# High intensity fluorescence of photoactivated silver oxide from composite thin film with periodic array structure

Chih-Min Chuang, Ming-Chung Wu,[a] and Wei-Fang Su[b]
*Department of Materials Science and Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei 106-17, Taiwan, Republic of China*

Kuo-Chung Cheng
*Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 106-08, Taiwan, Republic of China*

Yang-Fang Chen[c]
*Department of Physics, National Taiwan University, Taipei 106-17, Taiwan, Republic of China*

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We have fabricated a composite thin film that exhibits intense photoactivated fluorescence of silver oxide at 522 and 529 nm under the irradiation of a 488 nm laser. This film consists of a silver coated polymeric periodic array on indium tin oxide glass substrate. By adjusting the column diameters and lattice constants of the array to coincide with the excitation wavelength, an order increase in fluorescence intensity was obtained due to the surface plasmon polariton resonance of silver. This composite film has many potential applications in highly efficient optoelectronic devices. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2222252]

Recently photoactivated fluorescence was produced from nonluminescent silver oxide thin films by photoexcitation.[1–3] After local photoactivation of silver oxide films with UV or blue light, the possibility for exciting the fluorescence into the visible spectra represents an attractive prospect for advanced optical data storage.[4,5] Unfortunately, several studies report that metallic interfaces play complex roles in the basic interactions of an electromagnetic field with optically active materials.[6,7] For example, smooth metallic surfaces reduce the radiation from nearby organic dyes through nonradiative energy transfer, while molecules absorbed onto metallic electrodes show several orders of magnitude increase in surface-enhanced Raman signals.[8–10] Furthermore, quantum dots (QDs) located within the surface plasmon polariton (SPP) field of the metal also show a large photoluminescence (PL) enhancement.[11–14] Here, we report an approach to enhance the photoactivated fluorescence of metal oxide from a composite thin film with periodic array. The composite film is made from silver coated polymeric arrays on an indium tin oxide (ITO) coated glass substrate. By adjusting column diameters and lattice constants of the array to coincide with the excitation wavelength, the fluorescence was markedly enhanced. The increase is due to the efficient energy transfer from silver surface plasmon to silver oxide that is formed during the preparation of the composite film.

In this experiment, the polymeric periodic array was made firstly; a 250 nm thin film was made by depositing 2 wt % polymethylmethacrylate (PMMA) (Gredmann, molecular weight of ~996 000) in toluene on an ITO coated glass substrate at 3000 rpm followed by baking at 180 °C for 10 min. The PMMA film was exposed to electron beam (Hitachi, ELS-7500EX) and developed by using mixed solvent of methylisobutylketone and isopropanol (25:75 by volume) for 40 s, then isopropanol for 20 s, and finally, deionized water for 20 s. The resulting patterned polymeric film was coated with a 300 nm thick Ag film using a thermal evaporator (ULVAC) to make the composite film. The film size was typically $50 \times 50\ \mu m^2$.

Figures 1(a)–1(c) illustrate the film fabrication process. Figure 1(d) is a cross-section schematic of a typical finished sample. The fluorescence was generated by irradiating the patterns from the glass side at 488 nm and detected at normal angle. Figures 2(a)–2(e) show the scanning electron microscopy images of triangular arrays seen in a hole in the PMMA with five kinds of column diameters and lattice constants. The respective diameter and lattice constant are as follows: pattern 1, 145 and 200 nm; pattern 2, 170 and 200 nm; pattern 3, 75 and 300 nm; pattern 4, 240 and 300 nm; and pattern 5, 280 and 300 nm.

In our study, the silver oxide was likely formed at the interface between Ag and PMMA from residual oxygen present during the process. A Raman scattering measurement ($\mu$-Raman, Jobin Yvon-Spex, T-64000) was obtained to confirm the existence of $Ag_2O$ as shown in Fig. 3. The two peaks of $Ag_2O$ at 1365 and 1600 $cm^{-1}$ are consistent with previous reports.[15] The electron spectroscopy for chemical analysis (ESCA) study using monochromatized Al $K\alpha$ radiation (VG Scientific ESCALAB 250) also revealed the presence of $Ag_2O$ between the Ag metal and the PMMA.

The optical properties of absorbance and reflectance of the composite film were studied using a spectral microreflectometer (Mission Peaks Optics, MP100-M) equipped with an optical microscope. This instrument measures the interference between incident and reflected light with wavelengths ranging from UV to visible range (250–1000 nm). Unpolarized light was focused on the composite film to a spot size of <30 $\mu$m. For analysis all five patterns were fabricated on the same substrate. The reflected light at normal incidence from the composite film was analyzed and shown Fig. 4. Our results indicate how the SPP resonances of the patterns are

[a]Electronic mail: r91527017@ntu.edu.tw
[b]Author to whom correspondence should be addressed; electronic mail: suwf@ntu.edu.tw
[c]Electronic mail: yfchen@ntu.edu.tw

 

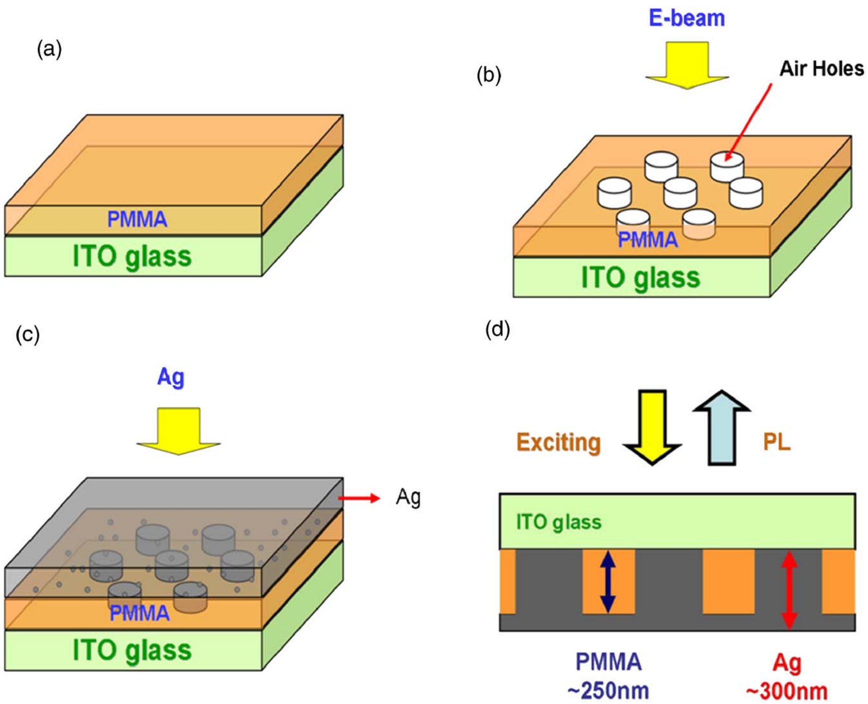


FIG. 1. (Color online) Schematic illustration of the fabrication process of silver coated polymeric array composite thin film on ITO substrate. (a) Spin coat 250 nm thick PMMA, (b) e-beam lithography, (c) deposit 300 nm thick Ag metal, and (d) schematic of a typical finished sample structure. Fluorescence is excited by a 488 nm laser on the glass substrate side and detected at parallel to the incident angle.

tunable by varying the geometrical parameters of the array. When we fixed the constant column height at 250 nm and the triangular lattice constant at 300 nm, the main SPP resonance was redshifted from 470 nm (pattern 3) to 505 nm (pattern 5) as we increased the column diameter. Therefore, the spectral properties of the surface plasmon resonance are critically dependent on the shape, size, and spatial arrangement of the metal.

Photoluminescence (PL) spectra of the composite film were characterized using a microphotoluminometer ($\mu$-PL, Jobin Yvon-Spex, T-64000) equipped with an optical microscope. All the spectra were obtained using an $Ar^+$ laser worked by a triple monochromatic and collected by a liquid nitrogen cooled charge-coupled device (CCD). Polarized light was focused on the film to a spot size of $<10\ \mu$m. Figure 5 shows the photoluminescence intensities of the film. Pattern 4 exhibited the strongest PL intensity, because its photon energy of the surface plasmon polariton resonance was close to that of the excitation and produced the strongest enhancement. When compared with pattern 3, the enhancement capacity of pattern 4 is ~20 times in 522 nm and ~14 times in 529 nm.

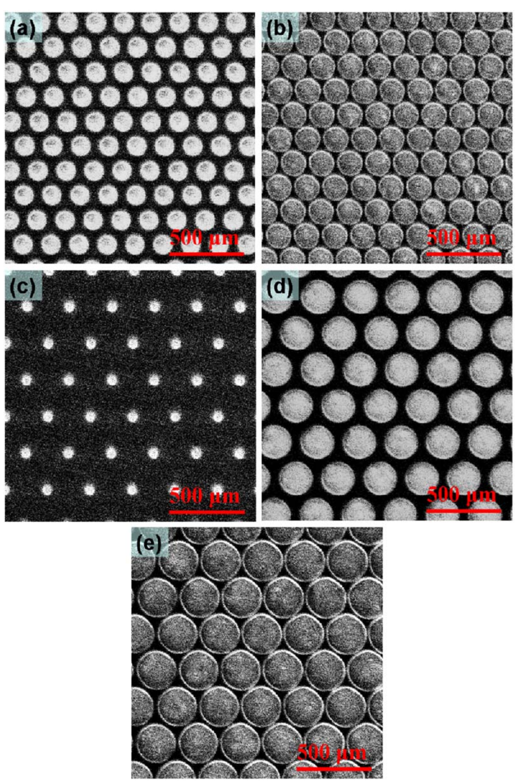


FIG. 2. (Color online) [(a)–(e)] Scanning electron microscopy (SEM) images of triangular array of holes of PMMA with five kinds of column diameters and lattice constants as (a) pattern 1, 145 and 200 nm; (b) pattern 2, 170 and 200 nm; (c) pattern 3, 75 and 300 nm; (d) pattern 4, 240 and 300 nm; and (e) pattern 5, 280 and 300 nm.

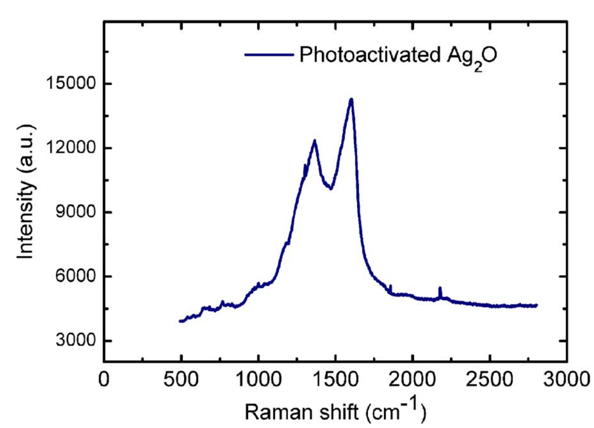


FIG. 3. (Color online) Raman spectrum of photoactived $Ag_2O$ from silver coated polymeric array composite thin film on ITO substrate.

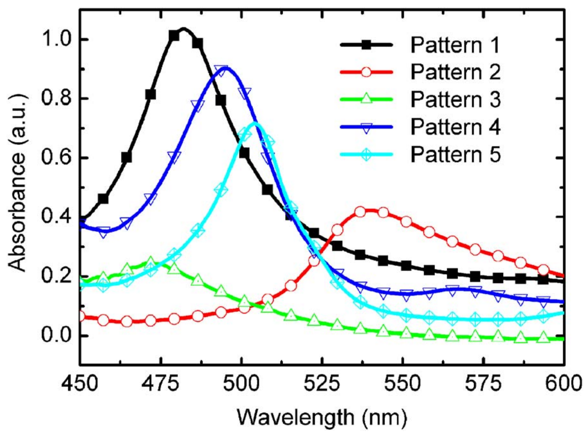


FIG. 4. (Color online) Normal incident absorbance spectra of the composite film with five different column diameters and lattice constants as pattern 1, 145 and 200 nm; pattern 2, 170 and 200 nm; pattern 3, 75 and 300 nm; pattern 4, 240 and 300 nm, and pattern 5, 280 and 300 nm.

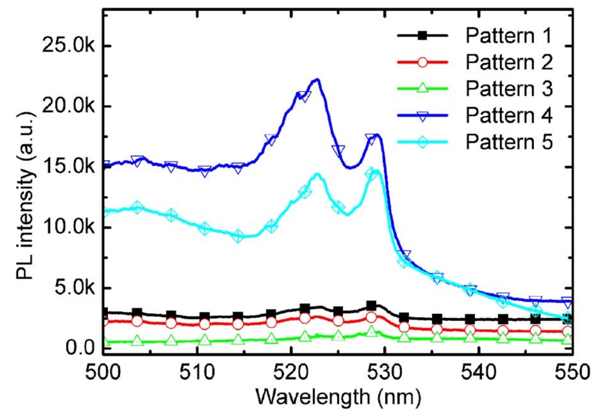


FIG. 5. (Color online) Microphotoluminescence spectra of the composite film with five different column diameters and lattice constants as pattern 1, 145 and 200 nm; pattern 2, 170 and 200 nm; pattern 3, 75 and 300 nm; pattern 4, 240 and 300 nm, and pattern 5, 280 and 300 nm.

In summary, we have fabricated a composite thin film consisting of silver coated polymeric periodic array on ITO substrate. This composite film exhibits intense photoactivated fluorescence of silver oxide at 522 and 529 nm under the irradiation of 488 nm laser. We can tune the surface plasmon polariton resonance by adjusting the lattice constant of the patterned array to coincide with the excitation wavelength. As a result of likely efficient energy transfer from silver surface plasmon to silver oxide, the film exhibited an enhanced fluorescence intensity up to ~20 times at 522 nm and ~14 times at 529 nm. Therefore, our approach provides excellent opportunities for using metal oxide in highly efficient optoelectronic devices.

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