Nanosphere Lithography for Nitride Semiconductors

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1. Introduction

Nanolithography has been widely studied in recent years, considering its wide-ranging applications in electronics and photonics. In the ideal case, lithography using short-wavelength electromagnetic wave through a pre-defined mask is probably the most desirable solution. However, as technology progresses further, traditional photolithography is becoming exceedingly complex and incurring higher cost associated with light source as the wavelength of light goes shorter. Therefore, other nanolithography methods become strong competitors excelling with lower equipment cost and simpler fabrication procedures. In particular, nanosphere lithography as a self-assembly bottom-up approach for producing periodic array of spherical particles is simple and inexpensive as compared to other lithographic methods.

Originally developed by Deckman et al. for defining a large area lithographic mask (Deckman & Dunsmuir, 1982), nanosphere lithography was further optimized by Hulteen et al. for applications involving surface-enhanced Raman spectroscopy (Haynes & Van Duyne, 2003; Hulteen & VanDuyne, 1995). Nanospheres that are used in lithography are commercially available in solution form, and through a simple coating procedure with optimized conditions, ordered hexagonal array of nanospheres can be naturally assembled as the nano-particles achieve equilibrium in an initially disordered system, i.e., a solution of nanospheres. Although only hexagonal array can be formed by this lithographic technique, the hexagonal pattern is useful for a range of applications, for instance, in nanophotonics where ordered hexagonal patterns can be used for the fabrication of photonic crystal (Han et al., 2005; Su et al., 2008) and also in plasmonics (Jensen et al., 2000; Malinsky et al., 2001; Stewart et al., 2006). With rivals like nanoimprint lithography (Byeon et al., 2007; Kim et al., 2007) and electron beam (e-beam) lithography (Berrier et al., 2004; David et al., 2006; Noda et al., 2007), the low cost and high through-put (albeit being less precise) nature of nanosphere lithography is especially suited for photonic applications.

Gallium nitride (GaN) semiconductors and devices thus serve well as a platform for nanosphere lithography. In recent years, GaN has emerged as the most successful semiconductor material in optoelectronics, delivering a range of commercialized products which has since revolutionized our lives, including violet laser diodes for ultra-high capacity optical storage and white light LEDs for solid-state lighting (Humphreys, 2008; Schubert & Kim, 2005). While GaN technology is becoming mature, there is still plenty of
room for further development. For instance, one major issue with GaN devices is the limited efficiency of light extraction. To tackle this problem, texturing of the surface in a regular manner has been adopted at the micrometer and nanometer scales (David et al., 2008; Han et al., 2006; Ng et al., 2008; Noda & Fujita, 2009). Therefore in this chapter, we will demonstrate the potential applications of nanosphere lithography including photonic crystals and surface plasmons. Several topics will be outlined in this chapter, including the various techniques of coating nanosphere arrays, together with a detailed analysis of their structural, morphological and optical characteristics. The possibilities of applying nanosphere lithography into practical GaN devices and beyond will be discussed.

2. Process of self-assembled nanosphere lithography

There have been intense efforts targeted at the formation of nanosphere into regular patterns. Although lots of variants of the process have since been developed, including the vertical deposition method (Gil et al., 2007; Jang et al., 1999; Ye et al., 2001; Zhou & Zhao, 2004), spin coating (Mihi et al., 2006; Ogi et al., 2007) and even merely dipping (Choi et al., 2009; Im et al., 2003), all these fundamentally rely on manipulation of the forces applied amongst nanospheres. Thus, most of these methods require precise control of ambient conditions such as temperature and pressure, together with the viscosity and evaporation rate of the fluid. These conditions could be varied in order to control the number of layers and degree of order of the assembled pattern, as well as the extent of coverage across the sample. It was found that the vertical deposition method yields a better quality of ordered nanosphere array (Wong et al., 2003) compared with others, therefore in this chapter we will concentrate on its discussion.

2.1 Vertical deposition

Known for its good orderliness and simplicity, the vertical deposition method has been adopted in many research studies employing nanosphere lithography (Chiappini et al., 2007; Kuai et al., 2004). A common and general setup for vertical deposition consist of an apparatus for maintaining a constant ambient temperature such as a dry-bath, or a basic oven, that is capable of providing a stable stream of air or gas, and a vial for holding the nanosphere in solution form with the sample to be coating lying upon the sidewall of the vial. A schematic diagram of a typical setup is illustrated in Figure 1. The solution typically consist of nanospheres suspended, and a water-alcohol mixture that controls the evaporation rate (Shimmin et al., 2006). Surfactants are sometimes used together to reduce the viscosity. As the nanosphere solution dries up, the nanosphere will be self-assembled into hexagonal close-packed pattern, adhering to the sample. Unfortunately, cracks often exist in the resultant nanosphere coating, regardless of the degree of order. The reason for the persistent formation of cracks is identified to be caused by the movement of “water line” as the water level changes during evaporation of solution. Also, since the concentration increases as the solution dries up, the thickness of the nanosphere coating, or the number of nanosphere layers, will usually be thicker towards the lower end of the sample than that at the upper end.

The problem of uneven layer distribution along the sample can be resolved by a modified vertical deposition method, namely the flow-controlled vertical deposition method. Instead of waiting for the solution to be evaporated, this modified method proactively scans the
water level along the entire sample by adjusting the relative position between sample and vial, while keeping the concentration changes to a minimum. This allows a much shorter processing time which also minimize possible sedimentation of nanospheres that will aggravate the unevenness during the deposition process. Thus, this method is ideal for maintaining a more even thickness of coating across the sample. For addressing the cracking problem, there have been attempts to use a chemical method in conjunction with vertical deposition method. L. Wang et al. have reported crack-free colloidal crystal by means of hydrolysis of a silica precursor during vertical deposition (Wang & Zhao, 2007). Silica species formed acts like a glue among nanospheres to avoid crack formation during evaporation. Other crack-free approach includes self-assembly at air/ water/ air interface which will form a free standing nanosphere films, although this is not an approach suitable for lithography.

3. Characterization of nanosphere coating

3.1 Topography of nanosphere coating

After deposition, a hexagonal close-packed nanosphere pattern can be observed under scanning electron microscope (SEM), as shown in Figure 2, if the coating is successful. Unless using very specific approaches to eliminate cracks as suggested in the last section, different kinds of defects, including but not limited to cracks and point defects, will be formed. As mentioned in the previous section, cracks formed through vertical deposition are most likely due to the movement of “water line” across the sample. However, there are also many other causes that could lead to a defect. For example, the vast amount of nanosphere that a solution contains cannot possibly be of identical dimensions. A single apparently larger or smaller nanosphere amongst many in an array is enough to give rise to point defects. Apart from dimensional non-uniformity, irregular nanosphere may also exist, that is, some of the nanosphere may not be perfectly spherical. Point defects will also be resulted from the protruding portions of irregular nanospheres. Due to the limitations in nanosphere synthesis and deposition, defects among nanosphere arrays are inevitable. Nevertheless,
with a low defect density, nanosphere lithography is adequate for many applications unless extremely high accuracy is required.

Fig. 2. SEM image of a monolayer of nanospheres, with occasional defects caused by non-uniformity in dimension of nanospheres.

One distinct advantage of nanosphere lithography is that nanospheres that self-assemble into a hexagonal close-packed pattern can produce features of nano- or even sub-nano scales, provided that the required dimensions of nanosphere are available. The voids between nanospheres are at least one order of magnitude smaller than the diameter of nanosphere itself; that is, for a 10 nm-diameter nanosphere, the void can easily be smaller than 1 nm.

Fig. 3. Transmission spectrum of hexagonal close-packed 192-nm-diameter nanosphere multi-layer array coated on a GaN wafer measured at 2 different angles with reference to an as-grown GaN sample. (with permission for reproduction from Institute of Physics Publishing)
3.2 Optical properties of nanosphere coating
The optical properties of a nanosphere coating are pretty obvious by observing it at different angles under broadband illumination – different colors of light are reflected at different angles, acting like a grating. In fact, the nanosphere coating is a 2-dimensional photonic crystal itself. In the frequency domain there is in fact a gap in the transmission spectrum, an example of which is illustrated in Figure 3. The existence of the gap indicates that certain wavelength of light is being reflected or scattered away. The spectral position of the gap varies according to the material’s refractive index, the size of nanosphere, orientation of coating and the number of layers. Typically the gap exists at a position at 2-3 times the diameter of nanosphere spectrally.

4. Nanosphere coating applications
4.1 Nanopillar photonic crystal LED
Besides using the nanospheres themselves directly, a patterned nanosphere layer can act as a good medium for further processing. Amongst different kinds of materials, silica-made nanosphere is especially suitable for etching process, since the good etch resistivity of silica renders the patterned monolayer of nanosphere a naturally good hard mask.
One of the most popular ‘secondary’ nanostructures derived from nanosphere lithography is the nanopillar array (Cheung et al., 2006; Li et al., 2007; Ng et al., 2008). After coating a monolayer of nanospheres onto a sample, the circular hexagonal close-packed pattern can be easily transferred to the sample by a subsequent dry etch. Figure 4 shows an example of the resultant nanopillar structure. An array of nanopillar is an effective approach to improve light extraction when fabricated on a GaN LED. Due to the high refractive index of GaN, LEDs without any light extraction strategy adopted will suffer from low light extraction efficiency, as a large fraction of emitted light is trapped within the GaN epilayer, propagating as guiding modes and subsequently re-absorbed. A nanopillar array integrated into the surface of an LEDs will have a surface-texturing effect. In one way, the nanopillars increase the total surface area of LED, thus increasing the probability for light to escape, and thereby decreasing photon re-absorption in GaN. At the same time, they reduce the effective refractive index such that total internal reflection is suppressed to a certain extent.

Fig. 4. SEM Image of a nanopillar array with diameter of 500 nm fabricated on GaN wafer.
In the research studies by W. N. Ng et al., a monolayer of silica nanospheres of 500 nm diameter, coated by spin coating method, served as a lithographic mask. Inductively coupled plasma (ICP) etching using a gas chemistry of Cl\(_2\) and BCl\(_3\) at flow rates of 20 sccm and 10 sccm respectively was carried out for a duration of 120 s. The silica nanosphere residual was removed by sonification to expose the nanopillar array beneath. The resulting nanopillar sample contributed to a two-fold enhancement of photoluminescence intensity in the normal direction. In their later studies, the authors successfully demonstrated light extraction enhancement from an electroluminescent LED with an integrated nano-pillar array. Significant improvement to the optical output was achieved compared to an unpatterned LED, as shown in the plot of \(L-I\) characteristics in Figure 5.

![Fig. 5. \(L-I\) characteristics of a nanopillar photonic crystal LED as compared with an unpatterned LED. (with permission for reproduction from Institute of Physics Publishing)](image)

To further extend the applications of nanospheres to GaN materials, an isotropic etching model with a monolayer of nanosphere has been reported by W. Y. Fu et al. Hemiellipsoid structures were been fabricated, as illustrated in Figure 6, using nanosphere coating mask with a modified recipe from the study in the previous paragraph, using a gas chemistry comprising 12 sccm of Cl\(_2\) and 9 sccm for CHF\(_3\). Compared to the etch recipe adopted by W. N. Ng et al., this modified recipe makes use of CHF\(_3\) that is particularly suited for etching of silica; as a result the dimensions of silica nanosphere in the array will slowly shrink as etching progresses. The etch rates of GaN and SiO\(_2\) can be controlled independently, allowing more freedom in the control of desired shape of the resultant arrays. This is useful for the design of different photonic dispersion characteristics that can be exhibited by photonic crystal structures. For example, a photonic bandgap based on an array of hemiellipsoid can be designed for light extraction purposes. From the angular PL emission plot as shown in Figure 7 (Fu et al., 2009), an obvious overall enhancement to the PL intensity is observed. By comparing the integrated PL intensity between an as-grown with the hemiellipsoid array an enhancement factor of over 3 times can be deduced.
4.2 Fluorescent nanospheres coated white LED

The white-light LED has become a widely available commercial product with numerous applications including solid state lighting, liquid crystal display (LCD) backlighting and signaling etc. There are two common approaches to achieve white light emission from an LED, either by spectral down conversion using YAG phosphor-coated blue LEDs (Pan et al., 2004; Schubert & Kim, 2005) or the mixing of discrete LEDs with the primary colors red, green and blue (Hui et al., 2009; Humphreys, 2008; Muthu et al., 2002; Steigerwald et al., 2002). Due to the technical difficulties of color mixing with three discrete LEDs without bulky optics, phosphor-coated white LED tends to be more widely adopted despite the large Stokes shift losses. Under this circumstance, fluorescent nanospheres coated white LED has been suggested as an alternative with some advantage over phosphor-coated white LED. A schematic diagram of such design of LED device is shown in Figure 8.
Nanospheres with fluorescent dyes incorporated internally have been demonstrated to act as an alternative to the conventional approach of coating phosphor on blue LED for white light emission. Commercially available in dimensions ranging from tens of nanometers to micrometers, polystyrene fluorescent-dyed nanospheres have been widely used in the chemical and biological areas (Bhalgat et al., 1998; Matsuya et al., 2003; Seo & Lee, 2004). The swelling and unswelling of the polymeric spheres during preparation ensures that the pores are able to entrap the fluorescent dyes physically, resulting in an enhanced dye photostability, with predicted lifetimes exceeding 36 months. Simply by adjusting the ratio between excited light emission from green- and red-colored nanospheres with respect to the blue light emission intensity from InGaN LED, white light emission can be achieved and the

![Fig. 8. Schematic diagram of a fluorescent nanosphere coated LED device. (with permission for reproduction from Institute of Physics Publishing)](image)

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![Fig. 9. (a) PL spectrum of the green microspheres, (b) optical image of fluorescence emission from green microspheres (with blue and red light filtered off). (c) PL spectrum of the mixture of green and red microspheres, and (d) optical image of fluorescence emission from green, yellow and red microspheres (with blue light filtered off).](image)

**Fig. 9.** (a) PL spectrum of the green microspheres, (b) optical image of fluorescence emission from green microspheres (with blue and red light filtered off). (c) PL spectrum of the mixture of green and red microspheres, and (d) optical image of fluorescence emission from green, yellow and red microspheres (with blue light filtered off). (with permission for reproduction from Institute of Physics Publishing)
color temperature can be easily adjusted, although the color conversion is still subjected to Stokes shift loss. However, the hexagonal close-packed patterned and spherical-shaped nature of nanospheres contributes to improved mixing of color both spatially and angularly, with a slightly better advantage on excitation of emission of other colors compared with conventional phosphors.

Figure 9 shows PL spectra and optical images of fluorescent nanosphere on GaN LEDs with blue emission as in the studies by K.N. Hui et al. (Hui et al., 2008). With different colors of fluorescent nanospheres, including green, yellow and red, emission spectrum of LEDs can be tuned to different shades of white light.

4.3 Surface plasmon

Induced by electromagnetic wave, when collective oscillations of free electrons, i.e., plasmons, are confined to surfaces and couples strongly with light, they are known as surface plasmon. This usually occurs at the interface between a metal (of negative dielectric constant) and a dielectric material (of positive dielectric constant). These surface plasmons are conducive to an important phenomenon, the localized surface plasmon resonance, which occurs when metallic nanoparticle is excited by light when in contact with dielectric material. This phenomenon is exhibited by a strong peak in the extinction spectrum. With GaN devices, localized surface plasmon resonance has great potential for improving light extraction efficiency of LEDs since it can significantly enhance the electric field strength near the surface of nanoparticle (Ross & Lee, 2008; Sundaramurthy et al., 2005).

Typically, when light emitted from multi-quantum wells of LED interacts with a metallic layer, a surface plasmon mode will be formed. This surface plasmon mode increases the density of states and spontaneous emission rate (Gianordoli et al., 2000; Hecker et al., 1999; Vuckovic et al., 2000), and thus helps to improve coupling from the multi-quantum wells (Neogi et al., 2002). There have been reports that successfully demonstrated enhancement in InGaN quantum well emission by means of enhancement of Purcell factor with surface plasmons making use of a metal film on top of an LED (Okamoto et al., 2004). However, light coupled to surface plasmon modes is trapped at the metal/dielectric interface despite the enhancement of internal quantum efficiency. To deal with this problem, localized surface plasmon resonance had been investigated, whereby a periodic metallic array, or plasmonic crystal, is adopted instead of a flat metal film to assist with extracting light from the surface plasmon polaritons (Cesario et al., 2007).

Since the resonance wavelength depends strongly on the size and shape of metallic nanoparticles, and that resonance at visible range often requires a feature size of less than 100 nm, nanosphere lithography is an effective method for the patterning of metallic nanoparticles, particularly because the requirement on orderliness is lower. By controlling the dimensions of the nanospheres, the dimensions of the resultant metallic nanostructures can be adjusted, thereby affecting the spectral position of resonance. With monolayer of nanosphere serving as a mask, deposition of desired metal, typically Ag, Al or Au, can be carried out to form an inverted metallic circular array (Jensen, Malinsky, Haynes & Van Duyne, 2000; Malinsky, Kelly, Schatz & Van Duyne, 2001), providing the metal can penetrate the void regions of the nanosphere array. Figure 10 shows an SEM image illustrating the resultant metallic nanoparticles after removing the nanosphere residual. According to the PL spectra of InGaN/GaN MQWs coated with an array of metallic nanoparticles using this nanosphere lithography method as reported by G.Y. Mak et al., it
was demonstrated that the metallic nanoparticles are indeed able to improve light extraction without changes of emission characteristics as demonstrated by Figure 11 (Mak et al., 2009).

Fig. 10. SEM image showing Au nanoparticles formed by deposition through a nanosphere mask. (with permission for reproduction from WILEY-VCH Verlag GmbH & Co.)

Fig. 11. PL spectra of LED with deposited nanoparticles of Au, Al and Ag. (with permission for reproduction from WILEY-VCH Verlag GmbH & Co.)

5. Summary

An inexpensive and simple approach as compared to other nanolithography methods, nanosphere lithography is able to play an important role in defining periodic-arrayed
lithographic mask for photonic applications. Although more optimization works needs to be done on thickness control, the availability of crack-free deposition method made it feasible for mass production with high yield. A few photonic applications have been addressed in this chapter. Fluorescent nanospheres provide an alternative way to produce white LED for solid state lighting with improved color mixing. Nanopillars derived from a monolayer of hexagonal close-packed nanospheres helps to texturize the surface of an LED in order to improve light extraction efficiency. Last but not least, localized surface plasmon resonance not only can improve light extraction, but also has potential sub-wavelength applications including optical energy transport and near field scanning optical microscopy.

6. References


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Lithography, the fundamental fabrication process of semiconductor devices, plays a critical role in micro- and nano-fabrications and the revolution in high density integrated circuits. This book is the result of inspirations and contributions from many researchers worldwide. Although the inclusion of the book chapters may not be a complete representation of all lithographic arts, it does represent a good collection of contributions in this field. We hope readers will enjoy reading the book as much as we have enjoyed bringing it together. We would like to thank all contributors and authors of this book.

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