

Metallic nanoparticle array on GaN by microsphere lithography

Giuseppe Y. Mak*, W. Y. Fu, Edmund Y. Lam, and H. W. Choi

Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong, P.R. China

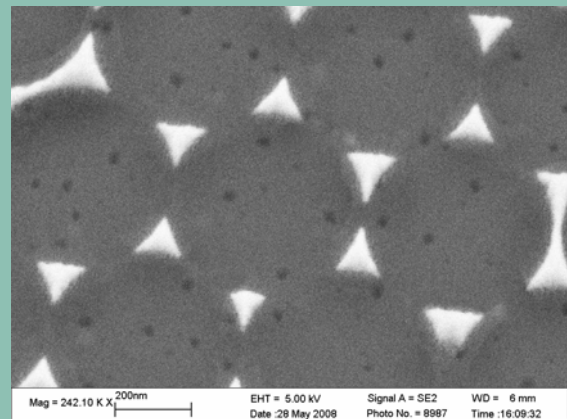
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* Corresponding author: e-mail yhgmak@eee.hku.hk, Phone: +852 97570875, Fax: +852 25170175

The optical characteristics of GaN blue-light (peak wavelength at 440 nm) light-emitting diode (LED) under the effect of localized surface plasmon (LSP) have been studied. Hexagonal arrays of triangular metallic nanoparticles deposited through a self-assembled silica microsphere mask have been fabricated using vertical deposition. By comparing the PL spectra of samples coated with Au, Al and Ag nanoparticles, it is found that Ag nanoparticles offer the most pronounced PL enhancement. The resonance wavelength was determined from optical transmission and verified by theoretical calculations. These results provide a cost-effective solution for improving the efficiency of LEDs.



Close-up view of Au nanoparticles.

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1 Introduction Plasmons are the collective oscillations of free electrons induced by an electromagnetic (EM) wave. When these oscillations are localized at the planar interface between a metal and a dielectric, they are known as surface plasmons (SPs). With recent advances in nanotechnology, SPs can now be confined to the surface of metallic nanoparticles [1]. These are often known as localized surface plasmons (LSPs). The advantage of LSPs over SPs is that LSPs do not require any special geometry for excitation. Another attractive feature of LSPs is that the electric field strength near the nanoparticle surface is significantly enhanced. Such local field enhancement can be exploited to improve the efficiency of light-emitting diodes (LEDs) [2, 3].

Such enhancement, however, is wavelength dependent. There is a resonance wavelength associated with metallic nanoparticles, which is dependent on the size, geometry as

well as the type of metal. In order to produce regular arrays of metallic nanoparticles, nano-patterning techniques including electron beam lithography (EBL) [4] and nanoimprint lithography (NIL) [5] have been used. Self-assembly methods have also been demonstrated. Yeh et al. formed Ag nanostructures through the deposition of a thin layer of Ag followed by thermal annealing [6]. Although the thickness of the Ag thin film can be readily controlled, the dimensions of nanoparticles are random in general. It is still a challenge in obtaining a regular array of nanoparticles over a large region using low-cost self-assembly techniques.

In this study, microsphere lithography was used to fabricate clusters of metallic nanoparticle array over large areas on GaN LED wafers (peak wavelength at 440 nm). The advantage of this technique is that the microspheres can be prepared with precise diameters and arranged in a regular,

close-packed array. This allows for relatively easy control over the dimensions of nanoparticles and the corresponding resonance wavelength. Regular ordering of nanoparticles also helps to provide a strong coupling of the LSPs among neighbouring nanoparticles. Another advantage is that the cost associated with microsphere lithography is significantly lower compared with conventional nanofabrication techniques, including EBL and NIL. Only a small amount of microsphere solution is needed for coating each sample, using basic laboratory apparatus.

2 Experimental details

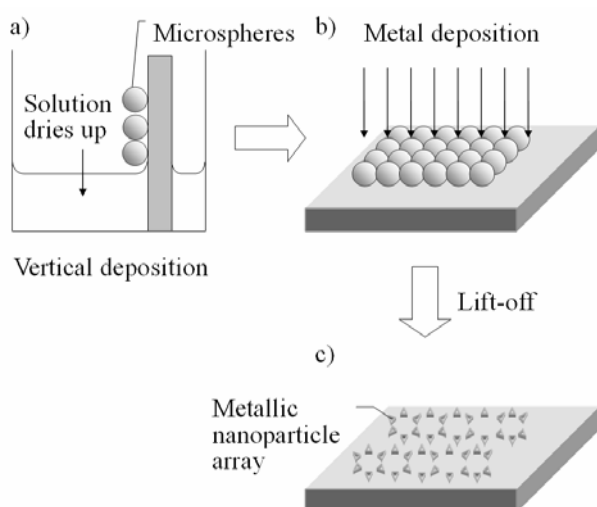


Figure 1 Schematic diagram of the fabrication process of metallic nanoparticles.

Figure 1 illustrates the fabrication process of metallic nanoparticles on a piece of GaN sample. To assemble the microsphere masking layer, the vertical deposition method as depicted in Fig. 1(a) was used [7, 8]. 100 μL of deionized water, together with 100 μL of methanol were mixed in a plastic vial. Silica microsphere colloid was subsequently added into the mixture for dilution. Depending on the microsphere concentrations, the volume of colloid added in each run varied between 10 μL to 20 μL . Finally, in order to lower the surface tension of the resulting suspension, a small amount of sodium dodecyl sulfate (SDS), an anionic surfactant, was added to the suspension. After mixing the colloidal suspension well, the LED sample was vertically dipped into the suspension. The entire assembly was placed into an oven at 40 $^{\circ}\text{C}$ to facilitate evaporation of the liquid. As the suspension dried up, the microspheres slowly adhered to the sample surface, self-assembling into an ordered hexagonal monolayer array, which also acts as a mask for the subsequent metal deposition.

Using an electron beam (e-beam) evaporator, a 100 nm layer of metal was deposited over the surface of the microsphere-coated sample. Since there are interstitial holes

amongst neighbouring spheres, metal atoms were able to penetrate through the voids to form triangular nanostructures. To ensure efficient penetration, a relatively fast deposition rate of about 4.0 $\text{\AA}/\text{s}$ was used. After the deposition, the microspheres were lifted off, leaving the metallic nanoparticles behind. The lift-off process was carried out by immersing the sample in deionized water followed by sonification for about 10 seconds. The resultant nanoparticle arrays are shown in the SEM picture in Fig. 2. It was observed that the dimensions of the nanoparticles are in the range of 105 ± 2 nm.

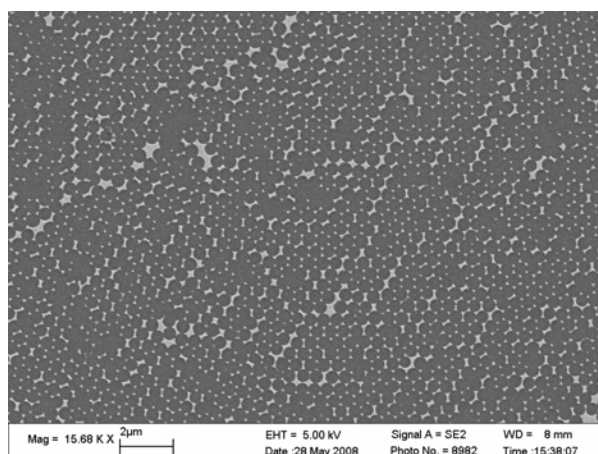


Figure 2 Au nanoparticle array.

3 Experimental results Figure 3 shows the photoluminescence (PL) spectra of metallic-particle-coated GaN LED samples, together with that of the as-grown sample. The Au and Al nanoparticles were fabricated with 500 nm silica microspheres, whereas the Ag nanoparticles were produced by silica microspheres of diameter 192 nm. In this PL experiment, a Spectra Physics diode-pumped solid-state (DPSS) laser at 349 nm was used as the excitation source, while the PL signal was coupled to a Princeton Instrument 150 mm spectrograph with a 1200 L/mm grating and detected with a Princeton Instruments TE-cooled CCD.

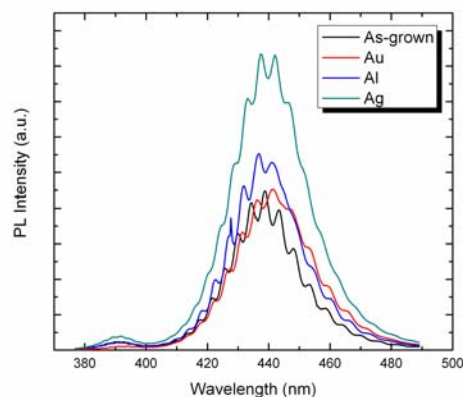


Figure 3 Comparison of PL spectra of as-grown GaN sample (black) and GaN samples with Au (red), Al (blue) and Ag (green) nanoparticles.

The intensities of the PL spectra for the samples with nanoparticles are higher than that of the as-grown sample. The largest PL enhancement is produced by the Ag nanoparticles. Intuitively, the resonance frequency of the Ag nanoparticles is most in sync with the MQW emission wavelength, which is 440 nm. To verify this, the optical transmission spectrum was obtained from the Ag-coated sample. A broadband tungsten-halogen lamp (VIS to NIR) was used to illuminate the samples via a fibre, and the transmitted signal was collected by another fibre and channelled to a spectrometer. Fig. 4 shows their transmission spectra. Indeed, a peak was observed in the region of 480 nm, correlating well with the PL data.

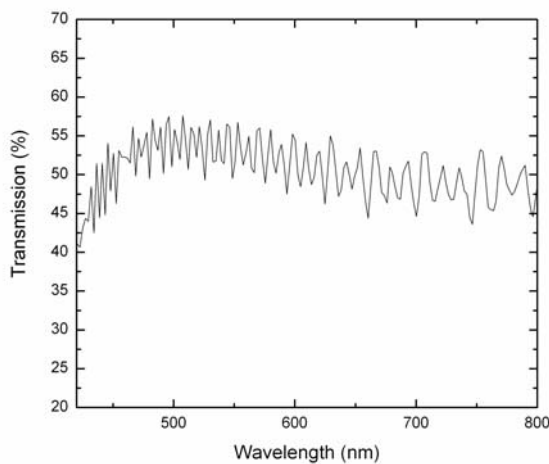


Figure 4 Transmission spectrum of GaN sample with Ag nanoparticles.

4 Theoretical calculations We attempt to verify the experimental results from theoretical calculations, beginning with the extinction coefficient of nanoparticles. The extinction coefficient (k_{ex}) for a particular substance is a measure of how well it scatters and absorbs electromagnetic radiation. For small and spherical particles, it is given by [9]:

$$k_{ex} = \frac{18\pi V \epsilon_h^{3/2}}{\lambda} \frac{\epsilon_2}{[\epsilon_1 + 2\epsilon_h]^2 + \epsilon_2^2}, \quad (1)$$

where V is the particle volume, λ is the wavelength of incident light, ϵ_h is the dielectric constant of the surrounding medium; ϵ_1 and ϵ_2 represent the real and the imaginary parts of the dielectric constant ϵ_m of the metal ($\epsilon_m = \epsilon_1 + i\epsilon_2$), which is a function of optical frequency ω . If ϵ_2 is small or weakly dependent on ω , then k_{ex} attains its maximum when $\epsilon_1 = -2\epsilon_h$. Thus, light absorption due to surface plasmon resonance is produced at the optical frequency when the resonance condition $\epsilon_1 = -2\epsilon_h$ is fulfilled.

In the case of noble metals such as Au and Ag, there are two contributions to the dielectric constant of the

metal: One is from the interband transition from the inner orbitals to the conduction band. The other is from the free electrons. The latter contribution, described by the Drude model [10], is given by:

$$\epsilon_m(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}, \quad (2)$$

where ω_p is the plasma frequency of the bulk metal, i is the imaginary unit, and γ is the damping constant that is inversely proportional to the nanoparticle radius r .

By applying the resonance condition $\epsilon_1 = -2\epsilon_h$ to Eq. (2), we can obtain:

$$\begin{aligned} \text{Re}\{\epsilon_m(\omega_r)\} &= -2\epsilon_h \\ 1 - \frac{\omega_p^2}{\omega_r^2 + \gamma^2} &= -2\epsilon_h \\ \gamma &= \frac{K}{r} = \sqrt{\frac{\omega_p^2}{1 + 2\epsilon_h} - \omega_r^2} \end{aligned} \quad (3)$$

where ω_r is the resonance optical frequency, and K is a proportionality constant to be determined empirically. For the 105 ± 2 nm Ag nanoparticles fabricated in our experiments, the resonance wavelength can be determined to be in the range of 448–500 nm, where K is found by using the absorption spectral data for Au nanoparticles in [11], and Ag is assumed to have the same value of K . The calculated value correlates well with the measured PL and optical transmission spectra. The slight discrepancy may be attributed to the dimensional non-uniformity of the metallic nanoparticles.

5 Conclusions Arrays of Au, Al and Ag nanoparticles were deposited onto GaN LED samples using microsphere lithography via the vertical deposition method. Photoluminescence data reveal an enhancement of emission intensity, the most significant of which comes from the Ag nanoparticles. The resonance wavelength of the Ag nanoparticle was determined from the transmission spectrum to be ~ 480 nm. From theoretical calculations, the resonance wavelength was predicted to be 448–500 nm, correlating well with the experimental result.

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