Design and fabrication of ultraviolet metal-oxide light-emitting devices

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Design and fabrication of Ultraviolet metal-oxide light-emitting devices

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Summary

Summary

Zinc Oxide (ZnO) has a wide bandgap energy (~ 3.37 eV) and high exciton binding energy (~ 60 meV) which is more than two times larger than that of Gallium Nitride (GaN). Therefore, ZnO has been recognized as a promising candidate of ultraviolet (UV) optoelectronic devices operating at room temperature or even at high temperature. Especially, the high exciton binding energy favors the excitonic stimulated emission in the application of lasers. However, ZnO has a wurtzite crystal structure, and thus two sufficiently smooth mirror surfaces are hardly to be cleaved to form Fabry-Perot cavity. The discovery and development of ZnO random laser successfully avoid this difficulty by forming the lasing resonance via multi-scattering in a closed-loop feedback. In order to realize electrically pumped ZnO random laser, a sufficient optical gain is needed to overcome the large scattering loss. The previous electrically pumped ZnO random lasers used either a *p-i-n* structure or an electron blocking layer to confine the carriers so that achieve a comparably large gain. However, there is only electrical confinement in the transverse direction realized, and the carriers are free to diffuse in the lateral direction. This hinders the gain enhancement, and thus results in a large threshold. Secondly, non-directional emission also impairs the usefulness of ZnO random laser. Thirdly, multiple lasing modes are excited from the ZnO random laser diode, especially under high excitation, which is not desirable. Therefore, in this thesis, work has been focused on enhancing the electron-photon-conversion efficiency so that to reduce the threshold, realizing

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directional emission and exploring the mode repulsion mechanism especially at high excitation.

A ZnO based index-guided heterojunction with buried waveguide structure has been employed to realize laser diodes. Both electrical and optical confinements in both transverse and lateral directions are formed. Consequently, the conversion efficiency is significantly enhanced. By forming highly disordered grains and voids as random cavities in the active layer of the index-guided heterojunction, electrically pumped ZnO random lasing has been demonstrated. The threshold is largely reduced with the buried rib waveguide. The off-axial scattering is significantly reduced, and a directional lasing emission is observed from the edge of the rib waveguide. More importantly, it is found the number of random modes is highly suppressed by employing the rib structure, as the number of the spatially repulsive closed loops is reduced with the area of the random media.

Mode repulsion mechanism is explored by forcing spatial overlap of the random modes, and enhancing the lateral coupling among them. In the designed random laser arrays with narrow spacing, it is found with strong lateral coupling between the adjacent random arrays, the obvious spectra repulsion at high excitation power could be achieved. Additionally, a significant output power enhancement is observed due to the increment of the spectrally coherent random emitters. In a further step, with enhancing the coupling among the random modes, and also make sure only the fundamental lateral mode is supported in the individual array element, a single-mode

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operation has been achieved in electrically pumped ZnO random laser array even at high injection.

Tin dioxide (SnO_2) has 3.6 eV bandgap energy and 130 meV exciton binding energy. This makes SnO_2 as a potential light-emitting device with high efficiency operating in the UV regime. Polycrystalline SnO_2 thin films were deposited onto 4H-SiC substrates by using filtered cathodic vacuum arc (FCVA) technique. The well-separate SnO_2 grains were realized by post annealing. The surface is hence widely exposed to the surrounding so that the surface area to volume ratio of the SnO_2 thin film is significantly improved. The large amount of shallow trapped states on the surface of the SnO_2 grains results in the UV emission at 387 nm.

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1. Introduction & Literature Review

1.1 Background and Motivation

Semiconductor lasers have prominent merit as compactness in unit cell size, easy integration with other semiconductor components and low cost of mass production by readily established semiconductor production techniques.^{1,2} The infrared laser diode (LD) has been well exploited and commercialized in the field of fiber-optic communication.³ Approaching to the visible regime, red semiconductor lasers are common in CD players, and the green LDs are now well used as laser pointers. In addition, the visible LDs have been extensively uses in the printing and imaging industry.^{4,5} Going to higher energy regime, the ultraviolet (UV) semiconductor laser has great potential application such as compact data storage, high resolution imaging, bar coding, sensing, water purifying and UV curing. More importantly, in the field of biomedical technology UV LDs have unique interest of application in compact bioagent detection.^{6,7} However, despite substantial progress in developing UV light emitting diodes (LED), there are very few commercialized UV LD in the market. This is because as the operating wavelength gets shorter, it is desired to have tinier laser cavity. It requires low loss waveguides with cladding layers featuring abrupt interfaces for optical confinement and efficiency carrier channelling mechanism. Another challenge is that when the wavelength keeps decreasing, it is harder and harder to realize sufficiently smooth mirror surfaces with very low loss and strong coherent feedback due to the physical properties of wide bandgap materials.

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Therefore there are still an eager desire and rich research value in exploiting and developing of semiconductor LD operating in UV regime.

1.1.1 ZnO as the UV material

To realize UV LD, The extensive research effort has been focused onto nitride-based wide bandgap material, such as GaN($E_g = 3.4$ eV)⁸, AlGaN⁹ and AlGaInN¹⁰. Multiple quantum well (MQW) has been developed based on the nitride compound to raise the density states of electrons to enhance the efficiency of lasing action.¹¹⁻¹³ However, in nitride compounds, to realize an efficient optical cladding layer with low refractive index, the large portion of AlN would results in high dislocation or even cracks, which severely harms the recombination efficiency. As Al concentration in the AlGaIn compound increasing, the compound will become more and more resistive. This generates another difficulty in current injection. Additionally, cleaving a low loss mirror surface in the Nitride material is another challenge. On the other hand, ZnO is another promising candidate. ZnO has band gap energy as $E_g = 3.37$ eV at room temperature. ZnO has a wurtzite crystal structure which is very similar as that of GaN.^{14,15} Both thin film and nano-structured ZnO with high crystal quality have readily been realized by various techniques.¹⁶⁻²² It has been demonstrated that the high quality ZnO could be deposited at comparably low temperature (<350° C) on latticed-mismatched substrate such as Si.²³⁻²⁵ This makes the crystal growth much simpler and cheaper than that of GaN, additionally it is easier to integrate with other Si-based optoelectronic devices. More importantly, ZnO has a high exciton binding energy of 60 meV compared to 25 meV for GaN.

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This implies the excitons are thermally stable at temperature as high as 700 K, which means excitonic stimulated emission is expected to occur at room temperature or even high temperature. If a ZnO-Mg_xZn_{1-x}O QW is used to concentrate the electrons, the free-excitonic gain was calculated to be 10^5 cm^{-1} , which is an order higher than that of the GaN-based QWs.²⁶ Therefore, it is believed that UV LDs with higher emission efficiency and simpler fabrication technology could be obtained from ZnO.

1.1.2 ZnO laser

The first ZnO laser operating at room temperature was demonstrated in 1997.^{27,28} High quality ZnO thin films were grown on sapphire substrates by microwave plasma-enhanced molecular beam epitaxy (MBE). The traditional Fabry-Perot (FP) cavity was formed by carefully cleaving the thin film into bars of cavity lengths in the range of 300-1000 μm . Optical pumping was carried out by a pulsed (10 Hz, 6ns) 355 nm Nd:YAG laser, and the excitation beam is focused into a stripe of 50 μm in width. Laser action has been demonstrated with a threshold of $\sim 240 \text{ KW/cm}^2$.²⁷ A very similar experiment has been conducted in single crystal GaN. The room temperature threshold intensity was characterized as $\sim 800 \text{ KW/cm}^2$, which is more than 3 times higher than that of ZnO laser.²⁹ Moreover, the ZnO-based quantum well structure could significantly further reduce the excitation threshold to $\leq 17 \text{ KW/cm}^2$.³⁰ Subsequently, from ZnO epilayers, stimulated emission from exciton-exciton scattering and electron-hole-plasma at temperature up to $\sim 550 \text{ K}$ ³¹ and lasing action up to 570 K³² were also observed. Therefore ZnO has great potential to realize room temperature operating UV LD with high emission efficiency. However, ZnO has wurtzite crystal structure, which brings difficulty in achieving strictly

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parallel and smooth mirror surfaces via cleaving.³³ The UV external mirrors are expensive. Therefore other feedback mechanisms are sought for lasing resonance.

1.1.3 ZnO random laser

As the development of nanotechnology, nanocrystals can be employed to pursue new feedback mechanism in ZnO²⁸ to avoid the formation of smooth mirror surfaces. Excitonic lasing action was sustained in hexagonal ZnO microcrystallites.^{34,35} The facets of all hexagons are parallel to those of others, forming Fabry-Perot lasing. A low threshold of 24 KW/cm² was obtained for 50 nm size nanocrystal. However, the resonance precisely relies on the arrangement of hexagonal structures and again the smooth facets are still difficult to achieve. Other methods were tried to realise the lasing feedback. Microdisk laser with SiO₂ microdisk and ZnO thin film on top supports whispering gallery modes.³⁶ Room temperature UV lasing was also observed from ZnO nanowires. The epitaxial interface between the sapphire substrate and ZnO and the sharp (0001) plane of the other end of ZnO nanowire form reflecting mirrors. 40 KW/cm² threshold was measured.³⁷ Besides the regularly arranged nanocrystals, there has been investigation and prediction that disordered media may result in more efficient operation of nonlinear optical devices³⁸. Therefore, nanocrystals acting as randomly distributed reflectors to improve the lasing efficiency have attracting a huge attention since the late 1990s.^{39,40} In 1998, Cao *et al* first observed lasing from polycrystalline ZnO films grown on amorphous fused silica substrate.⁴¹ Unlike the ZnO films epitaxially deposited on sapphire substrate which results in well-aligned hexagonal grains, the polycrystalline ZnO has

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highly disordered grains with irregular shapes, and size in the range of 50 ~ 150 nm. The randomly oriented polycrystalline grains results in strong optical scattering. With a sufficiently high scattering strength, the light could be reflected through multiple scattering and return to the position from which it was emitted. Thus the closed-loop path is formed as the resonant cavity, and the constructive interference inside the closed-loop path results in a large optical gain. The gain coefficient for the polycrystalline ZnO was measured as 100 cm^{-1} at an excitation of $2 \text{ } \mu\text{J}/\text{cm}^2$. As the gain exceeds the loss of the cavity, longitudinal modes would emerge. Subsequently, lasing action sustained by random gain medium has been demonstrated in oxidized Zn films,⁴² ZnO thin films fabricated by pulsed laser deposition (PLD),⁴³ annealed ZnO films,²⁵ ZnO micro random laser,⁴⁴ ZnO powder,^{45 46} and ZnO nanostructures such as nanowires,⁴⁷ nanoneedles,⁴⁸ nanorods,⁴⁹ and nanoparticles.⁵⁰ Therefore compared to Fabry-Perot cavity and the lasing cavity formed by hexagonal grains and microdisks, the ZnO lasing sustained by random cavities has advantages as no requirement of smooth mirror surfaces for the optical feedback as well as much less restriction on substrate choosing, thus results in simpler and cheaper fabrication. It is especially suitable for the materials which have difficulty to form facets with high reflectivity. It provides a cheap solution for realizing lasing in such material with less dependence on the substrate matching. Additionally, random laser has remarkable advantages as strong light localization and small mode volume, which enables the realization of micro laser. Nevertheless, as photons are scattered off the cavity by randomly distributed scatterers, ZnO random laser suffers from large scattering loss, which leads to lasing threshold $> 500 \text{ KW}/\text{cm}^2$. Moreover, non-directional emission

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is another disadvantage of random laser. In the following section the literature of ZnO random laser is reviewed. It will focus on the performance improvement of ZnO random laser, designs of electrically pumped ZnO random lasers to lower the threshold, enhance the emission efficiency, improve the emission directivity, suppress the side modes, and the choices of p -type substrate of the junction.

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1.2. Literature review

As a well-known laser source, an amplifying gain medium is enclosed within a resonant cavity. Most generally, the cavity is formed by cleaving or etching two parallel facets, or depositing reflective coating so that light is trapped inside, and be amplified. The phase coherence is satisfied as $m\lambda=2L$, where m is integer, λ is wavelength inside of the cavity material, and L is cavity length. Recently, a new kind of mirrorless laser has evolved, and known as the random laser. Random lasers do not require smooth facets with high reflectivity for the optical feedback. Photons are scattered by the randomly distributed scatterers, and some photon could get back to the same scatterer it encountered before. Therefore a “ring cavity” is formed, and if the “ring cavity” is assumed with a circular shape, it satisfies $\pi D=L$ to achieve the coherence.

1.2.1 History of random lasing

In 1968, V. S. Letokhov proposed an idea of scattering with negative resonance absorption.⁵¹ The possibility of lasing action in interstellar molecular clouds was pointed out, and theoretical studies on the threshold and spectral narrowing of the scattering media were initiated. In 1994, Lawandy *et al* firstly realized incoherent random lasing action experimentally by using solution containing rhodamine 640 perchlorate dyes in methanol and TiO₂ particles.³⁸ Multimode laser oscillation was firstly observed. There is an obvious linewidth narrowing from 70nm to 4 nm. There was a breakthrough of random laser in 1998 and 1999 when Cao’s group discovered coherent random lasing in ZnO polycrystalline thin film⁴¹ and ZnO powder.⁴⁵ The

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linewidth was reduced by more than 30 times from the incoherent random lasing. Comprehensive studies on the characteristics of the random laser such as modes number and threshold intensity were investigated. Since then huge amount of theoretic and experimental works have been devised to investigate the random lasers, improve the performance and pursue the application.⁵²⁻⁵⁸

1.2.2 Basic of random lasing: three scattering regions and coherent feedback

There are two types of random lasers namely the incoherent random laser and the coherent random laser. The distinction of the two types of random lasers is highly dependent on the scattering strength of the random material.⁴⁰ To analysis the lasing mechanism behind, some length scales are defined. The gain length l_g which is the path length over which the intensity is amplified by a factor e is defined to describe the amplification process. The transport mean free path l_t which is the average distance a wave travels before its direction of propagation is randomized is used to describe the scattering process. l_t could be characterized in a coherent backscattering experiment. The angular width $\Delta\theta$ of the backscattering cone is related to l_t as

$$\Delta\theta \approx \frac{0.7n_e(1-R)}{k_e l_t}, \text{ where } n_e \text{ is the effective refractive index of the random material,}$$

k_e is the effective wavevector of the probe light in the random material and R is the diffusive reflectivity of the sample material-air interface. From the measured $\Delta\theta$, l_t could be estimated.⁵⁹⁻⁶¹ Therefore light scattering could be quantized and classified into three regimes corresponding to different scattering strength, namely weakly scattering regime, diffusive regime, and localization regime.⁶² In the following

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paragraphs, the feedback mechanism of coherent and incoherent random lasers in the different scattering regime is introduced.

- a) If the scattering is very weak, that is $l_t \geq$ the sample size L , the scattering process occurs in weak scattering regime. The scattering process is trivial and has no much effect on the average length of light path in the gain medium, l_{path} . Under optical pumping, l_g decreases as the pump intensity increases. When the shortest l_g becomes equal to l_{path} , every photon generates a second photon by stimulated emission before leaving the gain volume. The light is amplified following $I = I_o e^{g l_{path}}$, where g is the gain. Thus the photon density at the frequency of gain maximum builds up quickly, which results in an apparent narrowing of the emission spectrum. It is clear that the light does not return to the original path after a trip, and hence there is no synchronization between the dwell time of the light and the lasing frequency, i.e. the lasing action is incoherent. From the measured spectra, as the pump intensity exceeds a certain value, the emission linewidth is quickly reduced to ~ 5 nm, meanwhile the peak emission intensity increase more rapidly with the pump intensity.⁶³ This describes the amplified spontaneous emission (ASE) in a random medium.
- b) If the scattering is stronger, that is $L \geq l_t > \lambda$, diffusion regime is reached. The interaction between scatters in diffusion regime becomes important and leads to multiple scattering. It is the multiple scattering significantly change the light propagation direction and hence increases l_{path} . Thus the pump intensity for achieving $l_g \sim l_{path}$ is lowered. In another word, the gain narrowing process and therefore the ASE process become much more efficient. Therefore for the

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scattering process in both the weak scattering regime and diffusion regime, the light is amplified along open trajectories, and scattering merely increases l_{path} . Incoherent feedback is related to the scattering process in the weak scattering and diffusion regimes.

- c) As the scattering strength is further increased to reach the situation that $l_t \sim \lambda$, which is also known as Ioffe-Regel criterion,⁶⁴ we reach localization regime, where Anderson localization of light is expected to occur.⁶⁵ Due to very strong scattering, recurrent scattering events arise. The light returns to a scatterer from which it was scattered before, thereby forming closed loop paths,⁶⁶ which is also explained by ‘ring resonator’ by Polson *et al.*⁶⁷ When the amplification along the loop is increased so that the gain of the closed loop cavity reaches the loss, lasing mode occurs. The lasing mode from individual closed loop cavity is sustained by the requirement of constructive interference with a phase delay of $2m\pi$, where m is an integer. This is verified by the measured spectrum when the scatterer concentration from the sample is largely increased. When the pump intensity exceeds the threshold, discrete peaks emerge in the emission spectrum. It is worth noting that the linewidth of these peaks is less than 0.2 nm.⁶⁶ When comparing to the spectrum width of ASE above threshold in the weak scattering and diffusion region, the linewidth in the localization regime is more than 20 times narrower. It is important to note that as the excitation position is moved across the sample, the frequencies of the sharp peaks changes. This phenomenon suggests that the emergence of discrete peaks corresponds to the resonance of spatially separated closed loop cavities. The spatial repulsion of random modes is

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consistent with the previous theoretical calculations.⁶⁸⁻⁷⁰ This has been verified by observing the separated closed-loop resonators in ZnO films.⁴¹ Thus, for the scattering process in the localization regime, coherent feedback is formed by bringing the light back to its original position to interfere so that to satisfy both the gain and phase conditions.

To distinguish the coherent and incoherent random laser, the average power Fourier transform (PFT) of the laser emission spectra could be employed. For the incoherent random lasing, the PFT spectrum exhibits a smooth curve; while for the coherent random lasing, the PFT spectrum contains a sharp, well-resolved Fourier component. These harmonics represent well-defined resonant cavities. Moreover, the harmonics of the PFT has an identical separation as $d_m = mnL/\pi$, where m is an integer denoting individual resonators, n is the refractive index of the random media, and L is the cavity length. So if the random cavity is treated as a circular shape, we have $L = \pi D/2$, which is half of the closed-loop length, where D is the diameter of the circular random cavity. Therefore, the size of the random cavity could be determined from the PFT spectrum.^{71,72}

1.2.3 Improve the performance of random laser

Similar to the traditional laser, the usefulness of the random laser is highly determined by the threshold, mode control and directivity. For the purpose of pursuing more application of random laser, a low threshold, single-longitudinal-mode operating, and directional emission are desired. Thus in this section, the

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literatures about reducing lasing threshold, limiting mode number and improving emission directivity are summarized.

1.2.3.1 Threshold

(a) Scattering strength

The threshold of a random laser is strongly related to the scattering strength. With an enhancement of optical scattering strength, i.e. reducing l_t , the feedback provided by scattering becomes stronger, thus the lasing threshold is reduced. l_t could be reduced by increasing either the scatter concentration, N or the scatterer size, R_s . Firstly, it has been found l_t is inversely proportional to N . In Cao's experiment, as the scatterer density N increases from 8×10^{10} to $6 \times 10^{12} \text{ cm}^{-3}$, l_t which is characterized in the coherent backscattering experiment reduces from $17 \text{ }\mu\text{m}$ to $0.4 \text{ }\mu\text{m}$, so that the scattering strength is enhanced. On the other hand, l_t could be reduced by increasing the scatterer size. The larger the scatterer size, the larger the geometrical scattering cross section of individual scatterer spheres, thus the stronger the coupling among them, so that there is higher chance of forming closed loop cavities.⁷³ It has been observed that l_t decreases drastically with increasing the sphere diameter of ZnO scatterer from 85 nm to 137 nm . The relation between the threshold pump I_{th} and l_t has been characterized. It has been found I_{th} decreases with l_t , and I_{th} drops quickly when l_t is approaching the optical wavelength λ , namely approaching the localization regime. This is quantitatively examined by Cao *et al*, revealing that $I_{th} \propto (l_t / \lambda)^{0.52}$ as shown in Figure 1.1 (a).^{54,74}

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(b) Pump area

I_{th} also depends on the pump area A_p . I_{th} has been recorded as a function of A_p for both a pump spot and strip. When A_p increases, I_{th} first decreases as $I_{th} \propto A_p^{-q}$, where $q=0.50$ and 0.62 for $l_t = 0.9$ and $9 \mu\text{m}$, respectively. In addition, there exists a critical A_p above which I_{th} is nearly A_p independent.⁷⁴ To explore the physics behind, the size of the random modes has been studied by the spectrally resolved speckle technique to map the spatial profile of the individual random mode.⁷⁵ The decay length of a lasing state, l_d which reflects the spatial extent of a lasing mode has been deduced from the measured speckle pattern. It is found that l_d is invariant with the pump intensity as well as A_p . The inversely proportional relation between I_{th} and A_p could be explained as: when A_p is smaller than the size of the lasing mode, the optical gain is not fully overlapped with the lasing mode. Hence, enlarging A_p increases the overlapped area and then results in the reduction of I_{th} . Once A_p covers the entire lasing mode, there is no further increasing of the effective gain for this mode, and thus the critical A_p is reached. From Figure 1.1(b), it is observed that the critical A_p is smaller for a random media with a smaller l_t . This is also expected as from the speckle pattern measurement, as l_t decreasing, l_d i.e. the size of lasing mode is also reduced,^{63,76} so the pump area required to fully cover the random mode is also smaller.

Besides A_p , there was also observation and arguments that lower I_{th} could be resulted from increasing the sample size, L . It is suggested that with larger sample

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size, there is higher probability of having optimum configurations of high quality cavities rather than the formation of larger cavities. Thus, if the cavity quality is sufficiently good, the design of an efficient random laser does not require a large L .⁷⁷

Figure 1.1 The incident pump intensity at the lasing threshold versus (a) l_t/λ and (b) the area of the pump beam spot on the sample surface. l_t are $0.9 \mu\text{m}$ (circles), and $9 \mu\text{m}$ (crosses), respectively^{54 74}.

(c) Scattering loss

The scattering loss is defined as the portion of photons be scattered out of the cavity. For a random media, the spatial inhomogeneity is large, so the scattering loss is of significance in determining the loss of a random laser. A conventional waveguide was employed to suppress the scattering loss.⁷⁸ The polycrystalline ZnO rib was buried inside of dielectric cladding layer, for example MgO, which has smaller

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refractive index. Since we have $g_{th} = \partial_{sca} + \partial_{cav} \approx \partial_{sca} + \chi L^{-1}$, where ∂_{sca} , ∂_{cav} , χ , and L are scattering loss, cavity loss, normalized cavity loss, and pump stripe length respectively. Hence, in Yuen's experiment, the threshold pump intensities were plotted against the pump stripe length. Therefore the scattering loss ∂_{sca} was obtained. It is important to note that with the MgO waveguide cladding, ∂_{sca} is reduced from 127 cm^{-1} to 70 cm^{-1} , and threshold pump intensity drops significantly from 0.69 MW/cm^2 to 0.61 MW/cm^2 .⁷⁸

1.2.3.2 Mode control

(a) Scattering strength

The mode number in a random material is strongly affected by the scattering strength. It has been experimentally found the number of lasing modes increases as l_r decreases, i.e. scattering strength increases. This is because when the scattering strength increases in a random material, the loss of the closed loop cavities decreases accordingly. Thus, there are more cavities with loss smaller than resonance gain, and more lasing modes would emerge under the same pump.^{41,54} However, to design a random laser which suppresses side modes, it is not desired to reduce the scattering strength, which increases the threshold. Moreover, it is really difficult to achieve a proper scattering strength which sustains only single mode operation by controlling the scatterer concentration N and the scatterer size R_s .

(b) Pump area or sample size

Other than reducing the scattering strength, side mode suppression could be achieved by reducing the pump area (i.e. A_p) or sample size L . As the lasing resonance occurs by recurrent scattering inside of a closed loop cavity, different lasing modes

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corresponds to different closed loop feedback paths, which are not spatially overlapped due to the gain competition.⁵⁴ Therefore when A_p or L reduces, there are less closed loop paths formed, and then less lasing modes emerges. This has been demonstrated by inspecting the saturated number of lasing modes of a random media with various sizes as described in Figure 1.2(b).⁵⁴ It could be clearly understood that the number of random mode could be excited is reducing with L . It has also been found that interestingly as A_p keeps decreasing to a critical area, laser oscillation stops. It means this critical area is too small to form a closed loop feedback. So in this way the size of a single random mode could be estimated.⁴⁵ Leong also demonstrated the lasing modes are roughly linearly proportional to the width of the ZnO rib waveguide.⁷⁹ Therefore it is clear that if we manage to confine the only few closed loop path inside of the gain medium, it is possible to efficiently suppress the side modes.

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Figure 1.2 (a) The number of lasing modes as a function of l , at the fixed incident pump pulse energy of 1.0 μJ , (b) saturated value of the number of lasing modes as a function of the sample size⁵⁴.

(c) Mode repulsion

As introduced in the upper section, each random mode occupies a certain area. Thus the localization of the random modes results in the mode repulsion spatially. This means the saturated number of lasing modes is proportional to the scale of the random media. Besides this, mode repulsion in spectral domain instead of in spatial domain could occur in a random media with inhomogeneous broadening. This is proved by Cao's group experimentally.⁸⁰ In preparing the disordered media, the different local strains and distortions in each individual dye molecule generate a large inhomogeneous broadening. It is observed from the spectra as shown in Figure 1.3(a), the number of lasing modes increases with the pumping intensity, and eventually, the wavelength spacing between the adjacent lasing modes no longer decreases at a further increase of pumping intensity. New lasing peaks can only emerge away from the gain maximum. As another evidence of spectra repulsion, the normalized spectral correlation function $C(\Delta\lambda)$ was examined. The oscillation period of $C(\Delta\lambda)$ gives the average separation between the adjacent lasing modes. From Figure 1.3(b), it is found the lasing modes are evenly distributed in the spectra with very similar wavelength spacing.

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Figure 1.3 (a) Spectrum of laser emission from the PMMA containing dye and microparticles. The incident pump pulse energy is 1.6 μ J. (b) Normalized spectral correlation function $C(\Delta\lambda)$ ⁸⁰.

Generally, there are two prerequisites for the occurrence of the spectral repulsion. Firstly, the spatial extent of lasing modes should be larger than the excitation area. In this way, to acquire gain, the spatial mode overlapping is forced to be formed. The spatial profile of the individual lasing mode was measured by the spectrally resolved speckle technique. It is interesting to find the lasing mode is larger than the size of the pump area. Secondly, it requires the frequency separation between two adjacent modes is smaller than one homogeneous linewidth^{81,82} of the gain media. This is because a lasing mode interacts only with the gain media whose transition frequency is in resonance with the lasing frequency.⁸⁰ So the lasing modes with frequency more than one homogeneous linewidth away would not be affected. Therefore the number of a random laser could be controlled with proper coupling design even at high excitation.

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1.2.3.3 Directional emission

Random lasers have a fatal defect as high scattering loss and off-axial emission due to the nature of the resonance mechanism. In a thin film material embedded with highly disordered scatterers, since the film thickness is close to the optical scattering mean-free path, but is much smaller than the lateral size of the excitation area, the lasing cavities formed by optical scattering are located in the plane of the thin film. Unlike the emission from the Fabry-Perot cavity, the emitted lasing light from different random cavities can go to different direction in the thin film plane. Moreover, as the film thickness is approaching optical scattering mean-free path, there are large chances for the emitted light to be scattered out of the thin film plane by intracavity scattering. This will again reduce the directional emission intensity and impair the usefulness of random laser as shown in the schematic diagram in Figure 1.4⁸³.

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Figure 1.4 A schematic diagram showing the random laser cavities in the ZnO thin film. (a) Laser output from the edge of the sample; (b) laser emission scattered out of the surface of the film⁸³.

Yuen has demonstrated that by defining a ridge waveguide on the highly disordered ZnO thin film with MgO capped layer, the scattering loss and off-axial emission from the ZnO thin film could be significantly reduced.⁷⁸ With MgO capped layer, the lasing emission detected from the edge of the waveguide is enhanced at the fixed excitation and a single bright-spot emission is observed from the exit of ridge waveguide. The reason of the improvement of directional emission is that since MgO has smaller refractive index (~ 1.75) than ZnO (~ 2.1), the MgO capped layer traps the light scattered from the ZnO grains and voids to the surface and to the sides of the ridge by total internal reflection. Therefore, the scattering loss is largely reduced and the emission is guided in the direction of ridge waveguide.

1.2.4 Random laser diode design

1.2.4.1 Three designs of conversion efficiency enhancement

For the design of laser diode, one of the most primary concerns is to achieve a high optical gain, so as to sustain the lasing action and carry out efficient electro-to-optical conversion. However, for achieving a sufficient optical gain, the largest obstacle in realizing the electrically pumped ZnO random laser is the low carrier accumulation in the gain media due to the poor injection efficiency and electrical

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confinement. In the following paragraphs, the previous effort on enhancing the carrier confinement and thus optical gain are reviewed.

(a) ZnO-SiO₂ nanocomposite heterojunction diode

By embedding ZnO powder in a SiO₂ matrix, nanocomposite clusters are formed as the scatterers to enhance the light extraction efficiency.⁸⁴ The ZnO-SiO₂ clusters have a strip pattern. With adjusting a proper strip width and spacing, the closed-loop zigzag paths are formed as the coherent feedback to sustain the lasing action. A *p-i-n* structure was used by sandwiching the intrinsic ZnO-SiO₂ nanocomposite layer between electron and hole injection layers (i.e. Al doped ZnO and *p*-SiC(4H) respectively).⁸⁵ In this way, the carrier concentration in the gain layer is significantly increased, so that the electron-to-photon conversion efficiency is enhanced.⁸⁶ In a further step, by choosing the hole injection layer as *p*-GaN which has relatively low refractive index, the transverse confinement has been achieved and the off-axial scattering to the surface has been reduced.⁸⁷

(b) Au/SiO₂/ZnO heterojunction diode

A metal-insulator-semiconductor (MIS) structure was employed to enhance the electron-photon conversion efficiency. 100 nm SiO_x ($x \leq 2$) is sandwiched in between an Au layer and polycrystalline ZnO layer with random oriented grains. As depicted in the band diagram in Figure 1.5(a), when the Au and ZnO layers are biased with positive and negative voltages respectively, electrons are injected

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towards the Au layer and blocked by the large energy barrier of SiO_x layer. Thus, the electron concentration in the downwards-bend region of the conduction band of ZnO is largely increased. This carrier confinement results in a significant gain enlargement.^{88,89}

(c) *n*-ZnO/MgO/*p*-GaN heterojunction diode

In this case, heavily doped *p*-GaN layer was chosen as the hole injector. A 30 nm MgO layer was sandwiched in between *p*-GaN and *n*-ZnO layers. When the heterojunction is forward biased, electrons are drifted from ZnO layer towards *p*-GaN side. However, due to large conduction-band offset between ZnO and MgO (i.e. $\Delta E_C = 3.55$ eV), electrons are blocked by the MgO layer, and accumulated at the ZnO/MgO interface. Thus the electron concentration is largely increased in the gain medium, namely *n*-ZnO layer. For the hole injection, it is important to note that the valence band barrier between *p*-GaN and MgO is only 0.9 eV. Additionally, the applied forward bias upwards bends the band of MgO layer. Therefore the large amount of holes could tunnel through MgO layer to ZnO side. The band diagram of the ZnO/MgO/GaN heterostructure is depicted in Figure 1.5(b). In this way, the electron-to-photon conversion efficiency at the surface of ZnO layer is significantly enhanced due to the increases carrier concentration. The low threshold current, i.e. 0.8 mA was observed, which is about 2-order lower than that of the Au/SiO₂/ZnO random laser.^{90,91}

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Figure 1.5 Band diagram of (a) Au/SiO₂/ZnO MIS laser diode⁸⁹ and (b) n-ZnO/MgO/p-GaN laser diode⁹⁰.

1.2.4.2 Choose hole injection material

Besides the electrical confinement reviewed in 1.2.4.1, the carrier injector also plays an important role in the carrier accumulation and thus the high gain realization in the design of an efficient laser diode. As ZnO is a native n-type semiconductor, the focus of searching the carrier injectors is on the hole injection material. In the following paragraphs, the performance of the light-emitting devices fabricated with n-ZnO and various types of hole injectors are reviewed.

- (a) Firstly, the ZnO-based homojunction was realized. Huge effort has been made in order to realize the p-type conducting ZnO by different groups all over the world. However, the stable p-type conduction is difficult to achieve. This is mainly due

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to dopants are compensated by native defects such as hydrogen and Zn interstitials. Additionally, low solubility of the dopants in ZnO host and deep impurity level causing resistance to the formation of shallow acceptor level are also the reasons that make it difficult to achieve *p*-ZnO.^{92,93} Despite of that, by making huge of effort there are some successful report on ZnO with *p*-type doping. A few groups reported *p*-type conduction in ZnO by doping nitrogen (N) as shallow acceptors. The hole concentration could be raised to the order of 10^{16} - 10^{17} cm⁻³.⁹⁴⁻⁹⁶ Group III element such as gallium, aluminum, or indium was chosen to codope with nitrogen so that the solubility of nitrogen is largely enhanced and the hole concentration could be pushed 10^{18} cm⁻³.^{97,98} The *p*-type conducting ZnO has also been demonstrated by doping other group V element such as phosphorus⁹⁹ and arsenic¹⁰⁰. With these developments of *p*-type doping techniques, several groups recently reported light emitting diodes (LEDs) based on ZnO *p-n* homojunction structures. However, in most of these homojunctions light emission is dominated by the deep-level emission.¹⁰¹⁻¹⁰⁵ This is because heavy doping of *p*-ZnO generates high concentration of deep-level defects, and consequently results in high intensity defects related emission. Thus the poor crystal quality and the unstable performance of *p*-ZnO impair the near band edge UV emission.

- (b) As there is lack of reliable *p*-type ZnO, researchers had to seek the alternative hole injectors to develop heterojunctions. Among the various materials, silicon (Si) has the prominent merit by its large hole concentration and mobility as well as the low fabrication cost. Firstly *n*-ZnO was deposited onto *p*-Si to form

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heterojunction. However, the EL emission spectra were dominated by a broad peak centered at 580 nm.^{106,107} The reason is that the crystalline of Si and ZnO differs a lot, and the lattice constant for Si and ZnO with wurtzite crystal structure are 5.43071Å and $a=3.249\text{Å}$, $c=5.206\text{Å}$ respectively. Large lattice mismatch results in a large number of deep-level defects at the interface of Si/ZnO. Hence, at forward bias, electrons on the conduction band of ZnO may first fall into these empty traps and subsequently recombined with the holes injected from *p*-Si side. In addition, the conduction band and valence band offset are calculated by Anderson model as $\Delta E_C = 0.4\text{ eV}$ and $\Delta E_V = 2.55\text{ eV}$ respectively.¹⁰⁸ The large difference between ΔE_C and ΔE_V makes much larger barrier for hole injection. Therefore, this raises the turn on voltage and impairs the emission efficiency. This could be repaired by adopting *n*-Si other than *p*-Si as hole injector. Under positive bias on *n*-Si side, the valence band of Si could be possibly lower down to get closer to the valence band of ZnO, therefore this makes holes easier to tunnel to the valence band of ZnO.¹⁰⁹ However, the high density of deep-level defects states generated by the lattice dislocation at the Si/ZnO interface is a remained problem which suppresses the near band edge emission. Moreover, the large number of non-radiative defects also impairs the conversion efficiency. The ZnO/Si heterojunction normally has turn-on injection current as high as $\sim 50\text{ mA}-100\text{ mA}$.

- (c) *p*-type silicon carbide (4H-SiC) substrate also attracts researchers' attention by its high hole concentration ($\sim 1 \times 10^{19}\text{ cm}^{-3}$) and carrier mobility ($\sim 120\text{ cm}^2/\text{Vs}$). Yuen has developed a heterojunction with *p-i-n* structure by sandwiching the

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active ZnO layer by *n*-type aluminum doped ZnO (ZnO:Al) and 4H-SiC.⁸⁵ The carriers are confined in the intrinsic ZnO layer which has good crystal quality, so that the emission efficiency is enhanced. 385 nm excitonic emission was observed with limited defects related emission. However, 4H-SiC has a hexagonal crystal structure with $a=3.073\text{\AA}$, $c=10.053\text{\AA}$,¹¹⁰ which has a large lattice mismatch with wurtzite ZnO. This requires a very fine deposition of ZnO layer to ease the interface dislocation. Moreover, the fabrication of 4H-SiC is costly which limits its application as the hole injector in the ZnO-based heterojunction.

- (d) In order to eliminate the deep-level defects generated from the interface dislocation, a hole injector with similar crystalline with ZnO is desired. Gallium nitride (GaN) has the same crystal structure (i.e. wurtzite structure) as ZnO. GaN has lattice constant as $a= 3.186\text{\AA}$ and $c= 5.178\text{\AA}$, and the lattice mismatch is only $\sim 1.8\%$ as summarized in Table 1.1¹¹¹.

Table 1.1 The comparison of the structural properties of ZnO and GaN

	Crystal structure	Bandgap energy (eV)	Lattice constant (Å)
ZnO	Wurtzite	3.37	$a=b=3.249, c=5.206$
GaN	Wurtzite	3.4	$A=b=3.186, c=5.178$

With the development of high quality *p*-type GaN by magnesium (Mg) doping, extensive study has been focused onto the *n*-ZnO/*p*-GaN heterojunction. These *n*-

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ZnO/*p*-GaN LEDs exhibit the improved carrier confinement compared to ZnO homojunction, which largely enhances the recombination efficiency. Moreover, due to the limited interface trap states, the turn-on current is less than 10 mA, which is substantially reduced by about 1 order compared to the ZnO/Si heterojunction. Blue-violet emission at 430 nm has been demonstrated by Alivov's group from *n*-ZnO/*p*-GaN LED¹¹². However, by comparing the EL and cathodeluminescence (CL), it reveals that the emission is mainly attributed to the recombination at GaN side due to excess electron injection from ZnO to GaN. This has been observed in other works of *n*-ZnO/*p*-GaN junctions.¹¹³⁻¹¹⁵ This could be understood by exam the band structure of *n*-ZnO/*p*-GaN heterojunction using Anderson model as shown in Figure 1.6^{115,116} The electron affinities (χ) of ZnO and GaN are assumed to be 4.35 eV and 4.2 eV respectively. The band gap energies (E_g) of ZnO and GaN are 3.37 eV and 3.4 eV respectively. Thus as shown in the band diagram, the conduction band and valence band energy barriers are calculated as $\Delta E_C = \chi(\text{ZnO}) - \chi(\text{GaN}) = 4.35 - 4.2 = 0.15$ eV and $\Delta E_V = E_g(\text{ZnO}) + \Delta E_C - E_g(\text{GaN}) = 3.37 + 0.15 - 3.4 = 0.12$ eV. Hence, it is clear that the barriers for electrons and holes across the junction are similar. However, the electron concentration in *n*-ZnO side ($\sim 1 \times 10^{18} \text{ cm}^{-3}$) is 1 order higher than hole concentration in *p*-GaN side ($\sim 1 \times 10^{17} \text{ cm}^{-3}$). This favours electron injection and inhibits the recombination in ZnO side.

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Figure 1.6 The band diagram of ZnO/GaN heterojunction¹¹⁵.

In the n -ZnO/ p -GaN heterojunction the recombination is usually dominated by electron injection due to larger carrier concentration and mobility in ZnO. To realize excitonic emission from ZnO junction, p - i - n structure has been exploited by inserting a high optical quality intrinsic ZnO in between the n -ZnO and p -GaN layers, so that the recombination process is restricted in intrinsic ZnO layer, and ZnO excitonic UV emission with comparably narrow FWHM has been achieved.¹¹⁷⁻¹¹⁹

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1.3 Objectives

1. The first aim is to design and fabricate a ZnO-based heterojunction to realize electrically pumped random lasing with high conversion efficiency and thus low threshold current.
2. It is to minimize the scattering loss from the random laser diode to achieve a highly directional emission.
3. It is to suppress the side modes in the random laser diode by controlling the size of the random media.
4. In a further step, it is to investigate the possibility of random mode suppression even at high injection by random mode spatial overlapping and interaction.
5. Subsequently, it is to enhance the output power of a random laser by increasing the number of spectrally coherent emitters.
6. Finally it is to achieve an electrically pumped single mode dominating lasing from ZnO random media at high current injection.

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1.4 Major Contributions

This research work focuses on improving the electrical-to-optical conversion efficiency, emission directivity, and suppressing the side modes so that to overcome the shortcomings of the random laser and realize a useful ZnO-based random laser diode operating in UV regime. Two mechanisms, namely reducing the area of random media and forming spatial overlapping between random modes via lateral coupling, have been employed to limit the random side modes. Ultimately, the electrically pumped single-mode operation at high current injection has been realized. To search other candidate of wide bandgap optoelectronics devices, the possibility to realize UV light-emitting diodes by using highly disordered SnO₂ thin film was also investigated. The following paragraphs summarized the contributions of this thesis.

1. An n -ZnO:Al/ i -ZnO/ p -GaN heterojunction with a 3- μ m rib waveguide has been fabricated by filtered cathodic vacuum arc (FCVA) technique. Electroluminescence with emission peak at 387 nm was observed which is due to the radiative recombination inside of the i -ZnO layer. The injection efficiency of carriers into the i -ZnO rib waveguide is significantly improved by suppressing the lateral diffusion of carriers through the use of SiO₂ cladding layer. Optically, scattering loss is largely reduced via total internal reflection from n -ZnO:Al and SiO₂ cladding layer. The directional emission was realized from the edge of the rib waveguide.
2. Al doping was used and the annealing temperature and time were carefully chosen. In this way the large grains and void, (i.e. random cavities) were formed inside of the i -ZnO layer, and the i -ZnO layer could maintain a comparably high

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electrical conductivity. Coherent random lasing action was achieved by electrical excitation. With the buried rib waveguide, the lasing threshold was reduced by 30% and collimated emission beam was realized from the edge of the laser diode. The number of lasing peaks was significantly reduced as the size of closed-loop cavity modes is limited by the width of the rib waveguide.

3. An index-guided ZnO random laser array with 1.5 μm wide ZnO core and with 0.8 μm wide ZnO:Al(3%) cladding layer were designed and fabricated to investigate spectral repulsion via lateral coupling between the random modes. With the ZnO:Al(3%) coupling layer, the number of lasing modes was significantly reduced at high excitation power, and the far-field beam with double-lobed pattern was observed, which verifies the strong lateral coupling of adjacent lasing modes. In addition, the output power was enhanced by the addition of the individual random lasers which are spectrally coherent.
4. $n\text{-ZnO:Al(5\%)/1 } \mu\text{m-wide } i\text{-ZnO:Al(3\%)} \text{ random cavities}/p\text{-GaN:Mg}$ heterojunction arrays was fabricated. Al_2O_3 (with 1 μm in width) was selected as the dielectric insulator to achieve strong optical interelement coupling between the adjacent random cavities. Stable single-mode operation has been obtained from the proposed laser diode arrays under high electrical excitation (i.e., $> 6 \times$ threshold current). The quality factor can reach 1200 at high injection. Single-lobed far-field pattern is maintained over the operation conditions indicating only fundamental lateral mode is supported in the individual laser element.
5. Highly disordered SnO_2 thin film was studied as another potential candidate for the application of wide-band optoelectronics devices. Polycrystalline n-type

Chapter 1 Introduction & literature review

SnO₂ thin film was deposited on to *p*-SiC substrate by FCVA technique. Post-growth annealing is proposed to generate the well-separate grains and voids randomly inside the as-grown SnO₂ thin film so that the surface area exposed to the environment is largely increased. Hence, the increase of surface states increases the shallow trapped states supporting the intense defect-related emission. The dominating emission peak at 392 nm was observed under forward bias from radiative recombination between electrons captured at the surface defect states of small SnO₂ grains and holes injected from the *p*-SiC substrate.

Chapter 1 Introduction & literature review

1.5 Organization

In chapter 1, the background and motivation of this research work are presented. Subsequently, literatures of the fundamental of coherent random lasing, guidelines of improvement on threshold, mode control and directivity of the random laser, as well as ZnO random laser diode design are reviewed. After that, the objective of this work is presented, and the contribution is summarized. Chapter 2 briefly introduces the fabrication, measurement, and characterization techniques used in this thesis. Chapter 3 demonstrates the electrically pumped random lasing, efficiency improvement and directional emission from $n\text{-ZnO}/i\text{-ZnO}/p\text{-GaN}$ light-emitting diode (LED) with a 2- μm buried rib waveguide. The suppression of side modes by employing the rib waveguide is also demonstrated and discussed in this chapter. In chapter 4, lateral coupling and spectra repulsion of random modes is investigated in an index-guided ZnO random laser array by optical excitation. In a further step, stable single-mode operation is demonstrated in a $n\text{-ZnO:Al}(5\%)/i\text{-ZnO:Al}(3\%)$ random cavities/ $p\text{-GaN:Mg}$ laser diode array in Chapter 5. As another candidate of UV optoelectronic devices, SnO_2 thin film with well-separated gains and $\text{SnO}_2/p\text{-SiC}(4\text{H})$ LED are fabricated and studied in Chapter 6.

Chapter 2 Fabrication and Characterization Techniques

2. Fabrication and Characterization Techniques

2.1 Fabrication Techniques

2.1.1 Thin Film Deposition Technique

The Filtered Cathodic Vacuum Arc (FCVA) technique is a physical vapour deposition technique. FCVA has advantages: good crystal quality with limited defects states and low temperature deposition. It could be understood by knowing the working principle of the FCVA technique. Figure 2.1 shows the schematic diagram of the FCVA system. The system consists of a cathodic vacuum arc source, anode-cathode coils, an off-plane double-bend (OPDB) plasma-filtering duct, and a deposition chamber^{120 121}. The target is located at the cathode. When biased, the act of striking the trigger onto the target produces cathodic arc spots and plasma discharge is formed. The plasma beam consists of macroparticles and neutral atoms. To control the fineness of the plasma, a magnetic filter is used in our deposition technique where the plasma ions are guided by a filtering-duct, as depicted in the right part in Figure 2.1 known as an OPDB filter.¹²² It has two-torus bends at 90° and 45° with respect to axis of the cathodic vacuum arc source. The exterior wall of the filtering duct is surrounded by a set of magnetic coils for the generation of magnetic field to guide the plasma ions from cathode source to substrate, while its interior is equipped with baffles that are designed to catch or to reflect macroparticles. Only the ions with desired mass, charge polarization and charge number could be guided by the magnetic field to substrate. More importantly, the OPDB filter is effective in eliminating macroparticle contamination in the deposited films with increasing

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number of macroparticles hitting the walls of the plasma duct. It is to be noted that under the large magnetic field ($\sim 0.1\text{T}$) inside of the duct, the ions make helical motion about the center of the toroidal duct at a very high speed.¹²³ Thus the energetic ions provide a kind of pseudotemperature for the synthesis of crystalline films by improving the mobility of surface atoms. This exchange of kinetic energy from the energetic ions to the atomic surface motion of ZnO film eliminates the need of substrate heating. We have estimated that the pseudotemperature of the energetic ionized Zn species is equivalent to the substrate temperature of $\sim 300\text{ }^{\circ}\text{C}$. The use of cathodic vacuum arc source and OPDB plasma-filtering duct is to generate high-energetic ionized species with supreme fineness. In the FCVA system in reference ¹²⁰, the gas pipe is inserted at $\sim 30\text{cm}$ away from the substrate. Hence metal oxide plume is formed 30cm length away and transported to the substrate. This implies that the formed metal oxide plume has a high chance to be bombarded by the remaining dense and energetic ionized metal species within the 30cm length before depositing on the substrate. In this case, high probability of metal interstitials can be formed inside the film and high substrate temperature is required for the removal of metal interstitials.¹²⁴ As for the modified FCVA technique for the metal oxide deposition, the gas curtain of O_2 is introduced only a few millimeters above the surface of the substrate. By surrounding the substrate with reactive O_2 , the density of ionized metal species is largely reduced and the change of bombardment on the metal oxide plume before deposition on the substrate by the ionized Zn species is reduced. Thus, the metal interstitial inside of the film could be largely suppressed without applying high substrate temperature. Therefore, metal oxide thin film with high crystal quality

Chapter 2 Fabrication and Characterization Techniques

could be deposited at low substrate temperature ($< 200^{\circ}\text{C}$). However, the disadvantage of the modified design is that the deposition rate is 5 to 15 times slower than that of the old design. Therefore, with the capability of fine filtering of macroparticles and high ion energy, the ZnO films deposited by FCVA technique exhibit strong UV emission with suppressed defect-related luminescence such as green emission which is originated from Zn interstitial (Zn_i).

Figure 2.1 Schematic of the FCVA system. The OPDB filtering duct is also depicted.

Besides ZnO, it is convenient to deposit other metal oxide semiconductors by the FCVA technique. In chapter 6, Tin (Sn) was used as the metal source. As the melting temperature of Sn is low, the Sn target would be melted under the high arc current. Thus as shown in Figure 2.2, a copper cup was designed as the target holder to

Chapter 2 Fabrication and Characterization Techniques

contain the liquid metal source. A boron nitride ring was also designed to shield the top surface of the copper cup to avoid contacting the striker and generating the copper plasma. It is worth noting that to tune the exit angle of the plasma, especially for the heavy ions such as Sn ion, another set of electric coils were placed at the exit of the filtering duct denoted by * as shown in Figure 2.1.

Figure 2.2 The photo images of the copper cup target holder and the boron nitride shielder for the Sn target

2.1.2 Device Fabrication Techniques

(a) Photolithography

AZ 5214 was used as positive photoresist. A Quintel Corporation Q4000-4 mask aligner was used for making waveguide patterns on the deposited thin film. The mask used is the quartz mask with chrome patterns.

(b) Ion Beam Sputtering

Chapter 2 Fabrication and Characterization Techniques

A Kaufman ion source¹²⁵ is used for dry etching after the photoresist pattern is made. With the argon (Ar) gas flowing, a thermionic cathode filament provides a source of electrons to support a magnetically confined plasma discharge. The impact of the ions erodes the target, abrading away the areas not covered by the photoresist. The cathode voltage is ~ 800 V. Since the ion beam etching has high anisotropic directionality, it is able to accurately provide much smaller feature size and define better vertical side wall than the wet etching technique. Moreover, the cost is not high and the etching rate (i.e. a few nm per minute for ZnO etching) is acceptable.

(c) Electron Beam Evaporator

An electron beam is used to heat the source material inside a vacuum chamber to the temperature point at which it starts to boil and evaporate. The evaporated material is then condensed on the substrate.¹²⁶ For this thesis, two electron beam evaporators (E-beam) are adopted for SiO₂ and metal contact deposition. The working pressure for SiO₂ and metal is $\sim 2 \times 10^{-5}$ and 8×10^{-6} Torr respectively. For both the material, 7 kV accelerating voltage is applied to generate electron beam with high kinetic energy. Most ($> 85\%$) of the kinetic energy is converted into thermal energy as the beam bombards the surface of the material ingots, and thus transform the material into the gaseous phase and then precipitate into solid form on substrate.

Chapter 2 Fabrication and Characterization Techniques

2.2 Characterization and measurement Techniques

2.2.1 Photoluminescence (PL) Spectroscopy

Figure 2.3 Photoluminescence measurement setup

The tripled-frequency pulsed Nd:YAG laser with 10 Hz pulse rate and 6 ns pulse duration is adopted as the optical excitation source. One filter for 352 nm light is used to filter the 532 nm excitation so that the pumping wavelength is 355 nm. As described in Figure 2.3, one cylindrical lens is used to focus the excitation light to a strip with variable width. The divergent emission from the excited device is collected

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by a spherical lens and the emission wavelength is detected by the monochrometer. One photomultiplier tube (PMT) multiplies the current produced by the incident light to make low-noise and high-sensitivity detection possible. Signal and reference frequency, which can be detected by a frequency detector attached inside of the laser source, are input to a lock-in amplifier. The component of the signal with distinct frequency and phase are filtered out so as to further improve the signal-to-noise ratio. The output readings are recorded by a Labview program.

2.2.2 Electroluminescence (EL) Spectroscopy

Figure 2.4 Electroluminescence measurement setup

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The EL measurement was conducted by driving the sample with a pulse voltage. This is to prolong the lifetime of the sample and reduce the noise level of the signal with the lock-in technique. A pulse modulating circuit is built by using a BJT (BDX33C) and resistor (10K Ω) as shown in the Figure 2.4. A pulse form from a function generator biases the base of the BJT. The pulse bias is taken from the collector. It has the DC power supply as the magnitude. The wavelength detection and signal magnification mechanisms are the same as that in PL measurement except that the reference frequency signal is proved by the lock-in amplifier.

2.2.3 Field Profile Measurement

(a) Near Field Measurement

The excitation of the sample is the same as that described in the PL measurement. In order to tell the wave mode from a light-emitting device, the size and shape of the emission pattern within the Fresnel zone need to be characterized as near field profile. Since for lasers operating in the UV regime, the size of the aperture is further reduced, an optical microscope is used to magnify the near filed pattern as shown in Figure 2.5. The objective lens is focused onto the emission facet of the sample. With maximum $\times 100$ and $\times 10$ magnifications from the objective lens and eye lens respectively, the emission pattern with a few μm size could be observed clearly.

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Figure 2.5Near field profile measurement setup

(b) Far Field Measurement

In order to characterize the divergence of the emission beam, far field pattern of the emission is measured. When the far-field pattern was excited optically by a laser, black paper plan with 1 mm slit was placed in front of the emitter to only let the emitted light penetrate through, while block the exciting laser light. The emitter is placed far away from the focal length of the lens, and the white paper plane is located at a distance from the lens which is slightly larger than the focal length. The relation of $1/u + 1/v = 1/f$ is followed. The setup configuration is described in Figure 2.6.

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Figure 2.6 Far field profile measurement setup

2.2.4 X-ray Diffraction (XRD)

The X-Ray diffraction pattern was measured by the Siemens D5005 diffractometer with $\text{CuK}\alpha$ ($\lambda = 0.154 \text{ nm}$) radiation (40 kV, 40 mA).¹²⁷ The incident angle was fixed at 1° . The detection mode (2θ) mode was employed. X-ray diffraction is guided by the Bragg equation, $2d \sin\theta = n\lambda$, where d is the spacing of the atom planes, 2θ is the Bragg diffraction angle, n is an integer and λ is the wavelength of the incident x-ray. Thus, by detecting θ , d corresponding to different crystal orientation can be determined from the equation, and the crystal structure and lattice constant can thus be determined. Additionally, The grain size (D) could be estimated using Scherrer equation, $\frac{0.9\lambda}{B \cos\theta}$,¹²⁸ where B is the line broadening at half the maximum intensity (FWHM) of the diffraction peak in radians.

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2.2.5 Microscopy

Scanning electron microscopy (SEM)¹²⁹ and Atomic force microscopy (AFM)¹³⁰ were used for characterizing the surface morphology of the thin films.

- 1) Scanning electron microscopy (SEM) (JEOL JSM-6340F and JEOL JSM-5910 LV) was employed to investigate the film surface and cross-sectional view.
- 2) AFM was used to analyze the surface morphology of the films in tapping mode (Digital Instruments NanoScope IIIa). The resolution of root mean square (RMS) roughness is 0.1 nm.

2.2.6 Spectrophotometer

Transmittance of thin films were measured by UV-Vis spectrophotometer (HP 8453, 190nm ~ 1100nm).¹³¹ A bare quartz substrate was chosen as the reference. The transmittance was calibrated against the reference data. The transmittance, T , is expressed as $T = I_t/I_o = \exp(-\alpha \times d)$, where I_o and I_t are the incident and transmitted light intensity respectively, α is the absorption coefficient, and d is the thin film thickness. Thus, α could be obtained by knowing the transmittance. The bandgap energy could be determined from α , as α is linearly proportional to $\sqrt{E_g}$ for a direct bandgap semiconductor and E_g^2 for an indirect bandgap semiconductor.

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3. *n*-ZnO:Al/*i*-ZnO/*p*-GaN heterojunctions with buried rib waveguide

3.1 Introduction

As reviewed in Chapter 1, ZnO random media have been considered as the laser cavities to fabricate electrically pumped ultraviolet (UV) laser diode. This avoids the difficulty to realize sufficiently smooth facets, which would be more difficult as the operating wavelength getting shorter. However, only the light scattered going through a closed-loop feedback, and coming back to the original position contributes to the lasing output. In another word, high scattering loss of random media requires high optical gain to sustain random lasing action. Therefore, to realize electrically pumped random laser, there is a large necessity to diminish the optical loss and enhance the electrical and optical confinement. Hence, the use of ZnO-SiO₂ nanocomposite film, which has high electrical-to-optical conversion efficiency, was proposed to achieve random laser diodes.^{86,87} Alternatively, electrically pumped random laser was obtained from metal-SiO₂-polycrystalline ZnO film where the ZnO/SiO₂ interface forms an electron accumulation layer to improve radiative recombination efficiency of the polycrystalline ZnO film.⁸⁸ Similarly, a MgO thin film was used as an electron blocking barrier to confine the carriers at the MgO-ZnO interface, so that to enhance the conversion efficiency of the polycrystalline ZnO-GaN heterojunction laser diode.⁹⁰ However, the carriers are free to diffuse at the insulator-ZnO interface, i.e., there is no electrical confinement in the lateral direction. Additionally, by the nature of the random lasing mechanism, the light emitted is

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towards random directions. Hence, the external efficiency is again harmed by lack of optical confinement. Therefore a conventional index-guided laser structure with buried rib waveguide was used to form both electrical and optical confinement in both transverse and lateral directions. It is expected to achieve low lasing threshold and directional emission. In the section of 3.2, the ZnO-based index-guided heterostructure with buried rib waveguide was designed and fabricated. Its electrical and optical properties are investigated. In section 3.3, the buried rib waveguide was employed to reduce lasing threshold and achieve directional emission in electrically pumped ZnO random laser.

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3.2 Edge-emitting *n*-ZnO:Al/*i*-ZnO/*p*-GaN LED with rib waveguide

3.2.1 Design considerations

To design an index-guided ZnO waveguide, it is the prerequisite to achieve the desired electrical properties, refractive indices, and bandgap energy by element doping and bandgap engineering in ZnO, therefore the electron and hole injection layers as well as the cladding layer were properly chosen. The previous works have demonstrated that electrical and optical properties of ZnO could be tuned by Al doping as shown in Table 3.1.

Table 3.1 Bandgap energy, carrier concentration and refractive index of different layers of the heterojunction.

	Bandgap (eV)	Carrier concentration (cm ⁻³)	Refractive index
ZnO	3.37	10 ¹⁸	2.1
ZnO:Al(3%)	~ 0.05 blue shift ¹³²	10 ²⁰	~2.09 ¹³²
ZnO:Al(5%)	~ 0.07 blue shift ¹³²	10 ²¹	~2.08 ¹³²
GaN:Mg	3.4	5×10 ¹⁷	2.5 ¹³³
SiO ₂	8.9 ¹³⁴	-	1.45 ¹³⁵

The carrier concentration could be largely increased (more than 2 orders) by Al doping. This makes ZnO:Al as a good electron injector. In addition, due to Burstein-Moss effect the absorption edge of Al-doped ZnO is blue shifted by more than 0.05 eV, which could eliminate the emission re-absorption in the electron injection layer.

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More importantly, the refractive index of Al-doped ZnO is slightly reduced. Thus by properly choosing the Al doping concentration, the index guide in the transverse direction is realized. The use of *p*-GaN is due to its bandgap energy (3.4eV) and lattice constant (lattice mismatch ~1.8%) match with that of the ZnO as well as the irreproducibility and low quality of *p*-type ZnO as introduced in Chapter 1 section 1.2.4.2. In the lateral direction, SiO₂ was used as insulating and cladding layer for the buried ZnO waveguide. It confines the carriers and emitted light inside of the waveguide.

As an efficient waveguide, the dimensions are essential for realizing high electro-optical conversion efficiency. In order to compensate the loss in the waveguide and enhance the emission sufficiency, it is desired to have a large confinement factor Γ so that to ensure small g_{th} , where $\Gamma g_{th} = \partial_{int} + \partial_{sca}$. Here g_{th} , ∂_{int} and ∂_{sca} are threshold gain, internal loss in the cavity, and scattering loss. The confinement factor is defined as the ratio of power of the guided mode flowing in the active layer to the total power flow which is expressed in equ. (1) for a TE mode wave in a waveguide structure with the width as w .

$$\Gamma = \frac{\int_0^w |E_y(x)|^2 dx}{\int_{-\infty}^{+\infty} |E_y(x)|^2 dx} \quad (1)$$

Substituting equ. (A1) from Appendix A into equ. (1), the confinement factor for the wave in the lateral direction could be derived as

$$\Gamma_{lat} = \frac{k_o^2(w)^2(n_{eff2}^2 - n_{eff1}^2)}{2 + k_o^2(w)^2(n_{eff2}^2 - n_{eff1}^2)} \quad (2)$$

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,where n_{eff2} and n_{eff1} are the effective refractive index of waveguide core and cladding column respectively and k_o is free space wave vector. Different effective refractive indices n_{eff2} and n_{eff1} corresponding to different *i*-ZnO layer thickness are calculated by transfer matrix method as shown in Table 3.2

Table 3.2 Different effective refractive indices n_{eff2} and n_{eff1} corresponding to different *i*-ZnO layer thickness

<i>i</i> -ZnO thickness (μm)	n_{eff2}	n_{eff1}
0.05	1.8929	1.7998
0.1	1.9278	1.7957
0.15	1.9830	1.7950
0.2	2.157	1.7944

Therefore by estimating the transverse confinement factor $\Gamma_{tra} = 0.98$, the overall confinement factors in the form of $\Gamma = \Gamma_{lat} \cdot \Gamma_{tra}$ are plotted using equ. (2) versus the waveguide width *w* and the *i*-ZnO layer thickness in Figure 3.1. It is noted that as $w > 2 \mu\text{m}$, Γ is reaching a saturated value. Additionally, as the *i*-ZnO layer thickness $\geq 0.15 \mu\text{m}$, $\Gamma \sim 0.98$ which indicates good wave confinement could be achieved. Therefore 0.15 μm and 3 μm are designed as the transverse and lateral dimension of the waveguide structure respectively to achieve high field confinement and yet support minimum optical modes. It is worth noting that from calculation, by choosing 0.15 μm thick *i*-ZnO, the maximum number of transverse modes is less

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than 3. Additionally, 0.15 μm is closed to $\lambda/n_{\text{zno}}=0.39/2.1$ to provide a sufficient scattering cross section area. Large value of the thickness is not desired to avoid large resistance across the junction.

Figure 3.1 Confinement factor Γ versus the waveguide width w and the *i*-ZnO layer thickness (0.05, 0.1, 0.15 and 0.2 μm).

Therefore, the designed schematic of *n*-ZnO:Al/*i*-ZnO/*p*-GaN heterostructure with rib waveguide is as shown in the schematic below.

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Figure 3.2 Schematic of *n*-ZnO:Al/*i*-ZnO/*p*-GaN heterojunction with buried rib waveguide.

3.2.2 Fabrication process

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Figure 3.3 Fabrication procedures of the index-guided heterojunction with buried rib waveguide.

As shown in Figure 3.3, (a) a $4 \times 10 \text{ mm}^2$, $2 \text{ }\mu\text{m}$ (0001) *p*-GaN:Mg on sapphire substrate (purchased from Semiconductor Wafer, Inc) with hole concentration as $5 \times 10^{17} \text{ cm}^{-3}$ was used as *p*-type substrate. A 150 nm thick intrinsic ZnO (*i*-ZnO) film was deposited onto half of the *p*-GaN:Mg/sapphire substrate by using FCVA deposition technique. During deposition, substrate temperature and oxygen partial pressure were set to $\sim 150 \text{ }^\circ\text{C}$ and $2 \times 10^{-5} \text{ Torr}$ respectively.¹²⁴ (b) Subsequently, a line-mask (with width, thickness and separation equal to $3 \text{ }\mu\text{m}$, $0.8 \text{ }\mu\text{m}$ and $500 \text{ }\mu\text{m}$ respectively) was coated onto the surface of the *i*-ZnO film by photolithography technique. The recipe of the photolithography process is summarized in the Table 3.3. (c) The unmasked *i*-ZnO layer was then completely removed by ion-beam sputtering with an etching rate of $\sim 10 \text{ nm/min}$ for 15 min.⁷⁸ The recipe of the ion-beam sputtering is summarized in the Table 3.4. (d) Then, a 120 nm thick of SiO_2 cladding layer was deposited onto the sample by E-beam evaporation with substrate temperature set to be $50 \text{ }^\circ\text{C}$. (e) After the deposition, a lift-off process was carried out to remove the excess SiO_2 layer attached on the surface of the *i*-ZnO rib waveguides. The sample was rinsed with acetone in an ultrasonic cleaner for 5 minutes. (f) Finally, a layer of *n*-ZnO:Al (5%) with thickness of 100 nm was deposited onto the sample by the FCVA technique. The carrier concentration of *i*-ZnO and *n*-ZnO:Al (5%) films was verified to be about 10^{18} and 10^{21} cm^{-3} respectively. In addition, it is noted

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that the *n*-ZnO:Al (5%) film has a bandgap of ~0.07 eV wider than that of the *i*-ZnO film [10]. In this case, the *n*-ZnO:Al (5%) layer serves as a transparent injector of electrons. A 100 nm thick Au film was deposited onto the *p*-GaN:Mg/sapphire substrate as the *p*-type metal contact by E-beam evaporation. In addition, 100 nm Ni film was used as the metal contact on the *n*-ZnO:Al(5%) layer. For the purpose of comparison, another *n*-ZnO:Al/*i*-ZnO/*p*-GaN heterojunction LED without a rib waveguide structure was also fabricated.

Table 3.3 Recipe of photolithography process

Spin coating	Photoesist	Prebake	Exposure	Develop
4000 rpm, 30 sec	AZ5214	106°C, 1 min 45 sec	3 mW/cm ² , 24 sec	Developer/water=1:2, 1 min 10 sec

Table 3.4 Recipe of ion beam etching

Ar pressure	Ion beam	Cathode	Discharge	Accelerator	Neutralizer
4×10 ⁻⁴ Torr	800 V, 80 mA	6 V, 22 A	40 V, 0.4 A	300 V, 10 mA	10 V, 40 –50 mA

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3.2.3 Results and discussion

3.2.3.1 Optical and electrical properties of heterojunction with and without rib waveguide

Figure 3.4 gives the EL spectra of the heterojunction LED with rib waveguide at different bias voltages. A rectangle pulse voltage source (with repetition rate and pulse width of 7.5 Hz and 80 ms) was used to bias the LED. The emitted light was collected from the edge of the LED by an objective lens. The corresponding PL spectra of the i -ZnO and p -GaN:Mg layers are also plotted in the insert of Figure 3.4. For the PL measurement, the samples were excited by a 355nm pulsed source (10Hz, 6 ns). It is observed from Figure 3.4 that all the EL spectra exhibit only UV emission with peak at 387 nm, and this agrees well with that of the PL spectra of the i -ZnO layer. This indicates that radiative excitonic recombination occurs inside the i -ZnO layer of the heterojunction LED. As n -ZnO usually has higher carrier concentration than that of GaN:Mg, it is expected that a large portion of recombination will be taken place inside of GaN region. Therefore, some previously reports have detected emission from p -GaN:Mg layer of the ZnO/GaN heterojunction LEDs [5]. However, no emission was detected from the p -GaN:Mg layer of our proposed n -ZnO:Al/ i -ZnO/ p -GaN heterojunction LED. This is because the proposed p - i - n heterojunction confines radiative excitonic recombination inside the i -ZnO layer. The heterojunction LED without rib waveguide exhibit similar EL spectra (not shown in the figure) except that the emission intensity is lower than that with a rib waveguide. Figure 3.5(a) and 3.5(b) show the photos of the rib waveguide and its corresponding

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emission image respectively taken by a CCD cameral of electric microscope. It is confirmed that the emission is from the edge of the rib waveguides.

Figure 3.4 EL spectra of the heterojunction LED with rib waveguide. The insert shows the PL spectra observed from *p*-GaN and *i*-ZnO layers.

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Figure 3.5 Photographs of (a) the heterojunction LED with rib waveguide and (b) its corresponding EL emission image.

Figure 3.6(a) shows the current-voltage (I-V) characteristics of the heterojunction LEDs with and without rib waveguide. Both I-V curves exhibit rectifying diode behaviour. It is observed that the turn-on voltage of the heterojunction LED can be reduced from 6 to 3.5 V, and the positive-bias current is larger with the presence of a rib waveguide. This is because the transport of the injected carriers is highly confined inside of the narrow waveguide core. While at negative bias, the diode with rib waveguide has larger reverse-biased current. This may be attributed to that significant amount of surface defect states are created at the side wall of the rib waveguide. It may facilitate the diffusion of carriers through the junction. The insert of Figure 3.6(a) shows the I-V characteristics of the Ni-Ni metal contacts on n -ZnO layer as well as Au-Au metal contacts on p -GaN:Mg/sapphire substrate. It is observed that these two types of metal contacts have a relatively good ohmic property. The light-voltage (L-V) curves of the heterojunction LEDs with and without rib waveguide are also given in Figure 3.6(b). It is noted that the presence of a rib waveguide structure enhances the emission intensity by ~ 5 times and the turn-on voltage is reduced from 6V to 3.5V. This is because the rib waveguide strongly confines injection carriers (i.e., the high resistivity of SiO_2 cladding layer confines the carriers injected into the i -ZnO layer) and light (i.e., the refractive index of i -ZnO layer is slightly larger than that of n -ZnO:Al layer and GaN:Mg as well as higher than that of SiO_2 cladding layer so that light is confined along the lateral and

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transverse directions of the rib waveguide through total internal reflection) inside the *i*-ZnO layer so that the corresponding electrical-to-optical conversion is improved. The near field profiles of the heterojunction LEDs are also shown in the insert of Figure 3.6(b). Single light spot is emitted from the edge of *i*-ZnO rib waveguide. This indicates the emission is strongly confined by the rib waveguide and SiO₂ cladding layer, and the emission is directional.

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Figure 3.6 (a). I-V curves of the LEDs with and without a rib waveguide. The inset shows the I-V characteristics of the Ni-Ni electrodes on *n*-ZnO and Au-Au electrodes on *p*-GaN:Mg/sapphire substrate. (b) L-V curves of the diode with and without a rib waveguide. The inset shows the corresponding near field profile.

3.2.3.2 Polarization properties of heterojunction with and without rib waveguide

Polarization behaviour of the heterojunction LEDs is also studied in order to analyze the optical confinement characteristics of the rib waveguide which is designed to control the emission of a random laser. Figures 3.7(a) and (b) show the L-V curves and EL spectra respectively for the TE and TM polarizations of the heterojunction LED without a rib waveguide. It is noted from Figure 3.7 that the TE and TM polarizations have similar turn-on voltage, L-V curves and emission spectra. This is expected as the optical confinement is weak in the transverse direction. Figures 3.8(a)

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and 3.8(b) show the L-V curves and EL spectra respectively for the TE and TM polarizations of the heterojunction LED with a rib waveguide. It is noted that TE polarization has turn-on voltage reduced to 3.5V. Moreover, the EL intensity of TE polarization is improved by ~ 2.2 times higher than that of the TM polarization. This implies that good optical confinement is achieved by the ZnO rib waveguide with SiO₂ cladding layer, and the emission from a random laser could be manipulated well by a waveguide structure. From the effective index method calculation of the rib waveguide, it is found that the corresponding confinement factor of fundamental TE and TM polarizations is found to be 0.98 and 0.88 respectively. Hence, the ZnO rib waveguide has better confinement for the TE mode than that of TM mode. Near field emission profiles for the TE and TM polarizations are also shown in the inset of Figure 3.8(a). It is observed that both polarizations exhibit a single light spot. This indicates that only fundamental TE and TM modes are supported by the rib waveguide. In addition, light spot of TE polarization is much brighter than that of the TM polarization. This verifies that TE polarization received better electrical-to-optical conversion than that of TM polarization inside the rib waveguide.

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Figure 3.7 (a) L-V curves for the two polarizations of the LED without rib waveguide.

(b) Corresponding EL spectra for the two polarizations with bias at 5V (A), 7V (B) and 9V (C).

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Figure 3.8 (a) L-V curves for the two polarizations of the LED with rib waveguide. The insert shows the near field profile in TE and TM mode of the rib LED. (b) Corresponding EL spectra for the two polarizations with bias at 5V (A), 7V (B) and 9V (C).

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3.2.4 Summary

In conclusion, an edge-emitting UV *n*-ZnO:Al/*i*-ZnO/*p*-GaN heterojunction LED with a 3- μm wide rib waveguide was fabricated by employing index-guided structure with buried rib waveguide. The heterojunction LED exhibits room temperature UV EL radiation, which is related to radiative excitonic recombination inside the *i*-ZnO layer, with emission peak at $\sim 387\text{nm}$. It is found that the turn-on voltage of the heterojunction LED can be reduced from 6V to 3.5V and the corresponding emission intensity can be enhanced by ~ 5 times with the presence of rib waveguide. This indicates the conversion efficiency is significantly enhanced by employing the index-guided heterostructure with buried rib waveguide. In addition, directional emission can be observed from the edge of the rib waveguide. Only fundamental TE and TM polarizations are supported by the rib waveguide. The TE polarization has emission intensity ~ 2.2 times higher than of TM polarization.

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3.3 Directional and controllable edge-emitting ZnO UV random laser diodes

3.3.1 Design considerations

It has been demonstrated in section 3.2 that, by employing a properly designed index-guided heterostructure with rib waveguide, the electro-to-optical conversion efficiency could be largely enhanced in ZnO excitonic emission. In addition, the strong optical confinement in both lateral and transverse directions imposed by the rib waveguide structure results in highly directional emission from the ZnO/GaN heterojunction LED. Therefore, it is ready to enhance the optical gain and reduce the cavity loss in ZnO random media so that to achieve electrically pumped random lasing with low threshold. Moreover, it is expected to overcome the shortcoming of nondirectivity in ZnO random laser.

Table 3.5 Carrier concentration and electron mobility in as-grown ZnO:Al(3%) and ZnO:Al(3%) annealed at 900°C with different annealing time.

Annealing time (minutes)	Carrier concentration (cm ⁻³)	Electron mobility (cm ² /Vs)
as grown	4.7×10 ²⁰	4.3
5	3.6×10 ¹⁸	8.6
10	1×10 ¹⁸	11.3
20	5×10 ¹⁶	6-15
>20	cannot measure	cannot measure

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Firstly, to realize random lasing via electrical pumping, it is required to form highly disordered gains and voids with lateral facets. These disordered facets provide large refractive index contrast to form the closed-loop feedback. From the previous study, random lasing could be sustained with a ZnO grain size >100 nm. Therefore, post-annealing at 900°C was conducted to achieve the desired random structure. On the other hand, the electrical conductivity of the active layer has the strong effect on the carrier injection efficiency and thus the threshold voltage. Al-doping is employed to maintain a comparably high carrier concentration in the active ZnO layer. The electrical properties of ZnO:Al with different annealing time duration was studied carefully.

As summarized in Table 3.5, the carrier concentration reduces as the annealing time increasing, and there is an abrupt decreasing of conductivity to a very small value that cannot be measured by the available Hall measurement probe station as the annealing time is greater than 20 minutes. The surface morphology of the ZnO:Al(3%) layer annealed at 900°C for 20 minutes is checked by scanning electron microscopy as shown in Figure 3.9. It is clear that the highly disordered grain and voids with size > 100 nm are formed. This indicates by doping Al and choosing 20 minutes annealing duration, it is able to form the closed-loop feedback to sustain the random lasing and yet maintain the layer conductive.

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Figure 3.9 Scanning electron microscopy image of (a) as-grown ZnO:Al(3%) and (b) ZnO:Al(3%) annealed at 900°C for 20 minutes.

3.3.2 Fabrication process

Figure 3.10(a) shows a schematic of the proposed buried heterojunction rib waveguide laser. A *p*-GaN:Mg/sapphire substrate with hole concentration as $\sim 5 \times 10^{17} \text{ cm}^{-3}$ was used as the hole injection layer and substrate. A $\sim 150 \text{ nm}$ thick of ZnO:Al(3%) thin film was deposited onto half of the *p*-GaN:Mg/sapphire substrate by FCVA technique. During the deposition, substrate temperature and oxygen partial pressure were set to $\sim 150^\circ\text{C}$ and $\sim 2 \times 10^{-5} \text{ Torr}$ respectively.¹²⁴ To sustain random lasing action, the sample was annealed at 900°C for 30 minutes in open air to form highly disordered ZnO grains and voids.²⁵ Figure 3.10(b) shows a scanning electron microscope (SEM) image of the *i*-ZnO:Al(3%) rib waveguide after post-growth annealing. Highly disordered ZnO grains are clearly observed from the SEM image. In addition, the use of Al-doped ZnO film as the rib waveguide is to maintain

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electrically conductive after the annealing process. The annealed *i*-ZnO:Al(3%) is found to have electron concentration and mobility of $\sim 5 \times 10^{16} \text{ cm}^{-3}$ and $\sim 6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively. Subsequently, a line-mask (with width, thickness and separation equal to 2, 0.8 and 500 μm respectively) was coated onto the surface of the annealed *i*-ZnO:Al(3%) film by photolithography technique. The unmasked *i*-ZnO:Al(3%) layer was then completely removed by ion-beam sputtering with an etching rate of $\sim 10 \text{ nm/min}$ for 15 min.⁷⁸ Then, a $\sim 120 \text{ nm}$ thick of SiO_2 cladding layer was deposited onto the sample by E-beam evaporation with substrate temperature set to 50 °C. After the deposition, a lift-off process was carried out to remove the excess SiO_2 layer attached onto the surface of the annealed *i*-ZnO:Al(3%) rib waveguides. The SiO_2 cladding layer serves the purpose as an electrical isolation layer to prevent the lateral diffusion of injection carriers from the rib waveguide. Furthermore, as the refractive index of SiO_2 cladding layer ($n \sim 1.45$) is smaller than that of the *i*-ZnO:Al(3%) rib ($n \sim 2.1$), strong lateral optical confinement can be achieved¹³⁶. Finally, a layer of *n*-ZnO:Al(5%) with thickness of $\sim 150 \text{ nm}$ was deposited onto the surface of the sample by the FCVA technique to serve as electron injection layer. The deposition conditions are the same as that of the ZnO:Al(3%) layer. The carrier concentration of *n*-ZnO:Al(5%) film was found to be $\sim 10^{21} \text{ cm}^{-3}$. A $\sim 100 \text{ nm}$ thick Au (Ni) films were deposited onto the *p*-GaN:Mg/sapphire substrate (*n*-ZnO:Al(5%) layer) as the *p*-type (*n*-type) metal contact by E-beam evaporation. For the purpose of comparison, another *p*-GaN/annealed *i*-ZnO:Al(3%)/*n*-ZnO:Al(5%) heterojunction laser diode without a rib waveguide structure was also fabricated.

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Figure 3.10 (a) Schematic of a *p*-GaN/annealed *i*-ZnO:Al(3%)/*n*-ZnO:Al(5%) buried heterojunction rib waveguide laser. (b) SEM image of the rib waveguide structure.

3.3.3 Results and discussion

Figure 3.11 compares the photoluminescence (PL) spectra of the as-grown and annealed ZnO:Al(3%) layer deposited on GaN:Mg/sapphire substrate as well as a bare GaN:Mg/sapphire substrate under the excitation by a 355 nm frequency tripled Nd:YAG pulsed laser (10 Hz, 6 ns). It is observed that the as-grown ZnO:Al(3%) exhibits a broad spontaneous emission with peak located at ~385 nm. After annealing at 900°C in open air for 30 minutes, lasing modes (i.e. sharp peaks) at ~385 nm are emerged from the emission spectrum. This is because highly disordered ZnO grains and voids are generated from the ZnO:Al(3%) by thermal annealing. The size of the ZnO grains, which have an average diameter of ~100 nm,

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are sufficiently large to support coherent random lasing²⁵. On the other hand, the GaN:Mg layer shows an emission peak at ~367 nm.

Figure 3.11 PL spectra of the *p*-GaN:Mg layer, as-grown ZnO:Al(3%) layer and the annealed *i*-ZnO:Al(3%) layer.

In order to demonstrate the importance of the proposed buried heterojunction rib waveguide structure, lasing characteristics of the ZnO random laser diodes with and without a buried rib waveguide are compared. Figure 3.12(a) shows the edge and surface emission spectra of the ZnO random laser diode without a buried rib waveguide under various forward biases.

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Figure 3.12 (a) EL spectra of the laser diode without a buried rib waveguide measured from the edge and surface. (b) *L-I* (solid lines) and *I-V* (dashed line) curves of the laser diode. The insert shows the near field image of the edge emission. Schematic of a *p*-GaN/annealed *i*-ZnO:Al(3%)/*n*-ZnO:Al(5%) heterojunction laser diode without a rib waveguide is also shown in the figure.

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For the injection current, $I \geq 5$ mA, sharp peaks are emerged from the edge emission spectra at around 385 nm. In addition, the number of sharp peaks increases with the increase of I . This is attributed to the coherent random lasing action inside the annealed *i*-ZnO:Al(3%) layer. However, only spontaneous emission is observed from the surface of the laser diode. For $I \geq 8.3$ mA, the emission peaks observed from the edge and surface of the laser diode are blue-shifted to 375 and 370 nm respectively which are closed to the emission peak of GaN:Mg layer. This indicates that the injected electrons are drifted to the *p*-GaN:Mg layer and radiative recombination was taken place at the interface between the *p*-GaN:Mg and *i*-ZnO:Al(3%) layers. This implies that the transverse electrical confinement of the *p-i-n* heterojunction is deteriorated for the large value of I due to the current crowding effect.

Figure 3.12(b) shows the corresponding light-current (L - I) curves of the ZnO random laser diode without a buried rib waveguide. It is observed that there is an obvious kink at $I \sim 5.0$ mA in the L - I curve for the case of edge emission. This corresponds to the threshold current for the lasing modes emitted from the edge of the laser diode. Furthermore, the intensity of surface emission is less than that of edge emission. This indicates that the random lasing action is confined within the highly disordered *i*-ZnO:Al(3%) layer and the scattering of light from the surface and bottom of the annealed *i*-ZnO:Al(3%) layer is suppressed by the relatively low refractive indices of electron and hole injection layers via total internal reflection. The near field image of the diode laser, which verifies the transverse optical confinement of the laser diode, is also shown in the inset of figure 3.12(b). Nevertheless, lateral confinement of the laser diode has not been achieved.

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Edge emission spectra of the diode laser with a buried rib waveguide are plotted in Figure 3.13(a). For $I \geq 3.2$ mA, sharp peaks at around 387 nm are emerged from the edge emission spectrum. For further increase of I , the number and intensity of the lasing peaks are also increased. However, the number of dominant sharp peaks is less than that shown in figure 3.12(a). The corresponding surface emission spectra, which exhibit only broad spontaneous emission, are also plotted in the inset of figure 3.12(a). From the corresponding L - I curves shown in figure 3.13(b), it is noted that the intensity of edge emission (threshold current) is enhanced by ~ 9 times (reduced from 5 to 3.2 mA) when compared to that without the buried rib waveguide. Furthermore, at large value of I , the lasing peaks were excited electrically at around 387 nm which is closed to the emission peak of ZnO:Al(3%) film. This implies that the electrical confinement of the *p-i-n* heterojunction inside the annealed *i*-ZnO:Al(3%) waveguide is improved at large value of I and influence of current crowding is suppressed. Hence, the electrical-to-optical conversion efficiency of the laser diode is strongly enhanced by the presence of the 2- μ m rib waveguide embedded inside the SiO₂ cladding layer. The near field image of the edge emission is also shown in the inset of Figure 3.13(b). Only a single light spot is observed from the edge of the rib waveguide. Hence, these indicate that strong lateral and transverse optical confinement can be achieved simultaneously from the rib waveguide structure and the edge emission is highly directional.

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Figure 3.13 (a) EL spectra measured from the edge of the laser diode with a buried rib waveguide. The insert shows the corresponding EL spectra measured from the surface of the laser diode. (b) *L-I* (solid lines) and *I-V* (dashed line) curves of the laser diode. The corresponding edge-emission near-field image is also shown in the inset of Figure 3.12 (b).

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If the lasing mechanism of the laser diode is related to coherent random laser action, it is possible to deduce the cavity length, L , of the corresponding closed-loop cavity modes by power Fourier transform (FT) ⁷². Figure 3.14 shows the power FT of the laser diodes with and without a buried rib waveguide biased at 2 times of its threshold current. It is found the presence of rib waveguide reduces the value of L from ~ 6.8 to ~ 2.3 μm for the unpolarized light. This implies that the size of the closed-loop random cavities that can be formed inside the annealed *i*-ZnO:Al(3%) layer is limited by the width of the rib waveguide. As spatial overlapping of closed-loop cavity modes is not allowed inside a random medium due to the repulsion mechanism of lasing modes ⁸³, the number of excited lasing modes will be limited. This explains why there are much fewer dominant lasing peaks observed from the emission spectra of the buried heterojunction rib waveguide laser.

Figure 3.14 Power FT of the edge emission spectra of the laser diodes with and without a buried rib waveguide.

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3.3.4 Summary

In summary, coherent random lasing action is realized inside the annealed *i*-ZnO:Al(3%) rib waveguide due to the formation of ZnO grains and voids. Relatively low resistivity of *i*-ZnO:Al(3%) layer allows the effective injection of carriers through the *n*-ZnO:Al(5%) electron injection layer and *p*-GaN hole injection layer. In addition, the injection efficiency of carriers into the annealed *i*-ZnO:Al(3%) rib waveguide can be further improved by suppressing the lateral diffusion of carriers through the use of SiO₂ cladding layer as an electrical isolation layer. On the other hand, scattering loss of the annealed *i*-ZnO:Al(3%) rib waveguide is significantly reduced via total internal reflection from the electron and hole injection layers as well as the SiO₂ cladding layer. Hence, the *p-i-n* buried heterojunction rib waveguide structure has maximized the electrical and optical confinement along the lateral and transverse directions of the laser diode. The emission intensity (threshold current) can be enhanced (reduced) by ~9 times (~40 %). Furthermore, highly collimated emission beam is observed from the edge of the laser diode due to the strong optical confinement of the buried rib waveguide. As the size of closed-loop cavity modes is limited by the width of *i*-ZnO:Al(3%) rib waveguide, the number of lasing peaks that can be excited will also be restricted. Therefore, we have verified that the proposed UV emission *p*-GaN/annealed *i*-ZnO:Al(3%)/*n*-ZnO:Al(5%) buried heterojunction rib waveguide laser diode has high electrical-to-optical efficiency. The corresponding emission beam is directional, and the number of random lasing modes can be controlled by the presence of rib waveguide structure.

4. An index-guided ZnO random laser array

4.1 Introduction

We have demonstrated the suppression of side modes in ZnO random laser diode in Chapter 3. This is achieved by reducing the area of the random media so that the number of the random modes is reduced. However, the minimal size of the closed-loop feedback is too complex to be determined and it varies with the material fabrication conditions. This implies it is hardly to design a random laser which constrains only one random mode inside. Especially at high excitation power, the closed-loop paths with larger loss can form side modes. Hence, it is challenging to achieve high-power emission and suppression of side modes simultaneously from the random media. However, the discovery of spatial overlapping of random modes, which induces spectral repulsion of random modes as discussed in 1.3.2.2 in Chapter 1 can be applied to suppress the excitation of side modes at high pump power.⁸⁰ It is desired to have the random cavities spatially arranged closely so that the electric field from the individual random mode overlaps and interacts. Hence in the spectral domain, the modes with small frequency spacing are expected to repel each other. Therefore, we come out an idea to design an array of random cavities. Due to the strong lateral confinement of a waveguide, the lateral distribution of random modes can be described by the distribution of lateral waveguide modes, so that random modes from the adjacent random cavities can be forced to spatially overlap through the lateral waveguide mode coupling. Hence, in this chapter spectral repulsion in the random laser array was investigated.

On the other hand, we look at the output power from the random media. More

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random modes which are spectrally coherent are excited to lase as the excitation area increasing. Therefore the output enhancement is expected by increasing the excitation area, i.e. increasing the number of array elements, and yet the number of random modes is still restricted. This was also studied as another improvement of random lasing in this chapter.

4.2 Design considerations

Figure 4.1 Schematic of a weakly index-guided ZnO random laser array

Figure 4.1 shows the schematic of an index-guided random laser array using ZnO as the random cavities. By doping with Al, ZnO:Al(3%) has slightly

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smaller refractive index (~ 2.09) than that of intrinsic ZnO (~ 2.1).¹³² Hence, the as-grown ZnO:Al(3%) which does not sustain random lasing is chosen as the cladding and coupling layer between the waveguide core with random cavities. The width of the waveguide core, w and cladding layer, s are essential in determining the lateral mode and random mode coupling. For operating the ZnO random laser array at high power and yet with strong suppression of side modes, it is required that every individual ZnO random laser should optically couple to its adjacent neighbors. We calculate (i.e., by using effective index method) that the largest cut-off value of ' w ' to maintain single-lateral-mode operation in the individual random lasers with ZnO:Al(3%) cladding layer is obtained by $\sqrt{n_2^2 - n_1^2} k_0 w / 2 = \pi / 2$,⁸² where $n_2 = 1.7549$ and $n_1 = 1.7351$ are the effective refractive index of ZnO and ZnO:Al(3%) column, and $k_0 = 2\pi/\lambda$, here the operating wavelength, λ is ~ 395 nm. So the largest cut-off value of ' w ' for single-lateral mode is ~ 0.74 μm . This calculation has assumed that the index-guided ZnO waveguide and ZnO:Al(3%) cladding layer have the same thickness ' d ' equal to ~ 150 nm. However, 1.5 μm was chosen as the waveguide width under the restriction of the photolithographic technique to define fine waveguide stripes. This may lead to higher order lateral modes sustained in side of the waveguide. In order to achieve coupling of random modes between the adjacent random lasers, the lateral field is required to penetrate through the cladding layer. Figure 4.2 plots the lateral field profile of i -ZnO waveguide with ZnO:Al(3%) cladding. Here only the profiles of the fundamental modes are plotted. It is noted that if the width of cladding layer, s , < 1.2 μm , lateral mode can penetrate into the adjacent random cavities. Nevertheless, short value of s is required to

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maximize the coupling strength between the random cavities.⁸² It is noted that the shortest waveguide spacing, i.e. value of s for our photolithographic technique can be obtained is $\sim 0.8 \mu\text{m}$. Hence, if the values of w and s are chosen to be 1.5 and $0.8 \mu\text{m}$ respectively, minimum number of lateral-mode operation within individual waveguides and strong overlapping of lateral fields between the adjacent random cavities were expected to be achieved. In this way, the random modes are formed very close to each other with electric field overlapping and interacting. Hence, repelling of random modes with frequency spacing smaller than the homogenous linewidth of the annealed ZnO in the spectral domain is expected to be resulted.⁸⁰ From our experimental far-field patterns, we found that each array element operates in both the fundamental and 1st order lateral modes, which verifies the calculation of lateral mode confinement. (Details of the calculation are shown in Appendix A.) On the other hand, for the laser array without ZnO:Al(3%) cladding layer, ZnO random cavities will experience no coupling as the lateral waveguide modes from the adjacent waveguides are well confined and separated. From the waveguide theory, the coupling coefficient κ of waveguide arrays could be used to quantify the coupling of the lateral waveguide modes. κ is calculated as 30 cm^{-1} and $1.1 \times 10^{-6} \text{ cm}^{-1}$ for the ZnO laser array with and without ZnO:Al(3%). (The detail calculation is presented in Appendix B.) This verifies again the strong lateral waveguide mode coupling causes the random mode interaction and so random mode repulsion.

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Figure 4.2 Fundamental field profiles of ZnO random waveguide with (solid line) and without (dashed line) ZnO:Al(3%) cladding layer. The blue lines describe the waveguide regime. The array elements were assumed to only support fundamental lateral mode.

4.3 Fabrication procedures

The laser array was fabricated by depositing a ~150 nm thick of ZnO thin film onto a quartz substrate via FCVA deposition technique. The deposition conditions are the same as that in Chapter 3. The sample went through thermal annealing at 900 °C for 2 hours in open air. ZnO grains and voids can be formed inside the ZnO film to sustain random lasing action at wavelength, λ , equal to ~395 nm.¹²⁴ Subsequently, arrays of annealed ZnO of width and separation equal to w and s respectively were defined by photolithography and ion-beam sputtering technique as introduced in Chapter 3. As a result, highly disordered ZnO ridges were formed on the quartz substrate. Then, a ~150 nm thick of ZnO:Al(3%) film was deposited onto the sample by the FCVA technique. ZnO:Al(3%) was chosen as the cladding layer because it has refractive index

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slightly smaller than that of ZnO and the corresponding absorption loss at $\lambda \sim 395$ nm is low. It must be noted that the as-grown ZnO:Al(3%) layer does not sustain random lasing as demonstrated in Figure 3.11. After the deposition, a lift-off process was carried out to remove the excess ZnO:Al(3%) layer attached on top of the highly disordered ZnO ridges. Thus, index-guided waveguides with a planar configuration were realized.

Figure 4.3 shows a top view of the highly disordered ZnO ridges filled with ZnO:Al(3%) cladding layer. The rough (dark color) lines are the highly disordered ZnO ridges. It is clear that the uniformity of the fabricated ZnO array is good. For the purpose of comparison, another sample without ZnO:Al(3%) cladding layer was also fabricated. These samples form ZnO random laser arrays under optical excitation.

Figure 4.3 Top- view image of the laser array which was taken by an Olympus BH2-UMA microscope with $\times 500$ amplification. The strips in dark color are the ZnO waveguide arrays.

4.4 Results and discussion

In order to examine the coupling behaviour of random modes, lasing characteristics of the ZnO random laser arrays were studied. The samples (with $w = 1.5 \mu\text{m}$, $s = 0.8 \mu\text{m}$ and $d = 150 \text{ nm}$) with and without ZnO:Al(3%) cladding layer were excited by a 355 nm frequency tripled Nd:YAG pulsed laser (10 Hz, 6 ns). Excitation beam was focused on to the surface of the samples by a cylindrical lens. Length of pump strip onto the laser arrays was kept at $\sim 5 \text{ mm}$. Width of the excitation beam was measured to be $\sim 18 \mu\text{m}$. As the laser array has $s = 0.8 \mu\text{m}$ and $w = 1.5 \mu\text{m}$, about 8 highly disordered ZnO waveguides would be pumped simultaneously by the excitation beam. Edge emission of the laser arrays was then measured through a slit with $\sim 0.5 \text{ mm}$ in width.

Figure 4.4 (a) compares the light-light curves between ZnO random laser arrays with and without cladding layer. It is observed that the threshold pump intensity, P_{th} , of the ZnO random laser array with cladding layer is lower than that without cladding layer by approximately $\sim 30\%$. However, the slope efficiency of the light-light curves was observed to remain similar. We suggest that for the case without ZnO:Al(3%) cladding layers, there is significant nonradiative recombination at the side walls, which increases the threshold, but does not affect the slope efficiency of the lasers. It is worth noting that no random lasing action is sustained in the ZnO:Al(3%) cladding layer, which is supported by the PL result in Figure 3.11. Hence, adding the ZnO:Al(3%) cladding layer does not influence the gain of the laser array in a significant manner. Therefore the slope efficiency remains similar. Figure 4.4 (b) and (c) plot the emission spectra of the ZnO random laser arrays. It is observed that the number of lasing peaks is

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significantly reduced by the presence of cladding layer at and above P_{th} . As we know that the spectral repulsion of lasing modes in an inhomogeneously broadened gain medium (thermal annealed ZnO has large inhomogeneity) indicates spatial overlap of the lasing modes.⁸⁰ Hence, the reduction of lasing peaks observed in Figure 4.4 suggests that there occurs a strong lateral coupling of adjacent random modes. It is necessary to address that multiple fabrication and measurement of the laser arrays with different longitudinal dimension were made, and stable and consistent spectral feature was observed. This not only justifies the characteristic of random lasing, but also demonstrates the stable performance and reliability of the proposed random laser array.

The coupling behaviour can also be studied from the emission field patterns of the ZnO random laser arrays. The near-field patterns were captured by a microscope with $\times 500$ amplification. Thus the $1.5\ \mu\text{m}$ -emitters could be clearly seen. The far-field pattern was measured using the schematic shown in Figure 4.5. A cylindrical lens is to focus the emission in the transverse direction, while change little of the light path in the lateral direction. Therefore, the lateral profile of the output beam was studied.

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Figure 4.4 (a) Light-light curves of the ZnO random laser array with and without ZnO:Al(3%) cladding layer. Lasing spectra of the random laser array (b) with and (c) without ZnO:Al(3%) cladding layer under different pump power, P (Please be noted that the results in (c) have been magnified by 1.7 times).

Figure 4.6 (a) plots the near- and far-field patterns of the laser array with cladding layer. Photo of near-field pattern shows indistinguishable spots along the edge of the laser array pumped at $P = 0.6 \text{ MW}/\text{cm}^2$. This is expected as the lateral fields between two adjacent waveguides are coupled together. Photo of far-field pattern shows that the emission beam has a double-lobed profile, and the spatial separation of the lobes is about $\sim 6.3^\circ$. Evolution of the far-field pattern was also studied by plotting the corresponding lateral intensity profile versus pump power, P . It is noted that the double-lobed profile was formed for $P > P_{th}$. This indicates that strong lateral coupling of optical fields presents inside the laser array. However, there is no evidence of phase locking in the random laser

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array since the patterns do not have either the periodic features or the narrow beams that would indicate phase locking ¹³⁷. The observation of double-lobed profile which is similar to a single element laser operating with both the fundamental and 1st order modes, may be due to the excitation of 1st order lateral modes in the individual random cavities. This is because the array elements can support both the fundamental and 1st order modes at or above threshold as calculated in Appendix A. In addition, excitation of 1st order lateral mode is possible in some individual lasers. Furthermore, the lobe widths of the far fields are 4-5 times the diffraction limit, thus there should have several array modes in operation ¹³⁷.

Figure 4.5 Schematic of far-field pattern measurement in the (a) lateral and (b) transverse directions

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Figure 4.6 Plot of lateral far-field profile of the index-guided ZnO random laser array (a) with and (b) without ZnO:Al(3%) cladding layer versus pump power, P .

The insets show the near- and far-field patterns at pump power, P , equal to 0.6 MW/cm². The near-field profile was recorded by an Olympus BH2-UMA microscope with ×500 amplification.

Far-field pattern of the laser array without cladding layer was also measured as

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shown in Figure 4.6 (b). The far-field intensity is very weak, i.e. only $\sim 1/8$ of that from the laser array with cladding layer. Additionally, evolution of the far-field pattern with P shows no excitation of obvious dominant lobe. As shown in the left inset of Figure 4.6 (b), the image of near-field pattern shows 8 roughly distinguishable spots along the edge of the laser array pumped at $P = 0.6$ MW/cm². This verifies that there is no lateral coupling between adjacent waveguides in the laser arrays without ZnO:Al(3%) cladding layers.

In order to verify that the output power of the laser array can be increased with the number of random cavities, we repeated the PL measurement by using excitation strips of 32 and 50 μm in width (i.e., these represent the laser array has 14 and 22 random cavities respectively). Figure 4.7 (a) (b) and (c) plot the light-light curves and emission spectra respectively of the laser array with 8, 14 and 22 random cavities. It is noted that the output intensity is increased with the number of random cavities. Furthermore, the number of random modes observed from the PL spectra of the laser array with 14 and 22 random cavities is similar to that with 8 random cavities. Therefore, it is suggested that the total output intensity of the laser array can be increased with the number of random cavities and the number of side modes in the spectral domain, i.e. the number of excited random modes remains unchanged due to the lateral coupling of random modes.

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Figure 4.7 (a) Light-light curves of ZnO random laser arrays with ZnO:Al(3%) cladding layer with 8, 14 and 22 random cavities, and the lasing spectra of ZnO random laser arrays with ZnO:Al(3%) cladding layer with (b) 14 and (c) 22 random cavities.

Figure 4.8 compares the corresponding far-field profiles of the laser arrays. The observation of double-lobe profiles has indicated that the lateral coupling of random modes is presented between the adjacent random cavities in laser arrays with different number of array elements. However, the array elements may operate in both the fundamental and 1st order modes.

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Figure 4.8 Plot of lateral far-field profile of the ZnO random laser array with ZnO:Al(3%) cladding layer with (a) 14 and (b) 22 random cavities versus the pump power, P .

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4.5 Summary

We have shown that if random laser array is properly designed (i.e., every individual ZnO random laser is optically coupled to its adjacent neighbors), it is possible to increase the total emission power. Furthermore, the number of excited side modes can be suppressed at high excitation power. This is because the spectral repulsion of side modes occurs inside the laser array (i.e., due to the spatial overlapping of random modes arisen from the strong lateral coupling between adjacent random cavities) so that the maximum number of lasing modes is limited. It is important to distinguish the laser array discussed in this chapter with the conventional phase-coherent laser array,¹³⁷ as no phase locking phenomena has been observed from the proposed ZnO random laser array.

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5. ZnO random laser diode arrays for stable single-mode operation at high power

5.1 Introduction

It has been demonstrated in Chapter 4 that the random mode repulsion could be well achieved by spatially arranging the random modes very closely. This is achieved via overlapping and coupling of the lateral waveguide modes from individual waveguide array under optical excitation, as the lateral distribution of random modes confined inside an indexed waveguide can be roughly described by the distribution of lateral waveguide modes. This makes the random modes interact, and in the spectrum, the lasing frequencies with small spacing repel each other. Despite multiple realization of random laser array with different number of random waveguides has been done to verify the spectral repulsion, it is highly desired to investigate the mode coupling under electrical pumping to further verify the random mode repulsion mechanism. In addition, it is very interesting and useful to exploit the possibility of achieving single peak domination or even single-random-mode operation in random laser array by enhancing the interelement coupling between random modes. Thirdly, in Chapter 4, the measured far-field pattern exhibits a double-lobed profile. It is suggested that the excitation of 1st order lateral mode in the array element results in the double-lobed pattern. Thus, there is a large necessity to exam the evolution of the far-field pattern again from the random laser array elements which only support the fundamental lateral mode. Therefore, in this chapter, an array of ZnO random laser diodes with

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stronger lateral coupling was designed. The spectra characteristics and far-field pattern were investigated.

5.2 Design consideration

Figure 5.1 Fundamental field profile of $\text{Al}_2\text{O}_3/\text{ZnO:Al(3\%)}/\text{Al}_2\text{O}_3$ random waveguide (solid line). The field profile of $\text{ZnO:Al(3\%)}/\text{ZnO}/\text{ZnO:Al(3\%)}$ random waveguide discussed in Chapter 4 (dashed line) is also compared here.

Arrays of Annealed $\text{ZnO:Al(3\%)}$ with 1 μm in width are defined as the active region with random cavities. The spacing of the random arrays is designed to be 1 μm as well. Al_2O_3 instead of SiO_2 is chosen as the isolation cladding layer. This is because the refractive index of Al_2O_3 (~ 1.78)¹³⁸ is much larger than that of SiO_2 (~ 1.45).

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Thus it is expected that the interelement coupling of the random laser array can be enhanced via strong overlapping of lateral waveguide modes. *n*-ZnO:Al(5%) and *p*-GaN:Mg are chosen as the electron and hole injection layers for the same reason which has been introduced in Chapter 3. The effective refractive indices of *n*-ZnO:Al(5%)(100nm)/*i*-ZnO:Al(3%)(150nm)/*p*-GaN:Mg and ZnO:Al(5%)(100nm)/Al₂O₃(150nm)/*p*-GaN:Mg dielectric layers are calculated by transfer matrix method as 2.4411 and 2.4374 respectively at operating wavelength of ~385 nm. In this case, the penetration length of the evanescent wave into the isolation layer can be estimated to be ~0.8 μm. As the random cavities have a separation of 1 μm, strong interelement coupling should be obtained from this design of laser diode array. Figure 5.1 compares the calculated electric profile of the Al₂O₃/ZnO:Al(3%)/Al₂O₃ pair with the ZnO:Al(3%)/ZnO/ZnO:Al(3%) pair discussed in Chapter 4. It is clear that there is larger portion of leaky wave penetrating through the waveguide core into the cladding layer in the Al₂O₃/ZnO:Al(3%)/Al₂O₃ pair. This indicates stronger lateral coupling resulted in the design of ZnO random laser array diode. Inspecting the waveguide coupling coefficient κ , $\kappa=38.7 \text{ cm}^{-1}$ for the proposed laser diode array in this chapter, is larger than $\kappa=30 \text{ cm}^{-1}$ for the ZnO:Al(3%)/ZnO/ZnO:Al(3%) array in Chapter 4.

5.3 Fabrication procedures

Figure 5.2 shows a schematic of the proposed *n*-ZnO:Al(5%)/*i*-ZnO:Al(3%)/*p*-GaN heterojunction laser array. A ~150 nm thick *i*-ZnO:Al(3%) thin film was deposited on a *p*-GaN:Mg/sapphire substrate (purchased from Technologies & Device

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International Inc.) by FCVA technique at a substrate temperature of 150°C. The *p*-GaN:Mg layer is also used as a hole injection layer of the heterojunction. The sample was annealed at 900°C in open air for 20 minutes to obtain grains and voids inside the *i*-ZnO:Al(3%) layer to support coherent random lasing. An array of photoresist line-mask, which has 1 μm width and 800 nm thickness as well as 1 μm separation, was coated onto the *i*-ZnO:Al(3%) thin film. This is the smallest line-mask that can be formed by photolithography to fabricate the laser diode array. The sample underwent ion-beam etching for 15 minutes at an etching rate of ~ 10 nm /minute to form an array of highly disordered random cavities. A ~ 120 nm thick of Al_2O_3 was deposited as isolation layer onto the etched surface by electron-beam evaporation. After the removal of photoresist, a strip of ZnO:Al(5%) with length, width and thickness of 2 mm, 20 μm and 100 nm respectively was deposited by FCVA technique onto the sample as an electron injection layer. Hence, a heterojunctions array of ten highly disordered ZnO:Al(3%) random cavities was formed. The number of random cavities can also be increased with the width of the ZnO:Al(5%) stripe. Subsequently, a ~ 100 nm thick of Ni and a ~ 100 nm thick of Au were coated onto the *n*-ZnO:Al(5%) strip and *p*-GaN:Mg substrate respectively by electron-beam evaporation.

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Figure 5.2 Figure 1 (a) Schematic of a ZnO random laser diode array.

5.4 Results and discussion

Figure 5.3 shows the light-light curve and photoluminescence (PL) spectra of the sample without the deposition of metal contacts. The sample was excited by a 355 nm pulsed (10 Hz, 6 ns) Nd:YAG (yttrium aluminum ganet) laser at room temperature. The laser beam was focused to a strip with $\sim 20\text{ }\mu\text{m}$ width by a cylindrical lens and the lasing emission was collected from the edge of the sample. It is observed that a kink appears in the light-light curve for pump intensity, P , equal to a threshold value of $P_{\text{th}} \sim 0.26\text{ MW/cm}^2$. Furthermore, a single peak is emerged from the broadened emission spectrum for P larger than P_{th} . These imply that the sample exhibits random lasing action under optical excitation. For P increases to $\sim 3 \times P_{\text{th}}$, which is the maximum damage power of the sample, stable single-random-mode operation in the spectral domain can still be maintained. The emission spectra of the sample at $P \sim 1.1 \times P_{\text{th}}$ and $\sim 3 \times P_{\text{th}}$ are also shown in the inset of the figure. Stable single-mode operation of the laser array at large value of P has indicated that 1) only

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one dominant random mode is excited from each of the random cavities and 2) the dominant random modes supported by the random cavities have the same wavelength due to the strong interelement coupling of the laser array.¹³⁹

Figure 5.3 Light-light curve and PL lasing spectra measured from the edge of the ZnO random laser array under optical excitation. Metal contacts have not been deposited to the sample for this optical experiment.

Figure 5.4 plots the voltage-current and light-current curves as well as Q-factor versus current of the ZnO laser diode array. The diode array was driven by a rectangular pulse voltage source with repetition rate and pulse width of 7.5 Hz and 80 ms, respectively. The diode array exhibits a diode-like rectifying current-voltage characteristic with a turn-on voltage of ~ 5 V. It is also observed that a kink appears

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in the light-current curve for injection current, I , equal to a threshold value of $I_{th} \sim 1.1$ mA. This is consistent with the measured Q -factor of the heterojunction as for $I \sim I_{th}$, the value of Q -factor jumps from ~ 40 to ~ 1000 and reaches ~ 1200 at $I \sim 6.7$ mA.

Figure 5.4 Voltage-current curve, light-current curve and Q -factor versus injection current of the ZnO random laser diode array.

Figure 5.5 shows the electroluminescence (EL) spectra of the diode array. There is only one dominant peak emerged from the EL spectra at I equal to or larger than I_{th} . In addition, full-width at half-maximum (FWHM) of the lasing peak, $\Delta\lambda$ decreases from 0.4 nm at $I \sim 1.4$ mA to 0.32 nm at $I \sim 6.7$ mA. This implies that the electrical energy is only channeled to the dominant random mode so that $\Delta\lambda$ decreases with the increase of I . On the other hand, although the position of the dominant mode is stable

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(i.e., the corresponding value of $\Delta\lambda$ approaching the noise limit) at a value of I , hopping of dominant mode is observed for the change of I . This may be due to the carrier induced refractive index change inside the random cavities as the thermal effect is less significant for the laser diode array under pulsed operation.

Figure 5.5 EL spectra measured from the edge of the laser diode array at different bias conditions.

Near-field pattern (circle) measured from the edge of the ten ZnO:Al(3%) highly disordered random cavities under electrical pumping at $I \sim 6 \times I_{th}$ is plotted in Figure 5.6. The near-field pattern, which has a single-lateral-mode profile with a FWHM of $\sim 10 \mu\text{m}$, was recorded from an Olympus BH2-UMA microscope with $\times 1000$

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magnification. The near-field pattern reveals no fine structure that could be used to identify the individual random cavities. Figure 5.6 also shows the calculated fundamental near-field pattern (solid line) by using effective index method¹⁴⁰ and the effective refractive index profile of the laser diode array used in the calculation. It is noted that envelop of the calculated near-field pattern is roughly matched with the measured near-field pattern. Hence, the array of ten highly disordered random cavities supports stable fundamental-lateral-mode operation and the design of laser diode array has substantial interelement coupling. The observed near field pattern demonstrates the enhanced lateral waveguide mode interaction between the adjacent laser arrays. It suggests that the side longitudinal mode (i.e. random mode) suppression and stable single random mode operation even at high pump intensity are resulted from the lateral waveguide mode overlapping and coupling.

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Figure 5.6 Measured (circles) and calculated (solid-line) near-field patterns from the edge of the laser diode array biased at 6×threshold current. Lateral distribution of effective refractive index used for calculation is also shown in the figure.

Figure 5.7 plots the normalized far-field emission patterns versus different bias conditions. Single-lobed far-field pattern is maintained over the operation conditions and the variation of the FWHM of the far-field pattern is less than 1°. Hence, we have proved that the proposed ZnO laser diode array can sustain stable single-beam operation at high power. Moreover, this further confirms the suggestion that the double-lobed far-field beam observed in the ZnO random laser array in Chapter 4 is the result of the coexistence of fundamental and 1st order later modes in the individual laser elements.

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Figure 5.7 Normalized far-field patterns measured from the edge of the laser diode array under different bias conditions.

It is expected that the lasing spectra observed from the laser diode array is arisen from the strong interelement coupling of the dominant random modes. The dominant random modes, which are generated from the ten individual highly disordered ZnO:Al(3%) random cavities, should have the same wavelength and closed-loop cavity length, L , to achieve stable single-mode operation. Hence, it is possible to deduce the value of L by power Fourier transform (FT).

Figure 5.8 Power FT of the edge emission spectra of the laser diode array at different bias conditions. The inset diagram explains the interelement coupling of closed-loop random modes between adjacent random cavities.

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Figure 5.8 shows the power FT of the laser diode array versus bias voltage. It is observed that L reduces with the increase of bias voltage and is saturated at $\sim 4.1 \mu\text{m}$. If we assume that the closed-loop random modes have a 2-dimensional circular shape locating inside the plane of the heterojunctions, the shortest diameter, $d (= L/\pi)$, will be $\sim 1.3 \mu\text{m}$ wide, see also the insert of Figure 5.8. This value of d , which is closed to the width of the random cavities, represents a closed-loop random mode with the highest modal gain. However, the excitation of side random modes with L larger than $4.1 \mu\text{m}$ will be suppressed due to their relatively low modal gain. This finding of d from the laser diode array is consistent with the assumptions that the ten individual random cavities have the same wavelength and L . Otherwise, if L is smaller than $4.1 \mu\text{m}$, excitation of side modes can be observed due to the 1) increase of the modal gain of the side modes and 2) reduction of interelement coupling. Furthermore, if L is larger than $4.1 \mu\text{m}$, threshold of the laser diode array can be significantly increased.

5.5 Summary

In conclusion, we have fabricated arrays of $n\text{-ZnO:Al(5\%)/}i\text{-ZnO:Al(3\%)}$ random cavities/ $p\text{-GaIn:Mg}$ heterojunctions. The waveguide core with random cavities has $1 \mu\text{m}$ in width. $1 \mu\text{m}$ wide Al_2O_3 was selected as the dielectric insulator in order to achieve large electrical isolation and strong optical interelement coupling between the adjacent random cavities. Room-temperature stable single-mode operation has

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been obtained from the proposed laser diode arrays under high electrical excitation (i.e., $> 6 \times$ threshold current).

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6. SnO₂/p-SiC heterojunction light-emitting diode

6.1 Introduction

Tin dioxide (SnO₂) is an *n*-type semiconducting direct bandgap metal oxide. Compared to ZnO, SnO₂ has wider bandgap energy of ~3.6 eV, and more importantly, SnO₂ has an exciton binding energy of ~130 meV at room temperature which is more than two times of than that of ZnO (60 meV).¹⁴¹ Therefore SnO₂ is recognized as a good candidate for realizing UV luminescence with high-efficiency at room temperature or even high temperature. However, due to the dipole forbidden nature of SnO₂, the band-to-band emission is hard to achieve,¹⁴² instead, the report of luminescence from SnO₂ are all defects-based emission. The orange luminescence with emission wavelength ~ 600 nm has been observed from SnO₂ nanowires,¹⁴³ nano-ribbons¹⁴⁴ and nano-rods¹⁴⁵. It is suggested that the oxygen vacancies which are located at the surface interact with the interfacial tin vacancies, and lead to the formation of a large amount of trapped states within the bandgap. It is worth nothing that the high-intensity emission is usually observed in nano-structured SnO₂. This is because the large surface to volume ratio in the nanostructures favors the formation of surface defects, like oxygen vacancies. It is interesting to note that electroluminescence (EL) at 590 nm has been obtained from SnO₂ thin film, which consists of clusters of wormlike grains with area of ~1 μm × ~200 nm. These nano-clusters largely increase the surface to volume ratio, so that result in high-intensity emission.¹⁴⁶ Recently, the UV radiative recombination has been observed from SnO₂ nanowires which have superior quality and limited concentration of deep level

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defects.^{147,148} The shallow trapped states at the surface can capture high concentration of bound excitons, which results in high intensity of UV emission.¹⁴⁹ However, the nano-structured SnO₂ is not suitable for device fabrication and integration. Therefore in this chapter, it is proposed to grown polycrystalline SnO₂ thin film with high crystalline and limited deep level defects by FCVA technique. To enrich the surface states, post-growth annealing is employed to realize the small, closely packed, and well-separated SnO₂ grains. The light-emitting heterojunction was made and the electroluminescence was studied.

6.2 Fabrication procedures

SnO₂ thin films were deposited onto 4H-SiC and quartz substrates by using FCVA. In the experiment, substrate temperature and oxygen partial pressure were set to 350 °C and 7×10^{-5} Torr, respectively. A Sn target with 99.99% purity was used as the source target. In order to generate Sn plasma, arc current of 80 A was apply to the plasma source. However, Sn has a low melting temperature of ~230°C so that the Sn target will melt during the arcing process. Hence, the Sn target was inserted into a water-cooled copper cup of the plasma source to hold the liquidized Sn. The copper cup was shielded by a boron nitride plate to avoid the generation of copper plasma.

Low temperature deposition of SnO₂ thin films, which allows the effective growth of SnO₂ grains and voids through post-growth annealing, can be applied to realize shallow trapped states for the support of radiative recombination of captured excitons. The growth of SnO₂ grains (voids) inside the SnO₂ thin films can be explained as the

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merger (evaporation) of weakly bonded SnO₂ grains.^{85,150} Due to the creation of voids, the SnO₂ grains become loosely in contact and the corresponding surface are widely exposed to the surrounding so that the surface area to volume ratio of the SnO₂ thin film has been significantly improved.

Post-growth annealing of the samples in open air was carried out in a standard Linderg type furnace using a quartz tube reactor. Initially, the samples inside the furnace were heated up from room temperature to 900°C within 20 min. Then, the samples were annealed for a period of time, T_a , at a constant temperature of 900°C. Finally, the samples were cooled down to room temperature inside the furnace. This annealing process was used to minimize the buildup of thermal strain at the interface of SnO₂/SiC. The post-growth annealing temperature should be higher than that of the growth temperature in order to achieve effective formation of the irregular SnO₂ grains. This is because high annealing temperature enhances the generation of voids in SnO₂ film. As a result, a large number of shallow defects states, which support the intense defect-related emission, can be induced by the surface states of the irregular SnO₂ grains. Therefore, the generation of irregular grains is essential for the luminescence in SnO₂ thin film.

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6.3 Results and discussion

6.3.1 SnO₂ thin film

Figure 6.1 SEM images of SnO₂ thin films: (a) as-grown, (b) $T_a = 1$ min, and (c) $T_a = 1$ hr. The inset shows the AFM images of the SnO₂ thin films. The scale bar represents 1 μm.

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Figure 6.1 shows the scanning electron microscope (SEM) images and atomic force microscope (AFM) images of the samples before and after annealing at different T_a . The SnO₂ grains of the as-grown sample are closely packed. For $T_a = 1$ min, it is observed that the SnO₂ grains become loosely in contact with voids existing between the grains. For $T_a = 1$ hr, the size of the SnO₂ grains grow slightly further and almost all the SnO₂ grains are well separated from the others. The AFM images clearly reveal that the disordered grains grow both in and perpendicular to the substrate plane from ~ 50 nm for the as-grown SnO₂ to 150 nm for the SnO₂ after annealing. In this way, the surface-to-volume ratio is significantly increased via thermal annealing.

The crystalline structure of the SnO₂ thin films were studied by the X-ray diffraction measurement. As shown in Figure 6.2, for the as-grown SnO₂ film, the diffraction intensity is very low and no diffraction peak of the metallic Sn crystalline structure is detected. Diffraction peaks, which corresponding to SnO₂ (101) and (200) reflection of rutile structure, are observed at around $2\theta = 33.8^\circ$ and 37.9° for the sample with $T_a = 1$ min. The diffraction peak of the (101) direction at around $2\theta = 33.8^\circ$ is dominant in the XRD spectrum for the sample with $T_a = 1$ hr. Hence, this indicates that the sample after annealing for long enough T_a forms single crystalline grains have rutile structure of pure SnO₂ with a single orientation of (101) direction.

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Figure 6.2 XRD patterns of the SnO₂ thin films: (a) as-grown, (b) $T_a = 1$ min, and (c) $T_a = 1$ hr.

Besides the crystalline structure the optical properties of the SnO₂ film was also studied. The UV-visible optical transmittance of a post-growth annealed SnO₂ thin film deposited on quartz is plotted in Figure 6.3. It is observed that the average transmittance in the visible range is about 85%. The plot of the square of the absorption coefficient (α^2) as a function of photon energy ($h\nu$) is shown in the inset of Figure 6.3. The bandgap of SnO₂ film can be determined as about 3.6 eV by extrapolating the linear portion to the energy axis.

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Figure 6.3 Transmittance spectrum for the corresponding SnO₂ thin film. The insert shows the plot of α^2 versus $h\nu$ of the film.

In order to further analyze the optical property of the SnO₂ thin film, room temperature PL was measured by a fluorescence meter. The films were excited by a 300 nm source with maximum 5 nm full width at half maximum (FWHM). PL spectra of the samples are shown in Figure 6.4. For the sample with $T_a = 1$ min, a broad emission band spanned from 390 and 550 nm was observed. For the sample with $T_a = 1$ hr, a peak at ~390 nm was emerged from the emission spectrum. This indicates that the formation of SnO₂ grains and voids supports the generation of shallow surface defect states so the UV emission is observed in the PL spectrum.¹⁵¹ The PL spectrum for the sample with $T_a = 1$ hr could be fitted well by three Gaussian curves with peak wavelength at 389 nm (3.19 eV), 410 nm (3.02 eV) and 469 nm (2.64 eV). This verifies the there are three defects centers in the SnO₂ film. On the other hand, PL emission was not observed from the as-growth SnO₂ film. PL

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measurement of the *p*-SiC(4H) substrate was also conducted. No emission was detected from the SiC(4H) substrate even at high excitation intensity. This is expected as the SiC substrate has an indirect bandgap, which does not support radiative recombination. We believed that the PL spectra observed from the device are mainly due to the defective SnO₂.

Figure 6.4 PL spectra of the SnO₂ thin films after post-growth annealing at 1000 °C for $T_a = 1 \text{ min}$ and 1 hr .

6.3.2 SnO₂/p-SiC heterojunction LED

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Figure 6.5 (a) Schematic of a *p*-SiC/SnO₂ thin film heterojunction diode. (b) Cross-sectional and surface SEM images of the SnO₂ thin film.

To further investigate the excitonic related emission from disordered SnO₂ thin film, a SnO₂/*p*-SiC heterojunction was fabricated as depicted in Figure 6.5 (a). A *p*-doped single-side polished (0001) surface 4H-SiC wafer (purchased from Cree Inc) was chosen to be the substrate and the hole injection layer. This is because the *p*-doped SiC substrate has a hole concentration and a carrier mobility of $\sim 1 \times 10^{19} \text{ cm}^{-3}$ and $\sim 120 \text{ cm}^2/\text{Vs}$ respectively. More importantly, 4H-SiC is an indirect bandgap material, in which the radiative recombination hardly occurs. Thus it voids the difficulty in

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distinguishing the junction from which the light is emitted. As introduced in 6.2, FCVA technique was use to grow a 250 nm thick SnO₂ thin film onto the polished surface of the *p*-SiC. After the deposition, the sample was gone through thermal annealing at 900°C for 1 hr in open air. Figure 6.5 (b) shows the cross-sectional and surface SEM images of the SnO₂/*p*-SiC heterojunction. SnO₂ grains are clearly seen from the edge and surface of the film. Furthermore, a layer of 25 nm thick Al film and 150 nm thick Ti was deposited onto the rough surface of SiC as the *p*-type contact by electron beam evaporation. The sample was then subject to rapid thermal annealing at 800 °C in N₂ for 5 min in order to achieve a linear current-voltage dependence of the Al/Ti metal contact on the SiC.⁸⁵ A layer of 100 nm ITO was deposited onto the SnO₂ film by sputtering as the *n*-type contact. The *I-V* characteristic of the ITO/SnO₂/ITO structure is shown in Figure 6.7, which exhibits an ohmic behavior.

Figure 6.6 *I-V* characteristics of the SnO₂/ITO contact.

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The electroluminescence (EL) spectra of the SnO₂/p-SiC heterojunction LED were measured. A rectangular pulse bias with 13 Hz repetition rate and 60 ms pulse width was applied. Figure 6.7 shows the EL spectra of the LED at different forward-bias voltages. It is observed that intensity of EL spectra increases with the increase of forward bias. All the spectra have a dominant peak at 392nm wavelength. The previously reported peak located at ~590 to 605 nm which is commonly believed to be originated from oxygen vacancies,¹⁵² and interfacial tin vacancies was not observed. Furthermore, all the EL spectra can be fitted by three Gaussian curves with peak wavelength of 387 nm (3.20 eV), 413 nm (3.00 eV) and 464 nm (2.67 eV).

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Figure 6.7 EL spectra of the p-SiC/SnO₂ thin film heterojunction diode under different bias voltage. The inset shows the color photo taken for the diode under a forward bias voltage of 13 V.

The EL spectra provide a good agreement with the PL measurement results. This indicates that there are three defect-related radiative recombination centers in the fabricated SnO₂ thin film contributing to the EL emission. When compared to the PL spectrum of the film, it can be shown that the EL emission is contributed by the radiative recombination in SnO₂ film. The photo of the LED biased at 13 V was shown in the inset of Figure 6.7. Purple emission, which was located on the surface of the Al/Ti contact, could be clearly seen by naked eyes at dark environment.

Figure 6.8 plots the I - V and light-voltage (L - V) curves of the heterojunction. The I - V curve reveals a rectifying diode behavior with a very limited reverse-bias leakage current. It is observed that both the L - V and I - V curves exhibit a turn-on voltage of ~ 5.5 V. The inset of Figure 6.8 sketches the energy band diagram of the heterojunction under forward and reverse bias. The Fermi level of SiC (SnO₂) is estimated as 0.8 eV (1.0 eV) above (below) the valence (conduction) band. The electron affinity of SnO₂, $\chi(\text{SnO}_2)$ and SiC, $\chi(\text{SiC})$ are 4.53 and 4.05 eV respectively^{146 153}. From the transmittance measurement, the optical bandgap of SnO₂, $E_g(\text{SnO}_2)$ was measured as ~ 3.6 eV. In addition, the bandgap energy of 4H-SiC, $E_g(\text{SiC})$ is 3.26 eV. Hence the conduction band and valence band offset are obtained as $\Delta E_C = \chi(\text{SnO}_2) - \chi(\text{SiC}) = 0.48\text{eV}$, and $\Delta E_V = \chi(\text{SnO}_2) - \chi(\text{SiC}) + E_g(\text{SnO}_2) - E_g(\text{SiC}) = 0.82$ eV. Although ΔE_V is greater than ΔE_C , holes from SiC could still be injected

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into SnO₂ under certain forward bias due to large hole concentration and mobility in the p-SiC. According to the EL and PL measurement, there are mainly three defects states inside of SnO₂ at ~3.20, ~3.00 and ~2.67 eV above valence band. It is suggested electrons in the conduction band relax to the three defects states non-radiatively, and recombine with the holes injected from SiC. Therefore, emission at ~3.20 eV is mainly due to the radiative recombination of weakly bounded excitons at the shallow-trapped surface defect states; while emission at ~3.00 eV and ~2.67 eV are attributed to the radiative recombination of deep-trapped electrons and holes on SnO₂ side.

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Figure 6.8 Room-temperature L - V and I - V characteristics of the p -SiC/SnO₂ thin film heterojunction diode. The inset shows the schematic diagram of the energy band alignment of the heterojunction under forward and reverse biases.

6.4 Summary

In conclusion, post-growth annealing is proposed to generate grains and voids randomly inside the as-grown SnO₂ thin film. Hence, the increase of surface to volume ratio of the SnO₂ thin film increases the shallow trapped states for the support of captured excitons. As a result, UV emission can be observed from the SnO₂ thin film at room temperature. The SnO₂/p-SiC heterojunction is fabricated. Diodelike rectifying I - V characteristics, with turn-on voltage of ~ 5.5 V and reverse saturation current of $< 10^{-1}$ μ A, are measured at room temperature. The electroluminescent spectra with emission peaks at around 390, 410 and 464 nm are observed from the heterojunction under forward bias. Radiative recombination between electrons captured at the surface defect states of small SnO₂ grains and holes injected from the p-SiC substrate contributes to the room-temperature UV electroluminescence. When the forward biased is increased to 13 V, purple light emission can be clearly observed by our naked eyes from the surface of the heterojunction in a dark environment. Hence, this indicates that SnO₂ thin films can be used to realize UV optoelectronic devices provided that SnO₂ grains and voids can be realized inside the thin film.

Chapter 7 Conclusion and Future works

7. Conclusion and Future works

7.1 Conclusion

p -Ga $N:Mg/i$ -ZnO:Al(3%)/ n -ZnO:Al(5%) heterostructure with 3- μm wide rib waveguide has been realized. Al doping is adopted in the intrinsic ZnO layer so that to reduce the resistivity of the annealed ZnO. Carriers are highly confined inside of the i -ZnO:Al(3%) layer. In the lateral direction, carrier diffusion is prevented by the SiO₂ cladding layer. In this way, the large optical gain could be attained. In addition, the strong off-axial scattering light is eliminated via total internal reflection by the SiO₂ cladding layer in the lateral direction and the n -ZnO:Al(5%) layer in the transverse direction which has slight smaller refractive index than that of the active layer. Thus, the lasing threshold is largely reduced as a result of the reducing of scattering loss. At the same time, the edge emitting directional lasing action is observed consequently. More importantly, it is found that the number of the random modes is significantly reduced by employing the rib waveguide structure. This is attributed to the reduction of the area of random media where the random modes are spatially repulsive.

Besides the rib waveguide, ZnO:Al(3%)/ZnO/ZnO:Al(3%) random laser arrays are designed to force the individual random modes overlap each other via strong lateral coupling between the adjacent array element. Hence, spectral repulsion of lasing modes in an inhomogeneously broadened gain medium is observed. As a result of the increment of the number of spectrally coherent array emitters, the total output

Chapter 7 Conclusion and Future works

intensity is enhanced. Far-field patterns with double-lobed profile are measured for the pump intensity $P > P_{th}$. It is suggested that the double-lobed profile is attributed to the excitation of the 1st order lateral mode in the array elements. Nevertheless the double-lobed far-field beam indicates there is strong lateral coupling between the adjacent random arrays. To verify the mode repulsion mechanism and also improve the performance, p -GaN:Mg/ i -ZnO:Al(3%)/ n -ZnO:Al(5%) laser arrays with Al₂O₃ as the coupling layer, which has stronger interelement coupling among the random modes than the ZnO:Al(3%)/ZnO/ZnO:Al(3%) arrays is designed and fabricated. Single-mode operation is observed even at high injection as stronger interaction among the random modes exists. It is interesting that a single-lobed supermode far-field pattern is observed.

Polycrystalline SnO₂ thin film with small and well-separated disordered grains is studied as another candidate of UV optoelectronic devices. SnO₂ thin films are deposited by the FCVA technique at low temperature. Post annealing is employed to form disordered grains and voids so that to increase the surface area exposed to the surrounding environment. Therefore shallow states resulted from large amount of surface states give rise to the intense luminescence at near-UV regime. The electroluminescence at 3.2 eV is observed from the SnO₂/SiC(4H) heterojunction.

7.2 Future work

In the index guided ZnO random laser array, significant reduction of the number of random modes and the enhancement of output power have been demonstrated as a

Chapter 7 Conclusion and Future works

result of the strong lateral coupling of the neighbor random modes. However, the far field profiles suggest there is no phase locking presented in the random laser array. A more thorough study is needed in determining the phase condition of the laser emitters in the array. The study of the fringe visibility between the individual emitters is desired to quantize the spatial coherence of the two array elements.¹⁵⁴ The dependence of the random modes suppression, coherence of individual elements, far-field pattern and the beam divergence is needed to be studied comprehensively.

Although in Chapter 5, the stable single-mode dominated operation has been achieved even at high injection by strong coupling between the adjacent random cavities. To pursue more applications such as high resolution spectroscopy, the noise from the side modes should be further suppressed. More importantly, mode hopping introduces fluctuation in the operating wavelength at different injection level. This would impair the usefulness of the ZnO random laser diode. To heal the insufficiencies, longitudinal mode selection could be adopted into random lasers. The distributed Bragg reflector (DBR) or distributed feedback (DFB) laser structures are to be explored to realize the strong mode discrimination in random lasers. Grating with period as $\Lambda = \lambda / 2n_{eff}$ is to be etched onto one layer of the ZnO random laser diode with buried waveguide, or at the end of the intrinsic ZnO rib, where n_{eff} is the effective-mode index. Here Λ is to be adjusted to match with the dominating closed-feedback loop in the ZnO random media, so that to well suppress the side random modes and also lock the operating wavelength. Λ is estimated to be < 100 nm. Holographic photolithographic, focused ion beam and electron-beam

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lithography techniques could be used to form the grating with subwavelength features.

Some recent works have demonstrated that the coupling between ZnO emission and surface plasmons could be realized, and certain surface morphology could match the wave vectors of ZnO emission and surface plasmons.¹⁵⁵⁻¹⁵⁷ This inspires to utilize surface Plasmon coupling to improve the performance of the ZnO random laser diode. In resonance state, surface plasmon could enhance the emission efficiency by more than 1 order by increasing the spontaneous emission rate. Thus it is expected to enhance the lasing efficiency in the ZnO random laser diode by surface plasmon coupling. In addition, surface plasmon modes propagate in the metal/dielectric interface. It is actually a kind of nanometric confinement. This could be employed to further reduce the scattering loss of the ZnO random laser, and realize an excellent optical confinement. Moreover, as a waveguide, metal strips could provide a much more efficient confinement than the dielectric waveguide.¹⁵⁸ In a further step, if a periodic metal structure could be properly designed, the effective refractive index of the plasmon modes could be largely increased by modifying the dispersion property so that the confinement could be further enhanced.¹⁵⁹ So the surface plasmon waveguide could be designed to suit for the ZnO random laser diode to enhance the directional emission.

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From the above recommendation, it is clear that there is a potential to realize a useful ZnO random laser diode with precisely controlled single mode operation, high output power, nanoscale confinement, and directional emission.

Appendix A

Appendix A :Determine the ZnO waveguide width

Begin with Maxwell's equations.

$$\nabla \cdot E = \frac{\rho}{\epsilon},$$

$$\nabla \times E = -\frac{\partial B}{\partial t},$$

$$\nabla \cdot B = 0,$$

$$\nabla \times B = \mu\epsilon \frac{\partial E}{\partial t}.$$

Taking the curl of the curl function of the electric field gives

$$\nabla \times \nabla \times E = -\frac{\partial}{\partial t} \nabla \times B = -\mu\epsilon \frac{\partial^2 E}{\partial t^2}.$$

By using the vector identity

$\nabla \times \nabla \times E = \nabla(\nabla \cdot E) - \nabla^2 E = -\nabla^2 E$, therefore, we obtain the wave equation

$$\nabla^2 E - \mu\epsilon \frac{\partial^2 E}{\partial t^2} = 0.$$

The electric field inside of the waveguide takes the form of $E = E(x, y)e^{i(\alpha x - \beta z)}$.

Substituting the electric field into the wave equation, the wave equation has the form of

$$\nabla^2 E + k_o^2 n^2 E = 0, \text{ with } \mu\epsilon = \frac{c^2}{n^2}, \text{ and } k_o = \frac{\omega}{c}.$$

Appendix A

Figure A1 A symmetric slab waveguide.

In the waveguide structure in Figure A1 with refractive indices of core and cladding as n_2 and n_1 respectively, the electric field has the expression as

$$\text{Region 1: } E_y = [C \cos(hw) + D \sin(hw)]e^{-p(x-w)},$$

$$\text{Region 2: } E_y = C \cos(hx) + D \sin(hx),$$

(A1)

$$\text{Region 3: } E_y = Ce^{px}.$$

To satisfy the wave equation, we have

$$h = \sqrt{n_2^2 k_o^2 - \beta^2} \text{ and } p = \sqrt{\beta^2 - n_1^2 k_o^2}.$$

So we have

$$h^2 + p^2 = (n_2^2 - n_1^2)k_o^2.$$

(A2)

Appendix A

Next we require the tangential field component be continuous across the interface.

Hence

at $x=0$,

$$Cp = Dh, \quad (A3)$$

at $x=w$,

$$-p[C \cos(hw) + D \sin(hw)] = h[-C \sin(hw) + D \cos(hw)], \quad (A4)$$

(A3) and (A4) results

$$\tan(hw) = \frac{2ph}{h^2 - p^2}, \quad (A5)$$

which gives $\tan(h\frac{w}{2}) = \frac{p}{h}$ for the even symmetric modes, and $\cot(h\frac{w}{2}) = -\frac{p}{h}$ for

the odd symmetric modes.

A straightforward graphical solution is illustrated by Figure A2 and consists of finding the intersections in the $pw-hw$ plane of the circle $(pw/2)^2 + (hw/2)^2 = (n^2_2 - n^2_1)k^2(w/2)^2$ from equ. (A2) with the curve $pw/2 = hw/2 \tan(hw/2)$ and $pw/2 = -hw/2 \cot(hw/2)$ from equ. (A5). Each intersection like point A, B, C corresponds to a confined mode.

Appendix A

Figure A2 Plot of eigenvalue equations $p\frac{w}{2}=h\frac{w}{2}\tan(h\frac{w}{2})$ for even TE modes, $p\frac{w}{2}=-h\frac{w}{2}\cot(h\frac{w}{2})$ for odd TE modes, and the supplementary relationship

$$(p\frac{w}{2})^2+(h\frac{w}{2})^2=(n_2^2-n_1^2)k^2(w/2)^2.$$

It is noted directly from the graph that the frequency parameter $0 < \sqrt{n_2^2 - n_1^2} k_0 w/2 < \pi/2$ needs to be satisfied in order to sustain only the fundamental mode.

For the laser array in Chapter 4, the effective refractive indices of ZnO and ZnO:Al(3%) column are calculated as $n_2=1.7549$ and $n_1=1.7351$ by using transfer matrix method. Having $k_0 = 2\pi/\lambda = 2\pi/0.39\mu\text{m}$, the largest waveguide width for fundamental lateral mode operation is $w=0.74\mu\text{m}$. Similarly, from

Appendix A

$\sqrt{n_2^2 - n_1^2} k_o w / 2 < \pi$, the largest waveguide width for first order lateral mode

operation is $w=1.48\mu\text{m}$. This calculation matches well with the measured results.

For the laser array in Chapter 5, the effective refractive indices of $n\text{-ZnO:Al(5\%)/i-ZnO:Al(3\%)/p-GaN:Mg}$ and $n\text{-ZnO:Al(5\%)/Al}_2\text{O}_3\text{/p-GaN:Mg}$ column are calculated

as $n_2=2.4411$ and $n_1=2.4374$ by using transfer matrix method. Having

$k_o = 2\pi / \lambda = 2\pi / 0.39\mu\text{m}$, the largest waveguide width for fundamental lateral mode

operation is $w=1.45\mu\text{m}$. This calculation matches well with the measured results.

Appendix B

Appendix B :The coupling coefficient of different ZnO laser arrays

The coupling coefficient from the identical waveguide arrays is defined as

$$\kappa = \frac{\omega \epsilon_0}{4} \int_{-\infty}^{+\infty} [n_c^2(x) - n_a^2(x)] E_y^2 dx$$

, where n_a and n_c are effective indices of the individual waveguide and the waveguide arrays.

It can be simplified as

$$\kappa \approx \frac{2h^2 p e^{-ps}}{\beta(w + 2/p)(h^2 + p^2)} \quad (B1)$$

for TE modes.

Here $h^2 = n_2^2 k_o^2 - \beta^2$, $p^2 = \beta^2 - n_1^2 k_o^2$. For an individual waveguide, n_2 and n_1 are the effective indices of the waveguide core and cladding respectively as shown in Figure B1. β is the propagation coefficient of a uniform waveguide.

Figure B1 An identical waveguide array

Appendix B

(1) For the ZnO laser array with ZnO:Al(3%) cladding: $n_2=1.7549$, $n_1=1.7351$,

and $w=1.5 \mu\text{m}$,

$$\sqrt{n_2^2 - n_1^2} k_o w / 2 = \sqrt{1.7549^2 - 1.7351^2} \frac{2\pi}{0.39} 0.75 = 2.06.$$

From Figure A2, $pw/2=1.8$, $hw/2=1.1$. So we obtain $p=2.40$, and $h=1.47$. β can be calculated as

$$\beta = \sqrt{1.7549^2 \left(\frac{2\pi}{0.39}\right)^2 - 1.47^2} = 27.63.$$

Substitute the value of h , p , β and the waveguide spacing $s=0.8 \mu\text{m}$ into equ.

(B1), we have

$$\kappa \approx \frac{2 \times 1.47^2 \times 2.4 \times e^{-2.4 \times 0.8}}{27.63(1.5 + 2/2.4)(2.4^2 + 1.47^2)} = 30 \text{ cm}^{-1}.$$

(2) For the ZnO laser array without ZnO:Al(3%) cladding: we use $n_1=1$.

$$\sqrt{n_2^2 - n_1^2} k_o w / 2 = \sqrt{1.7549^2 - 1^2} \frac{2\pi}{0.39} 0.75 = 17.04.$$

From Figure A2, $pw/2=17$, $hw/2=1.5$. So we obtain $p=22.6$, and $h=2$. β can be calculated as

$$\beta = \sqrt{1.7549^2 \left(\frac{2\pi}{0.39}\right)^2 - 2^2} = 27.63.$$

Substitute the value of h , p , β and the waveguide spacing $s=0.8 \mu\text{m}$ into equ.

(B1), we have

$$\kappa \approx \frac{2 \times 2^2 \times 22.6 \times e^{-22.6 \times 0.8}}{27.6(1.5 + 2/22.6)(22.6^2 + 2^2)} = 1.1 \times 10^{-6} \text{ cm}^{-1}.$$

Appendix B

(3) For the ZnO laser diode array with Al₂O₃ cladding in chapter 5: $n_2=2.4411$,

$n_1=2.4374$, and $w=1\text{ }\mu\text{m}$.

$$\sqrt{n_2^2 - n_1^2} k_o w / 2 = \sqrt{2.4411^2 - 2.4374^2} \frac{2\pi}{0.39} 0.5 = 1.07.$$

From Figure A2, $pw/2=0.7$, $hw/2=0.75$. So we obtain $p=1.4$, and $h=1.5$. β

can be calculated as

$$\beta = \sqrt{2.4411^2 \left(\frac{2\pi}{0.39}\right)^2 - 1.5^2} = 39.3.$$

Substitute the value of h , p , β and the waveguide spacing $s=1\text{ }\mu\text{m}$ into equ.

(B1), we have

$$\kappa \approx \frac{2 \times 1.5^2 \times 1.4 \times e^{-1.4 \times 1}}{39.3(1 + 2/1.4)(1.5^2 + 1.4^2)} = 38.7\text{ cm}^{-1}.$$

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Author's publications

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