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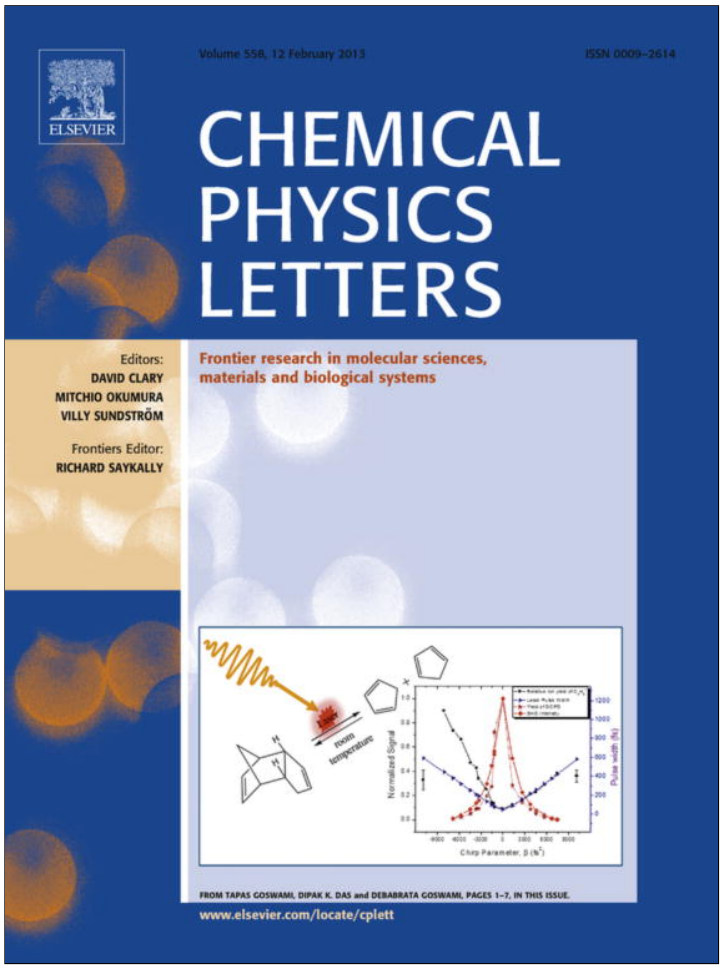

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Two-photon excitation by femtosecond laser in poly(*N*-vinylpyrrolidone) matrix doped with silver ions

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ABSTRACT

We studied the morphological behavior of two-dimensional (2D) structures fabricated by two-photon excitation of silver nitrate in poly(*N*-vinylpyrrolidone) (PVP) matrix. The 2D structures at two different positions toward depth direction were fabricated on a microscope stage. Obtained structures were investigated using an atomic force microscopy (AFM), a scanning electron microscopy (SEM), an energy dispersive X-ray spectrometry (EDX), and an X-ray photoelectron spectroscopy (XPS). AFM measurement showed the photo-induce structure on a cover slip. EDX and XPS measurements showed that the silver ion was photo-reduced and the photo-reduced silver was interacted with PVP, respectively.

1. Introduction

In recent years, two-photon induced microfabrication has been widely studied and developed for creating three-dimensional (3D) microstructures. This technique is one of the tools for creating periodic structures with micron or submicron scale. Combination of femtosecond laser and microscope with high magnification object lens with higher numerical aperture is a popular tool for the fabrication of micron scale structures.

Two-photon excitation was used for creating the structure in glass materials. For example, Glezer et al. investigated two-photon writing of bits in transparent glass materials and possibility of 3D optical data storage [1]. And this technique was also applied to photo-resist to fabricate the designed or patterned 3D structure, which Maruo et al. created 3D spiral structure [2] and Kawata et al. fabricated bull-shape 3D structure [3]. After they had succeeded to fabricate variety of the structure in solid, other study of two-photon excitation began. Katayama et al. [4] demonstrated femtosecond laser pulse induced crystallization in an amorphous inorganic (In_2O_3 + 1 wt.% TiO_2) film. The study was that the metal structure was fabricated by two-photon excitation without using photo-resist. Wu et al. [5], Kaneko et al. [6], Bladacchini et al. [7], Ishikawa et al. [8], and Vora et al. [9] successfully fabricated the metal structure. Wu et al. showed that the metal structure inside a sol–gel matrix. Gold material was used to create gold nanoparticle grating by Kaneko et al. The study of Refs. [7–9] was that a structure with silver was fabricated in two-dimensional (2D) or 3D to give electromagnetic functionality. In recently years, complex patterned structure was fabricated so that the fabricated structure has a functionality such as enhancement of electromagnetic field in visible range; Li et al. demonstrated the fabrication with scalable resolution along the beam axis by employing the deactivation beam and downed to a 40 nm minimum feature size [10], and Liu et al. reported high-Q polymer whispering gallery microcavities could be directly written by the two-photon polymerization of zirconium/silicon hybrid sol–gel [11].

We have already reported the 3D microstructures with submicron scale linewidth fabricated through two-photon photo-reduction of silver ions in PVP matrix using a femtosecond laser system as a past report [12]. However, previous study and other current study is only fabrication of structure and the mechanism of silver photoreduction without using femtosecond laser is known while the mechanism of silver photoreduction with using femtosecond laser is not known. So, to further analyze these fabricated structure, in this Letter, we studied the morphological behavior of 2D structures fabricated by two-photon excitation of silver nitrate in PVP matrix. Morphology of the photo-induced structures were measured using an atomic force microscopy (AFM) and a scanning electron microscopy (SEM), and analyzed using an energy dispersive X-ray spectrometry (EDX) and an X-ray photoelectron spectroscopy (XPS).

2. Experimental

Femtosecond laser at 508 nm directly excites carbonyl group of PVP through 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 cluster larger [13,14]. Femtosecond laser at 508 nm was driven from the sum frequency mixing of pumping beam of Ti:Sapphire and the signal beam from optical parametric amplification (OPA).

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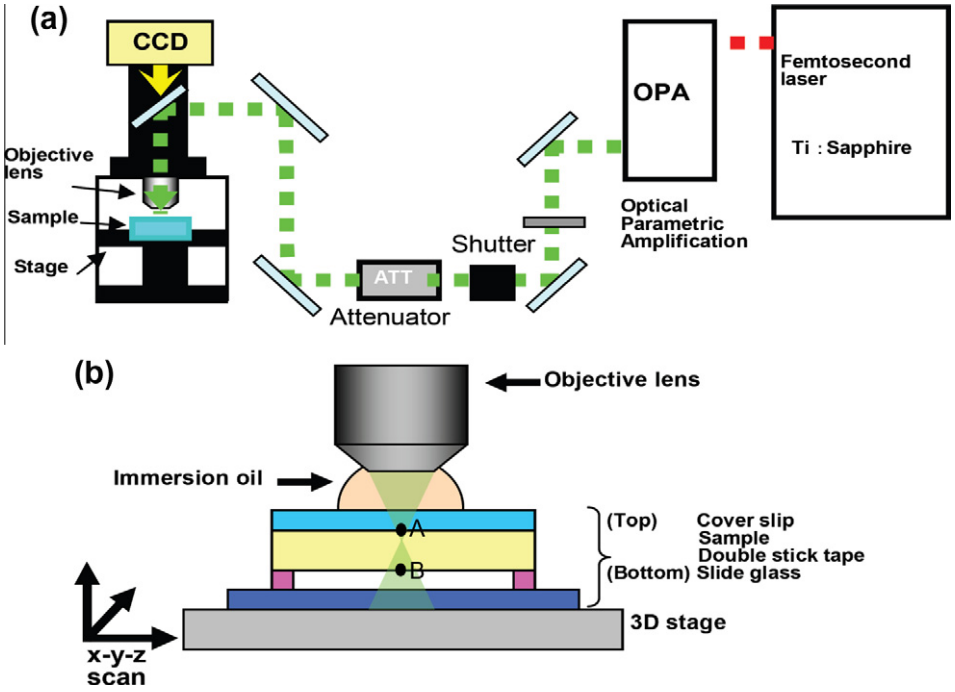

Figure 1. (a) Schematic apparatus of laser irradiation system. (b) Detailed configuration of sample under a microscope.

PVP with Mw = 10000 (Nacalai Tesque, Japan) was used as a matrix. 1.3 mol L^{-1} of PVP aqueous solution was prepared. 1.2×10^{-3} mol L^{-1} of silver nitrate ($AgNO_3$) (Wako, Japan) aqueous solution was prepared. Solution was cast at room temperature for one day under dark condition to prepare sample film with about 50 μm. In addition, this sample concentration is same concentration as the highest it in Ref. [12].

Schematic apparatus of laser exposure system is shown in Figure 1a. Light source is Ti:Sapphire laser system (Spectra Physics Hurricane) with an operating wavelength of 800 nm, a repetition rate of 1 kHz, and pulse width of 100 fs. Signal and idler beam are produced using an OPA system (Spectra Physics OPA-800C) pumped by Ti:Sapphire laser system. Sum frequency mixing light at 508 nm was produced in 0.2 mm thickness BBO nonlinear optical crystal with pump beam of 800 nm and signal beam from an OPA system. Wavelength of the sum frequency mix beam was monitored with a spectrophotometer (Ocean Optics USB4000-UV–vis spectrometer).

A detailed configuration of samples under the microscope is shown in Figure 1b. Structures were fabricated in two different positions toward depth direction in the sample: Near a cover slip (Position A) and on a sample surface (Position B). Positions A and B are shown in Figure 1b. Femtosecond pulse light at 508 nm is introduced to an optical microscope (Olympus BX51WI) and focused on a sample using an oil immersed object lens (Olympus UPlan FLN, 100×, NA = 1.30). Microstructures were fabricated near a cover slip (Position A) and on a surface (Position B) of sample film settled on 3D stages controlled by ALPS3861 software for 3D stage control.

For fabrication near a cover slip (Position A), laser scan speed of 20.0 μm s^{-1} was employed with laser power controlled from 50 μW using an attenuator, while laser scan speed of 2.0 μm s^{-1} with laser power of 10–70 μW was employed for the lines drawn through two-photon excitation on a sample surface (Position B).

To observe the structures fabricated near a cover slip (Position A), PVP matrix was removed. Structures were observed by an AFM (Pacific Nanotechnology Nano-R) and a SEM (Hitachi S-3000), and analyzed by an EDX (Hitachi S-3000) and a XPS (JEOL JPS-9010MC/SP).

3. Results and discussion

3.1. The structure on a cover slip

To measure the structures fabricated on a cover slip (Position A), PVP matrix was removed after laser irradiation. After removing PVP matrix, AFM and SEM measurements were performed. Figure 2 shows the AFM image of the remained structures on a cover slip and inset in Figure 2 shows the height profile of structures along white line in Figure 2. Figure shows structure with 650 nm height,

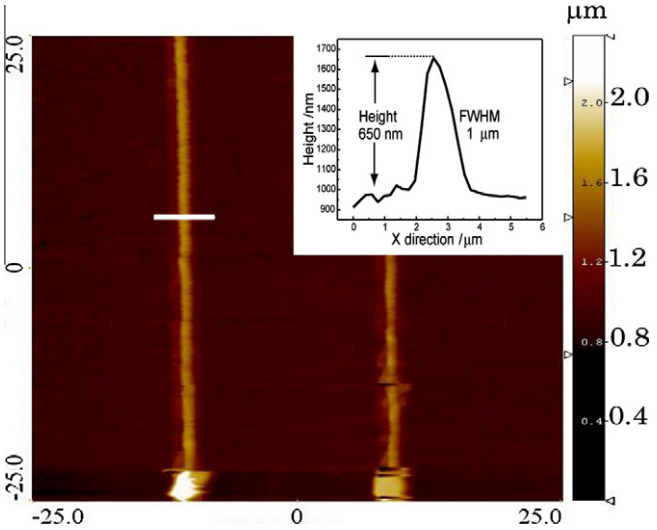

Figure 2. AFM image of the structures on a cover slip. Inset is profile along the white line in this figure.

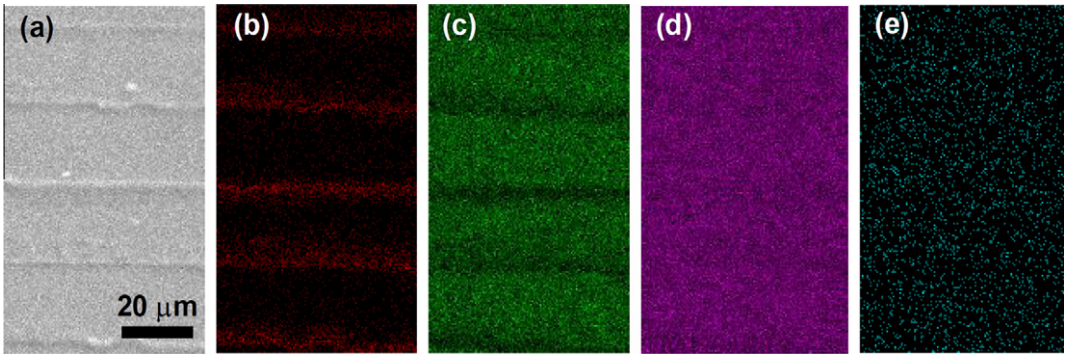

Figure 3. (a) SEM image of surface of the structures, and color mapping of (b) C, (c) O, (d) Si, (e) Ag.

and 1 μm linewidth from full width at half maximum (FWHM) in Figure 2.

SEM image of the line structures is shown in Figure 3a. To figure out the compositions of line structures, EDX analysis was performed. Color mapped image of carbon (C), oxygen (O), silicon (Si), and silver (Ag) detected by EDX measurement is shown in Figure 3b–e, respectively. EDX analysis shows carbon element is positive and oxygen and silicon elements are negative. Positive C line means the fabricated lines contain carbon element. O and Si are based on the glass cover slip substrate (SiO_2). Negative O line means that a structure was created on the cover slip with less O content. However, we observed not positive silver line but dispersed silver signal. This result was not expected one. Because of very low concentration of silver, it is difficult to separate the silver signal from the background EDX measurement which encompasses a volume.

To figure out the above issue that the silver signal could not be detected, XPS measurement was performed. Figure 4a shows a typical XPS spectrum of the fabricated structures. Figure 4b and c shows detailed XPS signal in the narrow binding energy region. C (1s) spectrum can be separated into four peaks by multiple Gaussian curves fitting. The peak positions at 285.0, 285.4, 286.4, and 287.6 eV are assigned carbon atoms from 1 to 4 shown in inset of Figure 4b, respectively [15]. The peak at 287.6 eV is attributed to carbonyl (C═O) oxygen in PVP repeated unit. Two peaks based on silver atoms (Ag 3d5/2 and Ag 3d3/2) were measured at 367.8 and 373.9 eV, respectively. The reason why this peaks can be detected is detection ability of XPS device is higher than it of EDX device. So, silver peaks do not appear in typical XPS spectrum but we detected it of detailed XPS spectrum in narrow binding energy. In Figure 4c, XPS data of free silver peak (Ag 3d5/2) in silver salt (silver nitrate) is also shown in comparison. The free silver peak (Ag 3d5/2) appeared at 369.2 eV, whereas the silver peak (Ag 3d5/2) in the structure was measured at 367.8 eV. It means that the silver peak in the structures is shifted to lower binding energy. It has been reported that the XPS spectrum of a silver nanoparticle which interacts with a carbonyl group was shifted to lower binding energy [16]. Thus, we think that the fabricated microstructures are interacted with PVP chains and make the silver contained PVP structure. The schematic picture of silver cluster interacted with PVP chain is shown in Figure 5.

Fabrication of structures in PVP matrix was also reported [9]. In that report [9], silver nitrate aqueous solution of 1.6 mol L^{-1}, which is quite higher than own case, was used and clear Ag signal was measured in EDX analysis because silver clusters are produced from high concentration of silver nitrate solution. In contrast to that report [9], the present results showed that the silver signal could not detect because the silver ions at lower concentration of silver nitrate were photo-reduced to produce silver atoms. It is known that silver ion is adsorbed to PVP and PVP prevents to grow silver cluster larger when the silver ion is dispersed in PVP matrix [13,14]. From these references and own results, we think that the silver ions adsorbed by PVP chain were photo-reduced and assembled together in this system. We assume that silver cluster is covered by PVP chain. In this case, we used low concentration of silver ion for investigation of Ref. [12]. But our goal is fabrication of completely metal structure. So we expect the completely metal structure will be created with high concentration of silver ion.

3.2. The structure fabricated on sample surface

We examined the difference between the structures on a cover slip (Position A) and on a sample surface (Position B). Line structures fabricated on a sample surface (Position B) were measured

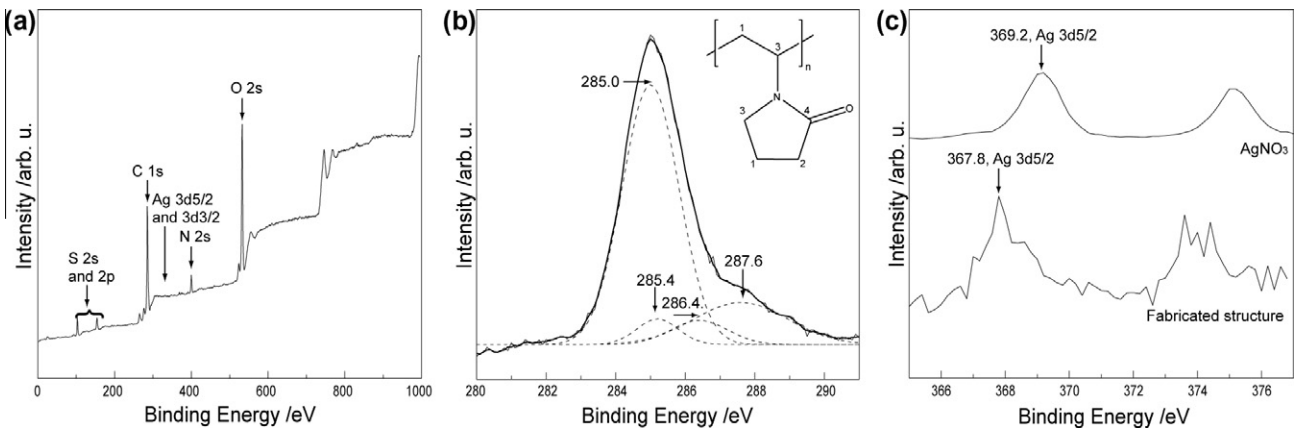

Figure 4. XPS spectra of the remained structures (a) in whole range, (b) C (1s) range, and (c) Ag (3d5/2 and 3d3/2) range with free silver peak in silver nitrate. Spectrum of (b) can be separated into four peaks by multiple Gaussian curves fitting. In (c), XPS data of free silver peak (Ag 3d5/2) in silver salt (silver nitrate) is also shown in comparison.

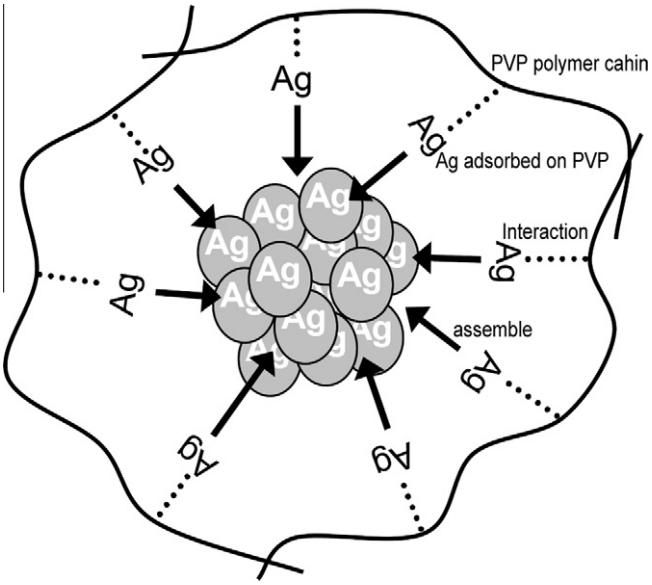

Figure 5. Schematic of Ag clusters interacted with PVP chains.

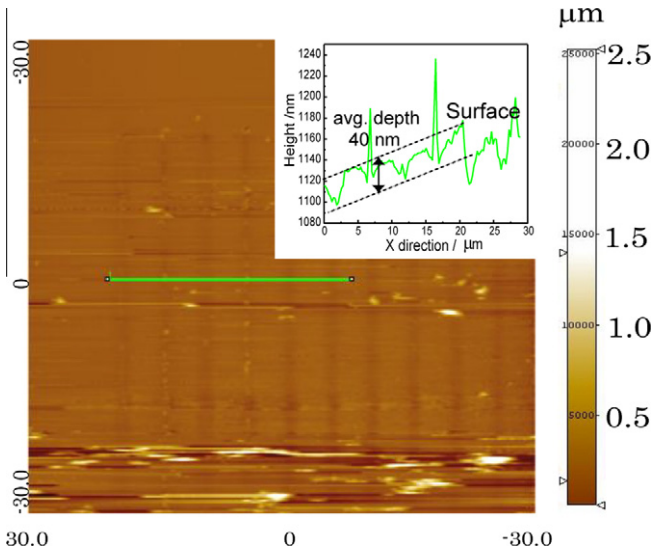

Figure 6. AFM image of the line structure fabricated on sample surface at 70 μW irradiation. Inset is profile along the green line in this figure. Upper broken line in inset is a sample surface. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

using an AFM. AFM image of the microstructures fabricated on a sample surface at 70 μW irradiation is shown in Figure 6. As shown in the figure, periodic line structures were measured. Inset in Figure 6 shows the cross-section image along the green line in Figure 6. Upper broken line in inset of Figure 6 is a sample surface and peaks over the upper broken line are structures fabricated. Cross-section image shows that fabricated structure accompanied with shallow but broad hollow. Linewidth of these structures is 0.57 μm from FWHM of the peak above upper broken line in Figure 6. We assume the reason of creation of hollow is as follow. Nanomovement was occurred when laser is irradiated to polymer [17]. Then polymer moved to irradiation point and made hollow. The depth of hollow was measured and plotted as a function of irradiation power in Figure 7. Depth is getting larger when laser

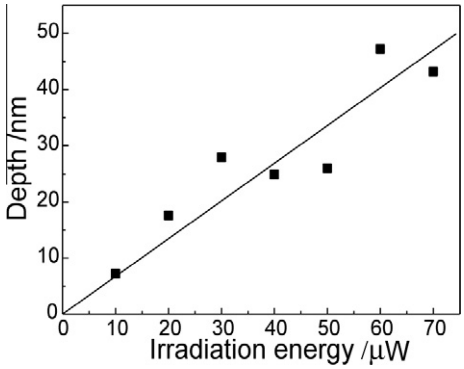

Figure 7. Plots of depth of hollow as function of irradiation power.

power increases. This is because the larger portion of polymer more moves to irradiation point, when the larger power of laser is irradiated. From this result and Section 3.1, we think that this nanomovement occurred with interaction between silver and PVP and these microstructures were created by PVP interacted photo-reduced silver. Comparing with AFM result in Section 3.1, linewidth of Position B is narrower than that of Position A. We assume only top of fabricated structure was measured because of existence of residual or unreacted PVP. If unreacted PVP is removed, we can measure entire structure.

4. Conclusions

In conclusions, we studied the microstructures fabricated through two-photon excitation of a carbonyl group in PVP matrix. EDX measurement indicated that fabricated structure mainly included carbon element. XPS measurement indicated that the reduced silver was contained in the line structure and had an interaction with carbonyl group of PVP. From EDX and XPS results, the structure was created by PVP interacted silver atom. And we assume that the silver contained PVP cluster is covered by PVP chain from these results.

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