

Fluorescence Patterning in Dye-Doped Sol–Gel Films by Generation of Gold Nanoparticles

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Received June 16, 1999

Revised Manuscript Received August 18, 1999

Glasses doped with nanoparticles of metal and semi-conductors have attracted much interest for potential applications as optoelectronic materials based on their nonlinear optical properties¹ as well as single-electron tunneling and charging phenomena.² On the other hand, organic molecules are alternative candidates for dopants into glass materials to give versatile photonic functions originating from their luminescent and photochemical properties.³ To utilize these functionalized glasses for practical devices, a new, simple method is necessary to embed and arrange doped species in a desired structure in thin films. A sol–gel technique⁴ is one promising method for incorporating a variety of functional species in glass films due to its low-temperature process involving hydrolysis and condensation reactions of metal alkoxides. In previous work, we doped rhodamine dye molecules in silica(SiO₂)/titania(TiO₂) sol–gel films and observed thin-film lasing action under optical pumping.⁵ We also prepared Au nanoparticles in SiO₂/TiO₂ films using photochemical reduction of Au(III) ions doped in the precursor sol solution.⁶ By means of this controllable photogeneration process, micropatterns of Au nanoparticles were fabricated in the films using a photomask. Furthermore, local reduction of Au(III)-doped SiO₂/TiO₂ films assisted by atomic force microscopy (AFM) enabled us to generate single Au nanoparticles, the size of which was controlled by bias voltages applied between a conductive cantilever and an indium–tin oxide (ITO)-coated glass substrate.⁷ This patterned production of metal nanoparticles would be a useful technique in

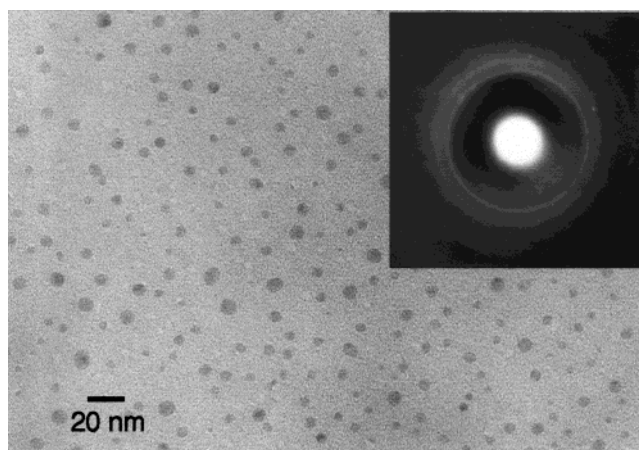


Figure 1. Electron micrograph and electron diffraction pattern of Au nanoparticles generated in UV-irradiated Au/RB–SiO₂/TiO₂ film.

constructing micro- and nanoscale optoelectronic assemblies in glass films. Moreover, incorporation of inorganic nanoparticles with photoactive organic molecules would lead to new functionalized materials. From this point of view, we have now studied SiO₂/TiO₂ sol–gel films binary-doped with Au ions and rhodamine molecules and found that fluorescence of rhodamine is patterned in the film by generation of Au nanoparticles.

In our sol–gel process, dip-coating films of SiO₂/TiO₂ containing chloroauric acid (HAuCl₄) and rhodamine B (abbreviated as Au/RB–SiO₂/TiO₂) were prepared on a glass substrate from an ethanol solution of tetraethyl orthosilicate (Si(OC₂H₅)₄)/tetraethyl orthotitanate (Ti(OC₂H₅)₄) mixture under an acid catalysis.⁸ The ratio of SiO₂:TiO₂ in the matrix films was optimized to be 2:1 to produce homogeneously doped films with optical flatness as well as to make generation of Au nanoparticles possible as mentioned below. A higher ratio of SiO₂ caused precipitation of rhodamine in the sol solution, while a higher content of TiO₂ resulted in opaque films due to fast hydrolysis reactivity of Ti(OC₂H₅)₄. Neatly coated films were transparent, having faint pink color due to an absorption band of the doped rhodamine dye at $\lambda_{\text{max}} = 565$ nm. Photogeneration of Au nanoparticles in the Au/RB–SiO₂/TiO₂ film was performed by UV irradiation at $\lambda = 365$ nm using a high-pressure Hg lamp. After irradiation for 20 min, the absorption spectrum of the film changed showing a shifted peak at $\lambda_{\text{max}} = 550$ nm and a broad tail at 500–550 nm, which was assigned to surface plasmon bands of generated Au nanoparticles.⁹ As shown in Figure 1, transmission electron microscopy of the UV-irradiated Au/RB–SiO₂/TiO₂ film confirms that spherical particles with an

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(8) A total of 6.7 mmol of Si(OC₂H₅)₄ and 3.3 mmol of Ti(OC₂H₅)₄ was added to 6 mL of a 0.05 M HAuCl₄ ethanol solution, and then 0.018 mmol of rhodamine B was dissolved and 0.2 mL of 2N HCl was dropped into the mixture while stirring. After this sol solution was hydrolyzed overnight at room temperature, the substrate was immersed into the sol solution, and then pulled out at 10 mm/s. For gelation, the coated Au/RB–SiO₂/TiO₂ film was dried at 150 °C for 15 s using a tube heater inside a desiccator. The film thickness measured by a stylus profiler was ~200 nm.

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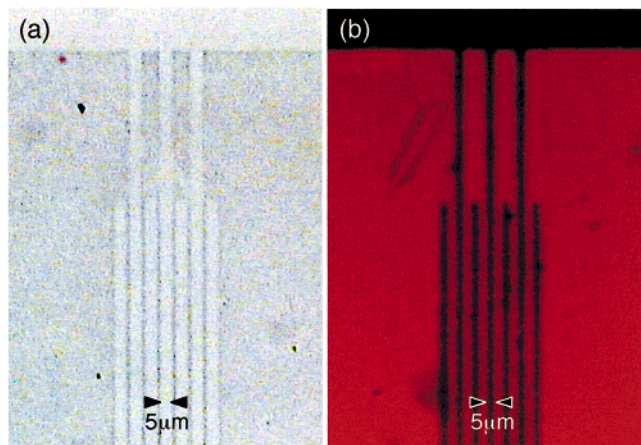


Figure 2. Transmission (a) and fluorescence (b) optical micrographs of Au/RB-SiO₂/TiO₂ film after UV irradiation through a comblike photomask.

average diameter of 7 nm homogeneously disperse in the film and its electron diffraction pattern indicates the (111) and (220) spacings of Au crystals. As previously reported,⁶ a film containing no TiO₂ (i.e., Au/RB-SiO₂) is not suitable for producing spherical Au nanoparticles. Its tightly cross-linked matrix structure, which is supported by the infrared spectrum showing lower O-H and Si-OH stretching peaks, results in networks of large, platelike and needlelike Au clusters due to limited diffusion of Au(III) ions in the film.

The difference in the visible absorption resulting from generation of Au nanoparticles is discriminated in a transmission optical micrograph of photopatterned films as shown in Figure 2a. The region UV-irradiated through a comblike photomask exhibits a higher optical density due to the broad plasmon band of the Au nanoparticles. The change of its optical properties is more clearly imaged in a fluorescence micrograph as shown in Figure 2b. Under excitation at $\lambda = 546$ nm, the UV-irradiated region shows red emission corresponding to fluorescence of doped rhodamine B while the region masked by stripes of 5- μ m gap exhibits no light emission. Rhodamine-doped SiO₂/TiO₂ (RB-SiO₂/TiO₂) films including no Au(III) ions are very emissive,⁵ whereas the present as-coated Au/RB-SiO₂/TiO₂ films before UV irradiation are not fluorescent. The intensity of fluorescence appearing in the Au/RB-SiO₂/TiO₂ film increased with UV irradiation time, but then saturated probably when all Au(III) ions are reduced to Au nanoparticles, as assumed from its photochemical process obeying the first-order rate law.⁶ From these findings, we conclude that the excited rhodamine molecules are quenched by the doped Au(III) ions in the as-coated Au/RB-SiO₂/TiO₂ films, but they are reactivated by photoreduction of the Au(III) ions to Au nanoparticles after UV irradiation.

On the basis of this photoresponsive reaction, any fluorescent pattern can be fabricated in the film using a UV laser. Figure 3 shows a representative fluorescent micrograph, in which each spotlike emission composing the word "KOBE" was formed by a single shot of a Nd:YAG pulse laser onto the Au/RB-SiO₂/TiO₂ film.¹⁰ The short pulse irradiation with duration time of several nanoseconds is enough to produce Au nanoparticles at a selected site in the film. The resolution of this laser

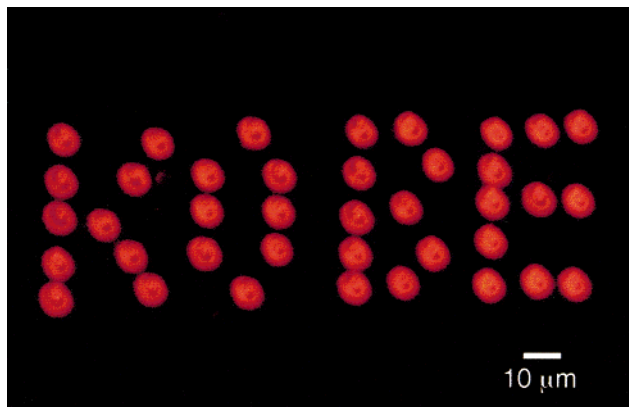


Figure 3. Fluorescence micrograph of laser-patterned Au/RB-SiO₂/TiO₂ film, where each fluorescent dot was formed by a single shot of a Nd:YAG pulse laser.

patterning would be improved up to the diffraction limit of light. Furthermore, the use of near-field scanning optical microscopy (NSOM) would break through the wavelength limit and realize fluorescence patterning at a resolution below several tens of nanometers.¹¹ Using NSOM in a previous study,⁶ we have imaged transmission contrast due the surface plasmon band of Au nanoparticles photogenerated in the Au-SiO₂/TiO₂ film. Introduction of UV light into a fiber probe of NSOM would be possible to locally generate Au nanoparticles and simultaneously detect their fluorescence by the near-field probe light. The resolution of the particle fabrication and optical characterization of the films by NSOM would then be approaching the tenths of the wavelength depending on the fiber probe aperture. Finally, it is interested in elucidating how an individual, single Au nanoparticle has an effect on optical properties of doped dye molecules in the film.

For the purpose of achieving nanofabrication of optical patterns in the sol-gel glassy films based on generation of individual Au nanoparticles, we here tried AFM-assisted local reduction method⁷ using a metal-coated conductive cantilever and an indium-tin oxide (ITO)-coated conductive glass substrate. An as-coated Au/RB-SiO₂/TiO₂ film was mounted on a piezo scanner, and an electric contact was made on one edge of the ITO surface with silver paste. The cantilever was approached to the surface, and local reduction of the Au/RB-SiO₂/TiO₂ film was carried out by scanning the sample in a certain square area under application of a negative bias voltage to the ITO substrate. Figure 4a shows a representative AFM image of the film surface after scanning reduction, where the center square area (20 \times 20 μ m²) of the film was locally reduced at -10 V. Before this procedure, it was confirmed that the surface roughness was less than a few nanometers. After the scanning reduction, in contrast, particlelike protrusions appeared in the scanned

(10) Laser patterning experiments were performed using an inverse fluorescence microscope equipped with a frequency-tripled Q-switched Nd:YAG laser ($\lambda = 355$ nm; pulse energy < 5 mJ; pulse width 4–6 ns). Under transmission observation, a laser spot of 10 μ m in diameter was focused on the specimen surface using a 100 μ m pinhole and a 10 \times objective lens. Each dot pattern was fabricated at a certain position of the specimen film by a singly fired laser shot. After formation of the pattern, its fluorescence pattern was imaged by excitation at $\lambda = 546$ nm using high-pressure Hg lamp.

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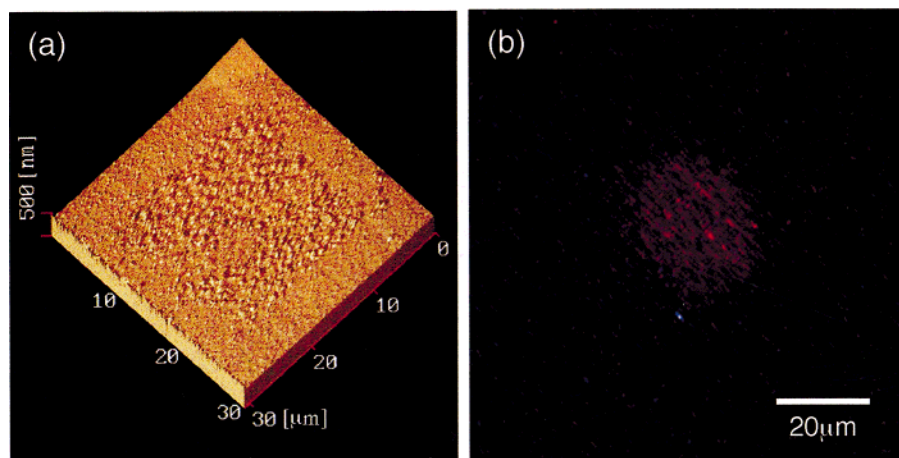


Figure 4. AFM image (a) and fluorescence micrograph (b) of Au/RB-SiO₂/TiO₂ film after AFM-assisted scanning reduction. The center square area (20 × 20 μm²) of the film was reduced by scanning two cycles at rate of 8 Hz.

area. Reduction of Au(III) ions to Au nanoparticles in the film was monitored from cathodic currents in the current–voltage curves at random points of the surface. The population of the surface protrusion due to generation of Au nanoparticles increased with an increase of the scanning rates and cycles, as previously reported.⁷ From its size larger than the photogenerated nanoparticles, each protrusion consists of numbers of particles aggregating and sticking out of the surface. The locally AFM-reduced area was observed by fluorescence microscopy, as shown in Figure 4b. The square area corresponding to the protruded topography in Figure 4a exhibits a weak red emission, whereas the surrounding as-coated region is not emissive. It demonstrates that the fluorescence of rhodamine in the AFM-reduced area can also be reactivated by generation of Au nanoparticles.

The present photoresponsive generation of Au particles enables us to form optically modulated structure in thin glassy films. Moreover, the AFM-assisted pro-

cedure provides us with a controllable fabrication of single nanoparticles, and consequently optoelectronic properties of the films can be modified in a nanometer scale. Such modification of thin glass materials based on generation of nanoparticles would be useful for nanofabrication of electrodes and nonlinear optical and single-electron devices.

Acknowledgment. The authors acknowledge Dr. A. Otomo and Dr. S. Mashiko for their help with fluorescence measurements. This work was supported by a Grant-in-Aid for Scientific Research (no. 10650043) from the Ministry of Education, Science, Sports and Culture, and by the Breakthrough 21 Basic Research Program of Support Center for Advanced Telecommunications Technology Research. This work was also part of a project performed under the Photonics Materials Program by the Venture Business Laboratory of Kobe University.

CM990382B