys. Lett. **83**, 1426–1428 (2003)
6. T. Baldacchini, A.C. Pons, J. Pons, C.N. LaFratta, J.T. Fourkas, Y. Sun, M.J. Naughton, Multiphoton laser direct writing of two-dimensional silver structures. Opt. Express **13**(4), 1275–1280 (2005)
7. T. Tanaka, A. Ishikawa, S. Kawata, Two-photon-induced reduction of metal ions for fabricating three-dimensional electrically conductive metallic microstructure. Appl. Phys. Lett. **88**, 081107 (2006)
8. A. Ishikawa, T. Tanaka, S. Kawata, Magnetic excitation of magnetic resonance in metamaterials at far-infrared frequencies. Appl. Phys. Lett. **91**, 113118 (2007)
9. Y.-Y. Cao, X.-Z. Dong, N. Takeyasu, T. Tanaka, Z.-S. Zhao, X.-M. Duan, S. Kawata, Morphology and size dependence of silver

microstructures in fatty salts-assisted multiphoton photoreduction microfabrication. Appl. Phys. A **96**, 453–458 (2009)

10. H.H. Huang, X.P. Ni, G.L. Loy, C.H. Chew, K.L. Tan, F.C. Loh, J.F. Deng, G.Q. Xu, Photochemical formation of silver nanoparticles in poly(N-vinylpyrrolidone). Langmuir **12**, 909–912 (1996)
11. M. Mostafavi, M.O. Delcourt, G. Picq, Study of the interaction between polyacrylate and silver oligomer clusters. Radiat. Phys. Chem. **41**(3), 453–459 (1993)
12. M. Maillard, P. Huang, L. Brus, Silver nanodisk growth by surface plasmon enhanced photoreduction of adsorbed [Ag^+]. Nano Lett. **3**(11), 1611–1615 (2003)
13. Y. Zhang, S. Ochiai, K. Kojima, Y. Uchida, A. Ohashi, Photochemical formation of silver nanoparticles in poly(N-vinylpyrrolidone) film and direct metal photo-patterning by a mask. Bull. Res. Inst. Ind. Tech. (Aichi Inst. Tech.) **8**, 43–48 (2006)
14. Z. Zhang, B. Zhao, L. Hu, PVP protective mechanism of ultrafine silver powder synthesized by chemical reduction processes. J. Solid State Chem. **121**(1), 105–110 (1996)
15. H.S. Shin, H.J. Yang, S.B. Kim, M.S. Lee, Mechanism of growth of colloidal silver nanoparticles stabilized by polyvinyl pyrrolidone in γ-irradiated silver nitrate solution. J. Colloid Interface Sci. **274**(1), 89–94 (2004)