IMPROVEMENT OF LED LIGHT EXTRACTION EFFICIENCY BY SILICA MICRO REPEATING STRUCTURE GROWTH

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IMPROVEMENT OF LED LIGHT EXTRACTION EFFICIENCY BY SILICA MICRO REPEATING STRUCTURE GROWTH

by

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LIST OF ABBREVIATIONS

2D	2 dimensional
Au	Gold
C	Carbon
CTAB	Cetyltrimethylammonium bromide
CRI	Colour rendering index
CCT	Correlated colour temperature
EDX	Energy dispersive x-ray
FTIR	Fourier transform infrared
IC	Integrated circuit
ITO	Indium tin oxide
IUPAC	International union of pure and applied chemistry
InP	Indium phosphide
InGaN	Indium gallium nitride
LEE	Light extraction efficiency
LED	Light emitting diode
lx	Lumens
M	Molarity
MRS	Micro repeating structure
MTF	Mesoporous thin film
MSTF	Mesoporous silica thin film

mm	Millimeter
nm	Nanometer
n	Refractive index
Na	Sodium
NaOH	Sodium hydroxide
OLED	Organic light emitting diode
RI	Refractive index
SiO_2	Silicon dioxide
SEM	Scanning electron microscope
SMRSG	Silica micro repeating structure growth
STFG	Silica thin film growth
TIR	Total internal reflection
TEOS	Tetraethyl orthosilicate
UV/Vis	Ultraviolet and visible light
Vs	Versus
XRD	X-ray diffraction

PENAMBAHBAIKAN KECEKAPAN PENGEKSTRAKAN CAHAYA LED DENGAN PERTUMBUHAN STRUKTUR MIKRO SILIKA BERULANG

ABSTRAK

Pengekstrakan kecekapan cahaya (LEE) adalah faktor yang sangat penting untuk penambahbaikan kecekapan diod pemancar cahaya (LED). Sehingga kini, kebanyakan kaedah penambahbaikan LEE melibatkan proses fabrikasi yang kompleks sama ada pada cip LED yang telah siap atau semasa pemprosesan LED. Dalam kajian ini, struktur berulang silika (MRS) dihasilkan menggunakan pertumbuhan struktur silika berulang (SMRSG) untuk meningkatkan kecekapan LEE. Berbeza dengan kaedah fabrikasi kompleks yang lain, SMRSG dilakukan melalui kaedah pertumbuhan larutan Stöber. Penyediaan larutan ini adalah mudah dengan hanya menggunakan tetraetil orthosilikat (TEOS), surfaktan dan pelarut. Hasil keputusan LEE pada LED dicirikan melalui spektrofotometer selepas SMRSG. Ianya menunjukkan purata peningkatan kecerahan sebanyak 0.77% pada permukaan LED licin. Satu kajian yang berasingan dimana proses pembersihan selepas fabrikasi LED menggunakan Sodium hydroxide (NaOH) juga dijalankan. Pembersihan singkat (30 saat) menggunakan NaOH ini adalah untuk membersihkan permukaan LED daripada bahan tercemar. Satu pemenuan baru dicapai dimana kecerahan LED telah meningkat sebanyak 5.05% dan 1.11% untuk LED permukaan kasar dan LED permukaana licin. Ini menunjukkan bahawa kehadiran SMRSG yang merupakan MRS dan pembersihan pada permukaan LED dapat mengubahkan LEE.

IMPROVEMENT OF LED LIGHT EXTRACTION EFFICIENCY BY SILICA MICRO REPEATING STRUCTURE GROWTH

ABSTRACT

Light extraction efficiency (LEE) is an important factor for Light Emitting Diodes (LED). As of today, most LEE improvement methods involve complex fabrication either on the finished LED chip or during the LED processing itself. In this study, micro repeating structures (MRS) are constructed using silica micro repeating structure growth (SMRSG) to improve LEE. In contrast to other complex fabrication methods, the SMRSG was done through a Stöber solution growth method. The solution preparation was relatively simple, using tetraethyl orthosilicate (TEOS), surfactant and solvents. The LEE result of the LED after SMRSG was characterized through using a spectrophotometer. It showed an average of 0.77% increment in brightness for unroughened LED. A separate study on using sodium hydroxide (NaOH) for post LED fabrication cleaning was also conducted. A new discovery was achieved where the brightness of the LED was increased by 5.05% and 1.11% for roughened and unroughened LED respectively. The short cleaning time (30 seconds) with NaOH was to clean the LED surface from contaminants. This suggests that the presence of the SMRSG which is an MRS and cleaning of the LED surface was able to change the LEE of the LED.

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CHAPTER ONE
INTRODUCTION

1.1 Research Background

There are many opportunities or potential for LED technology to grow and be explored. Improving an LED performance covers a wide range of topics such as improving the phosphor converter particle for better correlated color temperature, reducing chip size for better manufacturing density, change of package moulding material to prevent yellowing, thermal junction, temperature management for better lifetime of LED, increasing LED LEE and many more. The most widely studied topic on LED as of today is on increasing the LEE of LED. Improving LEE can reduce the wastage of energy to light up an LED to the required light output. Energy losses could be caused by compensation of light losses through increasing forward current to generate more photons. The LEE of LED is rather low due to light losses resulted from total internal reflection (TIR). The external quantum efficiency (EQE) of LED is only at 20% as of today (Möller and Forrest, 2002, Choi et al., 2012, L.Petti et al., 2013). This small percentage of EQE opens up ample of opportunity to improve LED LEE.

As a solution, there are many researchers out there who tried improving LEE of LED through growing a MRS either within the epitaxy structure or on top of the LED surface. The researchers tried growing periodical structures reported in different shapes, dimensions, materials used and methods of fabrication respectively. However, a similarity was observed in their fabrication where MRS were being achieved and reported in their own terminologies. Examples of such MRS fabrications are the use of ordered microlenses (Möller and Forrest, 2002), 2D photonic crystal (Yang and Cunningham, 2011), and Bragg's gratings (Ziebarth et al., 2004) to improve LEE whereas some uses abrupt patterns such as surface roughening and misfit repeating structures. Through this, a singular idea was obtained which any structure that is fabricated on an LED which is in the micron range and also repeating in periodic structure will be able to improve LEE of an LED.

Through the understanding of such MRS's impact on LEE, methods of growing MRS were reviewed through and found to be ample. Methods such as laser beam patterning to blast off material on substrate leaving base material and hole array (Teng et al., 2012, Gan et al., 2015), photolithography followed by wet etching for selective material area removal (Möller and Forrest, 2002) and radio frequency (RF) sputtering (Peng et al., 2004), focused ion beam lift off and many more (L.Petti et al., 2013). Such fabrication methods require expensive and complicated equipment setup in order to carry out studies on LED. A facile method to produce MRS was introduced with key advantages of being easily made and not involving complicated equipment. The method of producing MRS is through surfactant template SMRSG.

SMRSG through surfactant template is rather simple where a Stöber solution was prepared consisting of surfactant, catalyst, solvent and a precursor which is TEOS. Once mixed, the surfactant forms multiple micelles within the solution. The micelles displaces off precursor from its centre. Reaction of the precursor forming silica deposits takes place around the micelles while the centre of the micelles will be absent of the precursor, thus no silica formation will be found within the micelles area. After reaction of the precursor was completed, the removal of the micelles will leave multiple empty spaces and silica formation array. Formations of these arrays are also possible if it were to be transferred to atop of the surface of substrate or LED chip as the aiding base. These repeating arrays of empty spaces and silica deposits could be translated to periodical structures. Thus, it is a kind of MRS which could potentially improve the LEE of LED.

Besides that, an accidental discovery to improve LEE of LED was stumbled upon. Teng et al. uses sodium hydroxide (NaOH) diluted in water to clean the substrate without any sensitive epitaxy layer before conducting the SMRSG through a Stöber solution growth method. In conducting experiment for LED, the NaOH cleaning of the substrate surface was not conducted due to risk of interfering with the results of the silica micro repeating structure growth (SMRSG) on LED. LED consists of multiple metallization layers thus there is a possibility of the NaOH cleaning affecting the quality of the layers after treatment. As such, a standalone experiment of LED cleaning with NaOH to remove potential atmospheric deposited contaminants on the exposed LED surface was conducted and proven to be able to improve LEE. A discovery to improve LEE was achieved where cleaning of LED with a base solution was able to improve LEE of LEDs.

1.2 Problem Statement

The internal quantum efficiency (IQE) of an LED is nearing its potential 100% whereas the external quantum efficiency of light extracted out is only at 20%. This applies for both OLED and LED technology as both faces light losses mostly due to total internal reflection (TIR) (Möller and Forrest, 2002).

This research covers on the topic to improve LEE to help reduce energy consumption of an LED. Many methods are being used by manufacturers and researchers to improve the LEE of LED through the said method using ordered microlens (Möller and Forrest, 2002), 2D photonic crystal (Yang and Cunningham, 2011), and Bragg's gratings (Ziebarth et al., 2004) which was introduced earlier. These structure uses expensive, large and complicated equipment respectively to add LEE improving features into LED. Besides, these equipment consumes a lot of energy to power up and at the same time, uses other resources such as compressed air, vacuum and water supply. In some cases, dangerous chemical by products are being released after manufacturing. For an example photolithography process produces ethylene oxide, arsenic and formaldehyde which are carcinogenic (Kim et al., 2014).

With the ubiquitous challenges posing health hazards, high investments and complicated fabrication methods, it becomes a motivation to delve into much safer, cheaper energy efficient and facile processing methods. Besides that, recent world climate change due to emission of greenhouse gases through human activity (Solomon et al., 2010) had also been a great driver for the discovery of much efficient technologies out there. LED technology plays a vital role in helping to reduce greenhouse gas emission due to its lower energy consumption as compared to normal fluorescent lamps. Thus manufacturers are establishing much attention on LED technology development.

1.3 Objective of Research

The objectives of this research are:

i. To study the effect of MRS on light extraction efficiency of LED by SMRSG using Teflon and reflux growth methods.
ii. To examine the effect of NaOH as cleaning solution for LED to improve light extraction efficiency.

1.4 Scope of Study

The scope of exploration covers the use of a facile Stöber SMRSG method on the surface of 2 types of LED chip surface to improve LEE. The first type of LED chip surface to be studied is the roughened LED chip and the second type is the unroughened LED chip. Both types of LED chips were subjected to the same modification process to grow MRS through SMRSG. Prior to selecting the growth methods on LED, glass substrates were subjected to SMRSG using different apparatus to grow the structure. The apparatus to hold the Stöber solution were the Teflon flask and round bottom flask for reflux. The glass substrates were grown in horizontal and vertical position. Then after growth, the glass substrates were quickly inspected with naked eye and characterized through an ultraviolet and visible light spectroscopy (UV/Vis Spectroscopy), Fourier-transform infrared spectroscopy (FITR), X-ray diffraction spectroscopy (XRD), scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDX) to observe the changes that happens to the glass substrate in terms of optical, material and topographical responses.

After analysis was done on the glass substrate, the best SMRSG method on the LED units was selected. The Teflon flask and reflux growth were conducted on different batches of LEDs. The purpose of having an enclosed Teflon flask and also the reflux method is in order to prevent the dehydration of the solution which were heated up to 60 degrees Celsius (60°C) for 72 hours. The units were then subjected to surfactant extraction for 24 hours and dried in an oven for 24 hours to complete the growth process. Besides that, cleaning of the LED chip surface with a base solution was also studied. This was done by rinsing the LED units into NaOH solution for around 30 seconds. Then the units were rinsed with deionized water (DI water) to remove NaOH residue.

The emissions of the LEDs were characterized before and after experiments through a spectrophotometer to detect changes in the brightness of the LED. After brightness characterization was done, the units shall be subjected to SEM scan to study the surface topology changes in comparison with an untreated LED surface. An interrelationship between the MRS structure and effects on LEE could be drawn through theses characterization.

CHAPTER TWO
LITERATURE REVIEW

2.1 Introduction

At present many researchers have reported different methods of surface modification showing that MRS can improve the LEE of LED chips. Amongst the various MRS reported are embossed repeating microlens where the lens structure are periodically fabricated in the micrometer range (Tuohioja, 2006), 2D photonic crystal as seen in Figure 2.1 (Lee et al., 2003, Saxena et al., 2009), Bragg's grating which is a periodic variation of refractive index (RI) (Ziebarth et al., 2004), surface-roughening (Lee et al., 2005) and many more. The surface modifications to improve LEE of an LED are mostly done by employing repeating structures in the nano or micro scale.

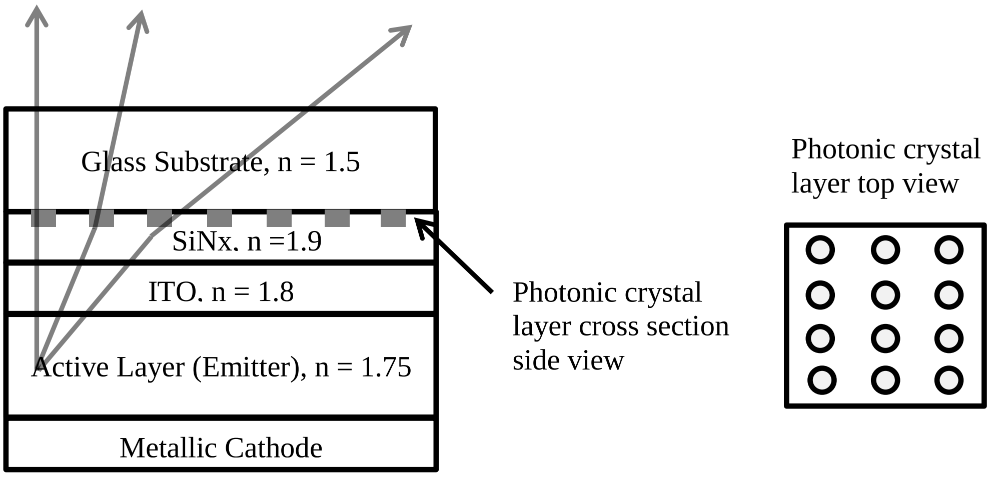


Figure 2.1: An example of MRS in the form of 2D photonic crystal pillar structure. (Lee et al., 2003, Saxena et al., 2009).

As an alternative, depositing mesoporous thin film (MTF) on LED chip is also thought to be possible to improve the final luminous flux of the LED. Luminous flux is measured in lumens (lx) which is the total quantity of light emitted by a source. This is because mesoporous materials could be fabricated to have some repeating structures which is a MRS. It is thus possible for MSTF which is an MRS to improve LEE because of the presence of an uneven surface for light wave to hit at random angles (Schreiber et al., 2005), act as a waveguide similar to microlenses (Lee et al., 2003) and a photonic crystal which is a periodical nanostructure to improve light extracted out from the LED chip (Saxena et al., 2009).

The motivation to improve LEE of LED technology will have a positive future prospect in the market. Positive features of LED’s are such as that it uses less energy (Sun and Lin, 2004), with efficiency far better than of incandescent lamps and is almost on par with fluorescent lamps (Kumar et al., 2006, Chen et al., 2010). In future it is expected to exceed all other lighting technologies ensuring that this technology will receive much attention. It can also show improved color rendering index (CRI) (Yeh et al., 2012) and has a long lifetime that goes up to 100,000 hours (Lin et al., 2009). By referring to the statistical analysis carried out by the Department of Electronics of Aalto University, about one fifth of the global electricity generated is used for lighting purposes. It is estimated that 90% of electrical energy could be saved by using smart lighting technologies combined with the usage of LEDs (Dehoff et al., 2010). A good example of energy saving can be seen in New York City where 70% of its traffic lights have been converted to LED technology, and the estimated annual savings for maintenance and electricity goes up to $6 million (Brown, 2011). The total estimated electricity savings in the US itself is estimated to be around $125 billion from 2005 to 2025 due to the usage of LED (Lin et al., 2009). Cumulative savings for the total amount of electricity and maintenance in the US is estimated to reach as high as $300 billion from 2009 to 2030 through LED enhancing LEE technology (Brown, 2011).

2.2 Light Extraction Efficiency in LEDs and its Measurement Methods

Light extraction in LED involves the emission of photons from the p-n junction of the LED semiconductor chip. It then goes through the packaging material and finally to the surrounding. The study of the electromagnetic wave or light emitted out from an LED is called analysis of LEE (Moreno et al., 2010). The measurement of LEE defines the characteristics and capability of the particular LED manufactured. Gauging of such capability is done through measuring luminous flux or photometric quantity of the LED by using a 2π integrating sphere. An integrating sphere is a spherical shaped instrument integrated with a photometer. The inner sphere is deposited with a reflective surface which acts as a diffuser for light to spread out while the photometer could be rotated on a goniometer to map out radiation pattern from the LED (Young, 2006).

Ultimately, manufacturers would demand to maximize LEE from an LED where lesser current or energy is required to generate out light. This reduces the electricity consumption which translate towards cost saving (Dehoff et al., 2010). There are many researches being done to improve LEE and thus such improvement needs to be measured for its effectiveness.

2.3 Mesoporous Thin Film Material and its Potential Application on Improving Light Extraction Efficiency

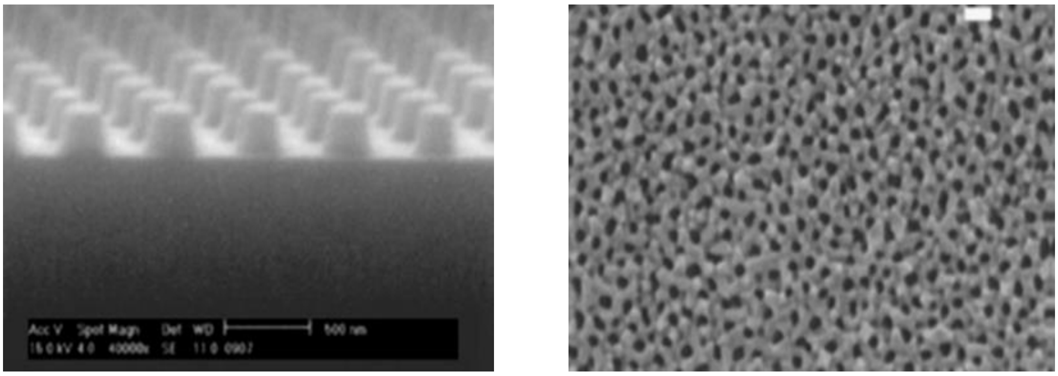
Mesoporous materials which could be in the form of film, bulk or powder forms are defined by the International Union of Pure and Applied Chemistry (IUPAC) as materials with pore sizes between 2 and 50 nm respectively (Meynen et al., 2009). The presence of pores in the base material reduces density, introduces a large surface area mostly used for catalysis, and in certain cases unleashes its ability to retain matter. In other words, it is a material which has different properties from its bulk material (Cheyssac et al., 2005a). Some researchers reported mesoporous thin film material as transparent (Wang et al., 2009, Zhao et al., 1998, Peng and Lu, 2008). There are many types of porous material films made out of metal oxides such as cobalt (ll, lll) oxide (Shu et al., 2009), titanium dioxide (Titania) (Ko et al., 2011), Zirconia (Wang et al., 2009), nickel oxide (Shi and Wu, 2013), zeolite materials such as mordenite (Jin et al., 2012), carbon (Lin et al., 2008) and silica (Zhao et al., 1998). There are also many applications that are possible for these mesoporous materials where they are being used in LED to enhance LEE. They are used as optical waveguide (Yim et al., 2005, Konjhodzic et al., 2006) or as a periodical structure to improve LEE (Peng et al., 2004) which is an MRS.

Mesoporous material can also be an MRS due to the presence of repeating air and base material array. Thus by exploiting this characteristic, a new application which is to improve LEE on LEDs could be possible. Many researchers reported periodical structures with a certain dimensions or shape could improve the LEE from and LED. The structure could either be protruding out from the LED chip surface as seen in Figure 2.2a or it could be intrusive in towards the LED chip as seen as Figure 2.2b.

Besides that, there are many structural shapes that could improve LEE provided they are repeating in nature. They could be in the shape of truncated pyramid as shown in Figure 2.2a (Do et al., 2004), shape of porous holes as shown in Figure 2.2b (Peng et al., 2004), microlenses where the shape is similar to a semi sphere as shown in Figure 2.3a (Möller and Forrest, 2002) or the shape of stacked hexagon as shown in Figure 2.3b (Choi et al., 2012). Figure 2.4 (Teng et al., 2012) show mesoporous structure fabricated through the use of surfactant template using Stöber growth which is similar to the as said MRS.

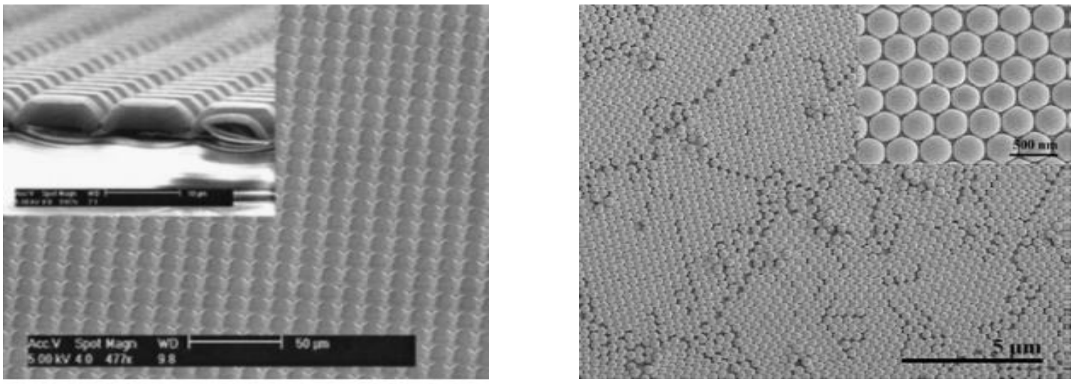
Stöber growth, a silicon dioxide (SiO_2) chemical growing method was popularized by Werner Stöber in 1968 (Stöber and Fink, 1968). It involves the hydrolysis of TEOS to produce ethoxysilanols which further reacts with other TEOS or formed ethoxysilanols. The reaction with other TEOS or ethoxysilanols itself produces a crosslinking of the silanol chains (Blaaderen et al., 1992). The nucleation of the SiO_2 formed after crosslinking are granular in shape which sizes could range from 50 nm to 2000 nm (Bogush et al., 1988).

Teng et al. improvised the Stöber growth method to produce SiO_2 with pores in the nano scale range (Teng et al., 2012). This was done through adding in surfactant into the Stöber solution. The fabricated sample by Teng et al. showed distinct repeating structures in the nano scale level. The structures are MRS due to the periodical SiO_2 and pore array. As such, the mesoporous silica structure fabricated through surfactant template which show MRS pattern is thus possible to improve LEE of an LED.



(a) (b)

Figure 2.2: MRS structures of (a) photonic silica crystals (Do et al., 2004) and (b) nanoporous anodic aluminium oxide (Peng et al., 2004).



(a) (b)

Figure 2.3: MRS structures of (a) microlenses made of poly-dimethyl-siloxane (Möller and Forrest, 2002) and (b) perforated tungsten trioxide (WO_3) hole structure (Choi et al., 2012).

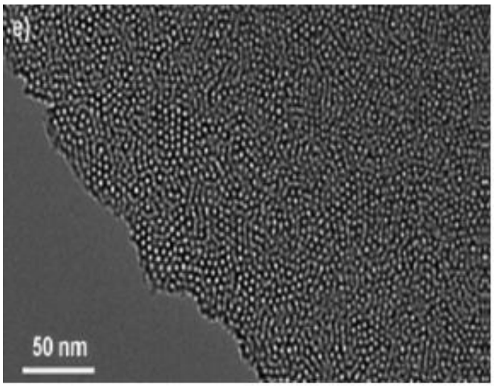


Figure 2.4: Mesoporous silica structure fabricated through surfactant template (Teng et al., 2012).

2.4 Micro Repeating Structure (MRS) on LED to Improve Light Extraction Efficiency

The IQE of an LED is nearing its potential 100% whereas light extracted out is only around 20% (Möller and Forrest, 2002, Choi et al., 2012, L.Petti et al., 2013). The rest are lost within the LED unit structure. Many inventions done by researchers to improve LEE are such as the making of 2D photonic crystal which looks similar to an optical waveguide in the shape of fibre optics. The photonic crystal 2D structure is analogous to the working principle of fibre optics, light wave is guided within the fibres through total internal reflection (TIR) as seen in Figure 2.5. TIR occurs if light wave is incident upon the interphase between the core and cladding of the fibre optics above the critical angle where the RI of cladding is lower than the core (Ghatak and Thyagarajan, 2000). It is thus possible to amplify the guided mode and the narrowing of emission respectively with a silica fibre (Marlow et al., 1999, Sims et al., 2011). As an alternative, Yi Et al. uses a different approach of a multidirectional reflecting waveguide by having a lower RI core covered by layers of alternating Si and Si_3N_4 with higher RI (Yi et al., 2005).

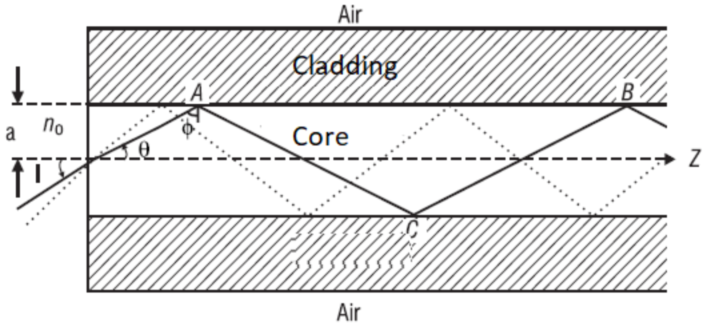
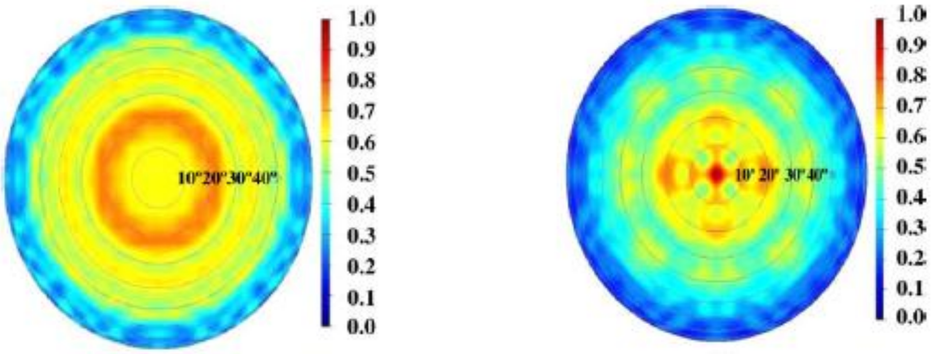


Figure 2.5: A fiber optics structure consisting of a central core and an outer cladding (Ghatak and Thyagarajan, 2000).

Researchers opt to grow MRS structures within or on the LED chip to improve LEE. An illustration is shown in Figure 2.7 to simplify the theory behind light being guided out through perpendicular porous structure from an emitter body which is an LED by Lee et al. and Mehta. (Lee et al., 2003, Saxena et al., 2009). The shape could either be a pillar rod as seen in Figure 2.7, a semi spherical shape, truncated pyramid shape or random grain structure with air hole array between them. This type of MRS is somewhat similar to a 2D photonic crystal, as seen in Figure 2.1 due to different RI of the pillar structure and the air hole array. Do et al. reported an increase of 50% of LEE through the use of 2D photonic crystal. The 50% increase of LEE was done on an LED that was estimated with an IQE of 20% (Do et al., 2004). Ziebarth et al. used Bragg gratings fabricated through soft lithography process (Ziebarth et al., 2004). The forward emission intensity was increased by 49% and 70% through the use of one-dimensional and two-dimensional gratings respectively. The quantum efficiency was increased by 15% and 25% respectively. The results published by Ziebarth et al. showed arbitrary values of LED light intensity between the improved and non-improved LED respectively. As such, the initial efficiency of the LED used for their experiment was unknown in order to judge the significant increase in LEE.

Tsai et al. states that by using a 2D photonic crystal, a 3.5 times in output power was observed within the angle of 25° (Tsai et al., 2010) due to the narrowing and concentrating of the LED emission. Tsai et al. optimized their LED to have a much more concentrated emission of photons in the centre instead of having a diffused emission which could be seen in Figure 2.6. Figure 2.6a shows that the intensity of photons emitted out from an LED without photonic crystals are spread out in an angle of 40° denoted by the orange and yellow color. Figure 2.6b shows the intensity of the LED with photonic crystals are concentrated in the centre below within 25° angle denoted by the red color in the centre of the chart.



(a) (b)

Figure 2.6: Radiation intensity of (a) LED without photonic crystals and (b) LED with photonic crystals.

Choi et al. selected colloidal lithography method to produce perforated structures with an increase of 39% in brightness (Choi et al., 2012). However Choi et al. also did not state out the initial value of the LED brightness and the improvement of LED brightness was reported out as arbitrary values. Kui et al. fabricated 2 types of photonic crystal one which is hole photonic crystal and the other a pillar photonic crystal on an InGaN LED (Kui et al., 2014). The experiment showed 40% improvement for hole photonic crystal structure whereas the pillar structure showed a 60% improvement in the LEE. The improvement was significant where it showed an increase from 100 milliwatt (mW) lighting up to 140 mW and 160 mW for the hole photonic crystal and pillar photonic crystal respectively. In comparison with the high powered UX:3 LED chip from Osram which is rated at 440 mW averagely, it could be judged that the LED used by Kui et al. does not have any LEE improvement features fabricated with it though both are of the same InGaN LED type. As such, implementing a simple LEE extraction structure improves the output significantly in Kui et al.'s LED.

Up until recently, photonic crystals are still being studied to improve LED LEE but with a different method of growth. Jeon et al. fabricated repeating zinc oxide (ZnO) nanorods on top of an InGaN LED (Jeon et al., 2015). The ZnO nanorods were fabricated through a two-step hydrothermal method. The first step is to grow a ZnO seed layer for a short period of time which is 5 minutes at room temperature using zinc acetate dihydrate ($(Zn(C_3H_3O_2)2.2H_2O$ in an ethanol solution. The second step is to grow the primary ZnO nanorods at a constant temperature of 85°C in solutions of zinc nitrate hexahydrate ($(Zn(NO_3)_2.6H_20)$ and hexamethylenetetramine ($(C_6H_{12}N_4)$). Jeon et al. was able to obtain a 28% increase in LEE for a low powered InGaN/GaN LED. Hronec et al. took the study of improving LEE in LEDs to the next step by introducing a method to enhance the features of an already fabricated photonic crystals (Hronec et al., 2016). This was done by coating a thin layer of gold (Au) around 5 µm on top of the photonic crystal structure on the LED. The initial LEE improvement of the LED with photonic crystal was at 45.6% while similar LED coated with the gold layer was able to yield a 59.0% which is a 10.4% increase over the non-coated LED. This gain was obtained from a low powered LED at a pumping current of 10 mA in comparison with the high powered Osram UX:3 chip with a pumping current of 350 mA.

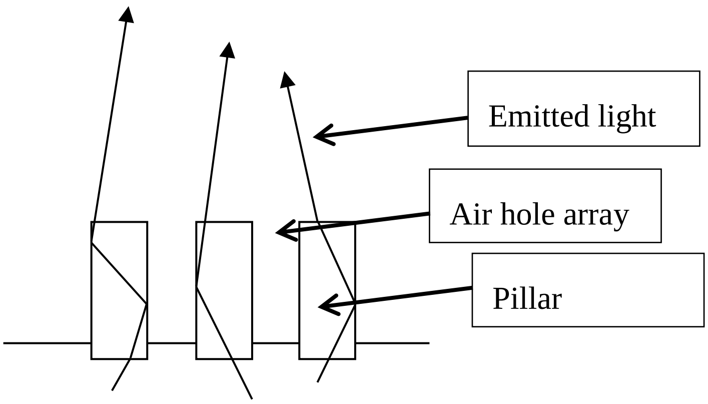


Figure 2.7: A simple illustration of a repeating pillar structure followed by air hole array. The arrow shows illustration of light being guided out of the repeating pillar structure.

Alternately from producing MRS on the chip, MRS structure could also be fabricated on the packaging material of the LED. This is done through embossing repeated microlens structure onto the encapsulant material of an LED package (Tuohioja, 2006). Aside from that, the packaging material used should have a RI in between the LED chip and air to further enhance LEE. RI of the LED chip is estimated to be n = 2.54 whereas RI of air is n = 1.00 (Choi et al., 2014). As such, the encapsulant material RI should fall between these numbers to provide an index matching through the intermediate modified layer. With this enhancement, light output could be collimated through narrowing the spread from a 108° to 45° angle and there was an increase in the luminous intensity by 70%. The narrowing of spread was described by Schreiber et al., which was a result from the reduction of stray light and increase in homogeneity of light (Schreiber et al., 2005).

Aside from that, 2D photonic crystal structure could be fabricated on the exterior ceramic converter layer (CCL) of the LED chip. A converter layer is widely used to convert emitted light from LED to achieve a desirable color in the LED industry. Rather than using the CCL to just alter emitted wavelength, it could be engineered to improve the LEE of an LED by having 2D photonic crystals on it. This could be done through the same method of colloidal lithography by Choi et al.. However, instead of using the as mentioned method to grow 2D photonic crystal within the LED, the 2D photonic crystal was fabricated on the CCL which will be placed on top of the finished LED (Park et al., 2011, Park et al., 2015). Park et al. was able to increase the average brightness of the LED by an average of 4%. With the proposed method, this increases the functionality of the CCL of having dual functionality as color converter and also to improve LED LEE.

On the contrary, a biomimicry study on a naturally occurring MRS was reported by Bay et al., whereby a rough misfitting surface at 3 µm height such as the abdominal structure of a firefly is much more efficient at extracting light compared to a smooth surface (Bay et al., 2013b). This abrupt pattern of repeating scales joined together produces diffuse transmission and it could improve LEE up to 55% where the LEE was increased from 100 mW up to 155 mW. Bay's evaluation showed that the period and height of the MRS should be 5 µm and 6 µm respectively (Bay et al., 2013a).

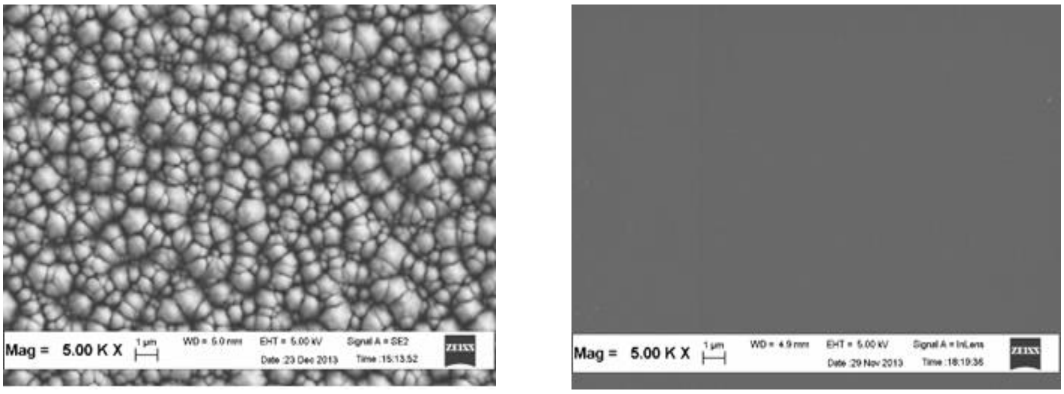
There are many methods being used to produce MRS be it through photolithography followed by wet etching (Möller and Forrest, 2002), RF sputtering (Shu et al., 2009), colloidal lithography (Choi et al., 2012), PECVD (Teng et al., 2012), electron beam lithography (L.Petti et al., 2013), hydrothermal growth method (Jeon et al., 2015) and several other methods. The projected improvement values by researchers could vary in comparison with one another. On top of that, several researchers mentioned above were able to project high and significant improvements in LEE for their LEDs where improvement ranges mostly from 40% of improvement up to 70% improvement. This happens due to the measurement method used, type of measurement instrument, type of LED whether is a high powered or low powered LED and method of LED chip fabrication (Jiang et al., 2016).

Each of the researchers reviewed above use low powered LED without any LEE improvement features for evaluation, thus they are able to project high LEE gains. In comparison, Osram UX:3 chip is a type of sapphire thin InGaN (150 µm) technology chip with the presence of LEE improving features such as a reflecting metallic mirror below its active layer and having favourably defined scattering surface for optimized LEE. It is a requirement by Osram to do so as the chips were designed to meet customer demands on producing LED with high efficiency. As such, studies conducted on these high powered UX:3 chip will potentially project out small percentage of improvement which is a significant enhancement to the already improved LED.

Besides that, researchers uses different current supply to light up their LED due to the different type of LED chip used for experiment to publish their results. For example Lee et al. used a pumping current of 150 mA on their LEDs (Lee et al., 2005) whereas Chen et al. used an injection current of 20 mA to power up their LED in their assessment (Chen et al., 2012). The different pumping current was used due to the different type LED used where Lee et al. used AlGaInP LED whereas Chen et al. uses InGaN LEDs. As such, the reported values could range from several percentages in brightness increment up to 25 times reported increment (Jiang et al., 2016) depending on the variation mentioned above. Nevertheless, it is still worthy to note that the photonic crystal which is an MRS fabricated on LEDs are able to improve LEE as reported by many researchers regardless of the magnitude of measured LEE improvement.

2.5 Micro Repeating Structure (MRS) through Etching on Light Emitting Diode Surface

Etching is a process of corroding into the surface of the material rendering it uneven or rough. The uneven surface produced had random and abrupt structures. Surface roughening through etching on actual Osram UX:3 chip could be observed in an SEM scan in Figure 2.8b. Figure 2.8a which is a mirror polished wafer was included for comparison. The surface-texturing was able to guide light out of the LED chip by allowing light to hit the interface at arbitrary incident angles (Do et al., 2004). This was termed as a waveguide similar to a 2D photonic crystal and also microlenses but reported by researchers in their own terminology. Texturing or roughening is popular technique to improve LEE of LED which is even used up to today's LED technology in Osram. The textured surface shows an average of 5% improvement in lumens over the non-textured surface.



(a) (b)

Figure 2.8: SEM images of LED chip of (a) roughened LED and (b) a mirror polished wafer.

Abrupt patterns made through 2D photonic crystal fabrication or embossing of microlenses were proven to improve LEE. Since abrupt patterns could improve LEE, surface-roughening through etching which produces repeating structure in different shapes was hypothesized to improve LEE. For example A well or inversed pyramid structure (Sun and Lin, 2004) or a truncated micro-pyramid (Sheu et al., 2006) formed on the LED chip top surface is reported to increase the LEE at 73% and 60% respectively. Another researcher uses wet etching on the n-side surface of aluminium gallium indium phosphide (AlGaInP) LED using phosphoric acid H_3PO_4 which produces a rough LED surface was able to yield 60% increment in LEE (Lee et al., 2005). Over the years, researchers still uses H_3PO_4 to conduct etching on AlGaInP LED where Park et al. was able to yield a 68% brightness increment for his LED (Park et al., 2014).

Sun and Lin projected a 73% improvement in LEE based upon a simulation calculation without any international systems of unit measurement (SI) provided. The LED used for measurement could be of low powered LED with very low light output which is true for both Sheu et al. and Lee et al.. Sheu et al. projected out a typical average increase of output brightness from 6 mW for a non-textured LED up to 10 mW for a textured LED (67% lEE improvement). Lee et al. reported the output brightness for a flat LED surface at 3.4 mW and a roughened surface projected out an improved output of 5.4 mW (59% LEE improvement). Park et al. which is another researcher projected an increase from 102 mW for a flat LED to 172 mW after roughening (69% LEE improvement). As such, highly projected LEE improvements in percentage could be significant for low powered LED rating as above in comparison with high powered Osram LED. Even Osram was only able to achieve 19% LEE improvement with the texturing method from 368 mW up to at 440 mW. On top of that, the chip power of the same type of LED used by the researchers is different for example both Lee et al. and Park et al. uses AlGaInP LED, however the power ratings are different at 3.4 mW and 102 mW respectively. Researchers also at times tend not to report out the SI unit used for measurement or uses arbitrary values for reporting. Such LEDs could easily show huge and drastic increase in LEE with any LEE structures fabricated within the LED structures. In summary, it depends on the measurement method and chip type used as reviewed earlier. Howbeit, the wet etching method still is the most popular method used until recently to produce MRS due to the low cost and simple method with high gains (Jeong et al., 2015).

2.6 Surfactant Template Mesoporous Silica Film properties and its Potential in Optoelectronic Materials

Silica (SiO_2), alumina (Al_2O_3) and indium phosphide (InP) are materials that could produce high quality pores (Wehrspohn et al., 2006). Mesoporous silica is a better material due to its promising characteristics in the growth of silicon-based optoelectronic devices (Xu et al., 2000). It was reported that mesoporous silica thin films (MSTF) fabricated through surfactant templates have elastic modulus conforming to integrated circuit (IC) which is an electronic device (Coquil et al., 2009). It is thus applicable in optoelectronics technology which is also an electronic device but producing light. Due to the conforming elastic modulus, it would not stress the optoelectronic device due to the minimal difference in coefficient of thermal expansion (CTE). This is because the chip passivation layers are fabricated from SiO_2. The MSTF is mostly reported to be transparent (Zhao et al., 1998, Peng and Lu, 2008), uniform and the thickness of the film ranges from 300 nm to a few hundred µm (Zhao et al., 1998) which is also applicable for optoelectronics devices.

Besides that, porous silica exhibits photoluminescence properties at room temperature (Cisneros et al., 2010) which opens up applications for optoelectronics. In recent times, silica mesoporous structures fabricated are being modified to exhibit multifunctional structure properties with luminescent properties (Sahay et al., 2014, Li et al., 2015). Multifunctional structures are composite materials where Nano reinforcements is executed making it electrically conductive and also having its optical properties modified (Gibson, 2011, Sahay et al., 2014, Li et al., 2015). Li et al. fabricated a multifunctional mesoporous structure with confined cadmium selenide (CdSe) quantum dots with luminescent properties (Li et al., 2015). The luminescent properties could be controlled by the changing the porosity of the silica structure. Zong et al. fabricated mesoporous silica structure with embedded gallium(III) oxide (Ga_2O_3) nanocrystal to produce a multi color emission material (Zong et al., 2014). The incident wavelength on the material could be varied in order to obtain a certain color of fluorescence. These structures by Li et al. and Zong et al. could potentially be used for light conversion purposes in LED with better LEE due to its MRS structure though not having any reported application yet as of today.

The porosity is mostly attributed through surfactant template growth (Yusuf et al., 2001) and myriad of researchers uses surfactant template growth. For example Yeh et al. utilizes ternary surfactant and silica condensation (Yeh et al., 2011), Johansson et al. produced large 18 nm mesopores with symmetric triblock copolymer which constitutes of polyethylene oxide and polypropylene oxide (P123) surfactant (Johansson et al., 2009) and Ko et al. fabricated mesoporous titania film with vertical pores using triblock copolymer consisting of a central hydrophobic block of polypropylene glycol flanked by two hydrophilic blocks of polyethylene glycol (F-127) surfactant in 1-butanol solution (Ko et al., 2011). There are also many reports on the use of surfactant templating method to fabricate ordered mesoporous silica. The potential uses of these surfactant template silica structures are mostly studied in the medical field for drug delivery (Farsangi et al., 2016, Escobar et al., 2017, Mehmood et al., 2017), in optical and electronic field (Sohmiya et al., 2015), multifunctional structure (Li et al., 2015) and several others. However, there is no actual industrial application reported yet on the use of mesoporous silica structures.

Surfactant template growth method produces mesoporous structure which could be made into thin film layers. The process is normally based upon a surfactant templating solution subjected to spin coating (Ko et al., 2011), casted (Huang et al., 2006) followed by evaporation induced self-assembly (EISA) method (Brinker et al., 1999, Zhang et al., 2007), Sol-gel method (Yusuf et al., 2001, Wu et al., 2013) or multi-step oxidation-etching process (Zhu et al., 2005). It could also be produced through sputter deposited film using radio frequency (RF) magnetron sputtering (Otomo et al., 2007, Otomo et al., 2006).

Pore alignment of the MSTF could be engineered in different directions. They could be deposited vertically or in a circular shape on the plane of growth (Wu et al., 2013). Richman et al. reported a method to fabricate vertical pores was through coating the substrate surface with a neutral material which does not have any affinity towards any of the surfactant blocks (Richman et al., 2008). It is important for the chemical reaction to be ideally slow for the vertical structure assembly to take place. A lower pH is preferable for slow reaction and ideally around pH 2 to 3 for regular and homogeneous films (Richman et al., 2008, Yeh et al., 2011, Wu et al., 2013). Yeh et al. reported that at pH 6, the mesoporous sheets become irregular and not controllable for a three component surfactant (Yeh et al., 2011). Putz et al. fabricated radially shaped mesoporous silica structure by combining 2 types of silica precursor which is TEOS and methyltriethoxysilane (MTES) grown in a solution mixture containing CTAB as surfactant (Putz et al., 2017).

Besides, MSTF is a versatile material due to the capability of having controllable amount of pores and adjustable pore structure and size, adjustable surface chemistry (Cheyssac et al., 2005a, Guo et al., 2011, Okamoto and Huang, 2012, Coquil et al., 2009), excellent chemical stability (El-Toni et al., 2012) and having well-organized pores (Liu et al., 2004/2005), it also has the flexibility for its pore structure to be manipulated. Thus the dielectric constant of the material could be