Nanosilver Colloids-Filled Photonic Crystal Arrays
for Photoluminescence Enhancement

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Abstract For the improved surface plasmon-coupled photoluminescence emission, a more accessible fabrication method of a controlled nanosilver pattern array was developed by effectively filling the predefined hole array with nanosilver colloid in a UV-curable resin via direct nanoimprinting. When applied to a glass substrate for light emittance with an oxide spacer layer on top of the nanosilver pattern, hybrid emission enhancements were produced from both the localized surface plasmon resonance-coupled emission enhancement and the guided light extraction from the photonic crystal array. When CdSe/ZnS nanocrystal quantum dots were deposited as an active emitter, a total photoluminescence intensity improvement of 84% was observed. This was attributed to contributions from both the silver nanoparticle filling and the nanoimprinted photonic crystal array.

Keywords Silver nanoparticles · Photonic crystal · Localized surface plasmon resonance (LSPR) · Nanoimprint

Introduction

Silver nanoparticles, which are among the most accessible and optoelectronically functional nanomaterials reported to date, can be applied directly to fabricate nanosilver dot arrays to produce localized surface plasmon resonance (LSPR)-coupled fluorescence enhancement. When a surface plasmon is formed on two-dimensional periodic arrays of nanosilver dots, the SPR energy is confined to each isolated dot, which is known as localized SPR (LSPR). The localized photoelectron energy in neighboring silver dots can be subject to electromagnetic field interactions. These lead to enhanced SPR effects with minimized in-plane propagation losses and provide improved sensitivity and coupled emission efficiency [1–3]. LSPR has therefore attracted considerable recent interest for applications in the fields of sensors and photo- and electroluminescence devices [4, 5].

One of the most active areas of research is the development of a method for fabricating silver nanopattern periodic arrays in a cost-effective, large area processible manner. Various top–down fabrication approaches have been proposed, including nanoimprinting followed by deposition [4] or lift-off [6, 7], and holographic lithography followed by reactive ion etching (RIE) [8]. Alternatively, self-organization methods have attracted increasing research interest due to their large area processing capability and more competitive production costs than the top–down process. It has been reported that randomly distributed silver nanoclusters can be self-transformed from the sputter-coated silver film by the dewetting phenomenon resulting from the increased surface energy at elevated temperatures. This can be achieved on either horizontally leveled substrates [9, 10] or angled substrates with ion beam sputtered surface morphology [11]. These randomly distributed array of nanosilver aggregates have been applied to introduce LSPR coupling effects in light emitting devices [12–15], antireflection [16, 17] and photovoltaics [18]. However, this mechanism involves elevated temperatures to induce restructuring, which imposes...
thermal constraints on the processing, and has issues with controllability of the nanosilver array and size.

As an alternative solution for improving the structural control and process repeatability of silver nanodots, nanosilver colloid can be used to fill the predefined hole array via various self-guiding assembly strategies, such as electrochemical deposition [19], surface chemistry modulation [20], and PMMA layer lift-off [21]. By applying different template pattern designs, various silver pattern array configurations can be reproduced successfully. Hence, with its enhanced patterning reliability, it should be an effective method for circumventing the technical limitations of the continuous metal thin-film self-transformation method described above. The predefined pattern can be generated by nanoimprint technology [19–21] with the template produced via either top–down fabrication or bottom–up self-organization methods. There have been a number of recent reports of self-organized template patterning, such as block copolymers, where an ionized nanosilver solution was introduced into the removed trench [22] and anodized porous alumina [23]. However, this is a less preferred means of controlling pattern configuration than the top–down fabrication method.

![Schematic illustrations of the fabrication process](image)

For the improvement in LSPR-coupled photoluminescence efficiency, the present study present a much simpler process strategy to achieve a controlled array of nanosilver dots by directly filling nanosilver colloids into the nanoimprinted hole array. No processing step was included for the removal of imprint residue. Multiple spin coatings were applied to increase the nanosilver colloid filling rate, followed by optimized thermal annealing and removal of the colloidal residue. In comparison with previous methods, we have achieved the photoluminescence enhancement efficiency of greater than 80% over the reference sample, which should be due to the silver nanoarray-induced localized SPR with a two-dimensional photonic crystal structural effect.

**Experimental**

Figure 1 shows an overview of the process. The first step was the preparation of a silicon master pattern. We used deep ultraviolet (DUV) lithography and subsequent RIE to fabricate the master pattern with a hexagonal array of nanosized holes, which were 300 nm deep and 270 nm in diameter. The silicon master pattern was then replicated.
onto a polytetrafluoroethylene (PTFE) polymer stamp by UV nanoimprinting to obtain the inverse pattern profile (i.e., an array of nanopillars). The patterns on the PTFE polymer stamp were then transferred to a UV-curable resin coating on a glass substrate via UV nanoimprinting. The hole array in the imprinted resin layer was then filled with nanosilver colloid through optimized spin coating. Our process does not include the removal of imprint residue, saving what is typically a demanding critical step in conventional nanoimprint.

A TEM image of the nanosilver colloid (DGP 40LT-15C; ANP Inc., Chungcheongbuk, Korea), 30–50 nm in diameter, is presented in Fig. 2. These were diluted to 3 wt% and then spin-coated on the hydrophilic-treated glass substrate at 3,000 rpm for 30 s, as shown in Fig. 1b. This multicycle programmed spin-coating condition proved to be the most effective in terms of filling efficiency. Thermal annealing at 200°C was used to sinter the silver nanoparticles after the removal of particulate nanosilver residue. Plasma-enhanced chemical vapor deposition (PECVD) of a SiO2 film 60 nm thick was then performed to prevent quenching of the QD photoluminescence on the nanosilver surfaces. As will be discussed in the Results section, the SiO2 layer was used to prevent quenching of the photoluminescence at the silver surfaces. The quantum dots were spin-coated to deposit the active layer, as shown in Fig. 1f. We prepared a colloidal suspension of CdSe/ZnS nanocrystal quantum dots (QDs) [24], with slight modifications, including further dispersion in chloroform. The QDs were approximately 5.5 nm in diameter, and the emission peak was at 614 nm.

Fig. 2 TEM image of as-received silver nanoparticles

Results and Discussion

Figure 3a shows a focused ion beam (FIB) image of the silver nanoarray (obtained using an FEI Helios Nanolab dual beam-FIB) and Fig. 3b shows a field-emission scanning electron microscope (SEM) image of the same silver nanoarray (obtained using an FEI Sirion 200) when the programmed three cycles of spin coating is applied. These images verified that the silver nanoparticles selectively filled the imprinted holes to be aggregated when sintered. From the atomic force microscopy (AFM) measurements (PSIA XE-100) shown in Fig. 4a and b, the silver nanoparticle-filled hole depth was reduced from the as-imprinted depth of 221.3 to 101.7 nm; i.e., the filling factor was approximately 55%. This is a much improved result in comparison with the one by ordinarily applied single step spin coating which produced the filling factor of only 10% through the comparative study I this work. This quantitative analysis also suggested that the selective filling efficiency in the recessed hole area is quite efficient.

Fig. 3 Images of the nanosilver-filled hole arrays: a FIB cross-sectional image, b SEM plane view image
Experimental data indicated that a SiO$_2$ layer of 60-nm thick on top of the silver-filled imprinted hole array provided the greatest performance enhancement. The surface plasmon-coupled emission (SPCE) efficiency depends on the separation between the silver and excited fluorophore [25, 26]. QDs excited photoluminescence quenches at close proximity distance between QDs and nanosilver pattern surface because the carrier transfer to metal occur in QDs before the radiation. However, if the thickness of the oxide layer is greater than the silver surface plasmon penetration depth, the surface plasmons resonance coupling becomes to be less effective because the momentum matching is required with excited photoluminescence additionally to light scattering. Then, the interaction between the silver and the QDs becomes weak for the LSPR-coupled field enhancement effect to be significant. Hence, it is important to optimize the SiO$_2$ layer thickness to achieve the maximum LSPR-coupled light extraction efficiency. The surface plasmon penetration depth ($Z$) can be estimated from the following equation:

$$Z = \frac{\lambda}{2\pi} \sqrt{\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1^2}}$$

where $\lambda$ is the wavelength of the pump light, and $\varepsilon_1$ and $\varepsilon_2$ are the real parts of the dielectric constant of SiO$_2$ and the silver nanoparticles, respectively. By trying several thicknesses of SiO$_2$ (ranging from 20 to 80 nm), we found that the maximum efficiency was 60 nm, in good agreement with Eq. 1 based on the theoretical value of 52.9 nm found in previous reports [26, 27].

The absorption spectrum of the QDs deposited on a glass substrate is shown in Fig. 5a. Figure 5b shows the absorption spectra of two different samples: sample 1 had the photonic crystal array of empty imprinted holes, which were filled with silver in sample 2. Sample 2 showed three absorption peaks at around 400, 525, and 720 nm, whereas sample 1 did not exhibit any peaks. The first peak at 400 nm probably resulted from the size-dependent spectroscopy characteristic of the silver nanoparticles, which indicated the presence of individual silver particles or aggregates. The second peak at 525 nm was attributed to the nanoimprinted photonic crystal array. The third primary peak at 720 nm resulted from the coupled LSPR effect of the nanosilver filled into the photonic crystal hole array.

The photoluminescence (PL) intensities of the processed samples are shown in Fig. 6. A 473-nm DPBL-9050 laser
was used to excite the quantum dot layer at an inclined angle, and the PL was collected from the same side. Figure 4 shows the PL intensity of samples having only QDs on glass (sample 3), QDs deposited on the patterned photonic crystal array (sample 4), and the photonic crystal array of holes filled with silver (sample 5). The inclusion of the photonic crystal array provided a 33% enhancement of the PL intensity (i.e., enhancement of sample 4 over sample 3), and an additional improvement of 38% was observed when the photonic crystal array was filled with silver. This suggests that both the localized SPR and the geometric effect of the photonic crystals had a substantial impact on the PL. The PL intensity enhancement was explained by (1) the enhanced density of the electromagnetic states near-field to the nanosilver dots field in the hole array that couple with the spontaneous emission rate from the active QD layer and (2) the improved extraction efficiency due to the two-dimensional photonic crystal array and the extremely low-refractive index of the gap-filled silver in the visible region. The nanosilver infiltration should sacrifice the transmittance (around 86% compared to the bare glass substrate), thereby compromising the emission efficiency. As a result, the achieved enhancement of the PL intensity implies the localized SPR and the photonic crystal structural effects dominate the reduction in transmittance.

For the emission enhancement in organic light emitting devices, previous papers have achieved around 50% improvement [28, 29] and 56% [30] by the photonic crystal effect only. In these studies, the high-refractive index dielectric oxide filled the photonic crystal structure to increase the out-of-domain light directionality, and for planarization to reduce the current leakage during the electroluminescence operation. As a result, they produced a larger photonic crystal effect than in the present study, 33%, where the oxide fill-deposition of dielectric oxide for planarization was not applied. Therefore, direct comparison of the photonic crystal effect between this and previous studies is meaningless. Rather, it should be noted that the present approach of filling nanoimprinted hole arrays with nanosilver colloids creates LSPR coupling as well as simultaneously providing the planarization effect that otherwise ultimately gives rise to current leakage and efficiency degradation. Consequently, the 84% increase in photoluminescence over the control is considerably more than that achieved in previous studies using only the photonic crystal effect [28–30].

Fig. 5 UV absorption spectra: a QDs on a glass substrate, b as-imprinted (sample 1) and nanosilver-filled hole arrays (sample 2)

Fig. 6 Photoluminescence spectra around the 618-nm peak. Sample 3 had QDs only on a plain glass substrate, sample 4 had QDs deposited on a patterned glass substrate, and sample 5 had QDs deposited on the silver nanoarray with a 60-nm SiO2 spacer layer was used to excite the quantum dot layer at an inclined angle, and the PL was collected from the same side. Figure 4 shows the PL intensity of samples having only QDs on glass (sample 3), QDs deposited on the patterned photonic crystal array (sample 4), and the photonic crystal array of holes filled with silver (sample 5). The inclusion of the photonic crystal array provided a 33% enhancement of the PL intensity (i.e., enhancement of sample 4 over sample 3), and an additional improvement of 38% was observed when the photonic crystal array was filled with silver. This suggests that both the localized SPR and the geometric effect of the photonic crystals had a substantial impact on the PL. The PL intensity enhancement was explained by (1) the enhanced density of the electromagnetic states near-field to the nanosilver dots field in the hole array that couple with the spontaneous emission rate from the active QD layer and (2) the improved extraction efficiency due to the two-dimensional photonic crystal array and the extremely low-refractive index of the gap-filled silver in the visible region. The nanosilver infiltration should sacrifice the transmittance (around 86% compared to the bare glass substrate), thereby compromising the emission efficiency. As a result, the achieved enhancement of the PL intensity implies the localized SPR and the photonic crystal structural effects dominate the reduction in transmittance.

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Conclusion

As a result of inserting nanosilver-filled photonic crystal structure array, the accumulated enhancement in the PL intensity from a layer of QDs, 84%, was achieved due to hybrid effect of silver nanoarray-induced localized SPR and outcoupling of wave-guided light in two-dimensional
nanopattern array. Even in comparison with many previous studies that have focused on developing the process of metal pattern array only for LSPR coupling, the present approach of utilizing colloids provide a unique and competitive method of realizing metal nanopattern array on predefined patterns. Such competitive advantages should be derived in view of the greater process accessibility and repeatability even over conventional nanoimprinting because it is based on highly efficient direct nanoimprint, further without requiring residual layer removal and separate planarization steps.

There are several other opportunities to further increase the enhancement factors, probably by a factor close to or above 2 by improving several of the processing steps, including the silver colloid filling rate, residual colloid removal, and optimization of the nanopillar configuration, all of which are currently under investigation.

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