

# Chapter 4

## Development of Fabrication Processes for III-Nitride Vertical-Cavity Surface- Emitting Devices

### 4.1 Introduction

Nitride semiconductors are quite promising materials considering their superior physical properties suitable for short-wavelength optoelectronic device applications. Nitride-based vertical-cavity surface-emitting lasers (VCSELs) have received much attention because of their various advantages such as a great potential for two-dimensional short-wavelength laser arrays, which provides the possibility of high-density, high-speed optical data storage. Since the first demonstration of optically pumped lasing of nitride VCSELs <sup>[15]</sup>, various efforts have been devoted to realize current injection operation in VCSELs and vertical microcavity LEDs (MCLEDs). One of the most difficult issues has been to grow electrically conductive nitride DBRs with high reflectivity. Though there have been several proposals on nitride vertical-cavity surface emitting devices, limitations on the device design coming from unavailability of electrically conductive nitride DBRs are troublesome. Since a highly-resistive, non-doped nitride DBR is just beneath the cavity, one must etch the p-i-n junction layers and expose the buried n-type nitride layer inside the cavity. Such a process requires rather thick p-i-n layers which is also served as a cavity. On the contrary, a conductive, epitaxial mirror through which carriers can be injected into the active region will be helpful to shorten the cavity length down to as thin as a half wavelength. It is also expected that the device fabrication process will be simplified by sequential formation of semiconductor mirrors and

the cavity. In this chapter, we demonstrate successful fabrication of blue InGaN vertical MCLEDs with a Si-doped n-AlGaIn/n-GaN DBR.

There are several proposals to realize electrically-driven nitride vertical cavity devices. One of them utilizes undoped nitride DBR as the bottom mirror, and hence thick n-GaN is placed beneath the active region and used as n-type contact layer [70]. In this case, thinner cavity suitable for microcavity devices such as single-photon sources is difficult to obtain, limited by controllability or reproducibility of etching procedures. Other proposals include double-dielectric-mirror structure or metal-hybrid structure [19, 20]. Both of them require very complicated and delicate process of epitaxial lift-off, which also might cause severe degradation of reflectivity at the lifted-off surface. Tawara et al. reported high quality factor in double-side dielectric mirror coated InGaIn microcavity and argued that interface roughness is negligible even at the lifted-off surface [20]. However, double-sided dielectric mirror coated devices have fundamental problem of lack of proper current injection method. Introduction of monolithic, conductive nitride DBRs is one of solutions to such structure design issues. From this point of view, we have tried to fabricate electrically-conductive nitride DBRs, of which growth details and characteristics will be given in chapter 3.

As for p-type DBRs, there are much higher technological barriers or obstacles due to inherent poor availability of high quality, high Al-composition p-AlGaIn. One practical solution may, thus, seem to be usage of combination of a p-GaN (or p-InGaIn) contact layer and a dielectric mirror [106]. Current injection method should be carefully optimized with such structures, because inside p-GaN layers hole current diffusion length is so short that usual ring-shaped metallic contact surrounding the dielectric mirror is not useful at all. One possible solution is transparent intracavity contact that enables us to inject hole current homogeneously into the cavity. With these issues kept on mind, we have fabricated nitride microcavity devices utilizing intracavity transparent contact. Fabrication and characterization of the microcavity LEDs will be further discussed in chapter 5.

Developments of fabrication processes for nitride vertical microcavity light emitting devices are presented in this chapter. The developed processes range from substrate preparation method for DBR growth to formation of transparent intracavity contact. As mentioned above, it is reasonable to utilize transparent intracavity contact to overcome design issues concerning efficient hole current injection. For this purpose, indium tin oxide (ITO) is used in this study. Rapid thermal annealing of sputtered ITO films under nitrogen ambient can improve both electrical and optical properties of the films. To improve process yield in photolithographic liftoff, new double-layer resist technique is developed.

Undercut resist profile favorable for liftoff as well as good adhesion onto nitride (and ITO) surface is available with this new method. Substrate preparation method to prevent thick AlGaIn/GaN DBR to crack is also established.

## 4.2 Development of Hole Injection Method

### 4.2.1 Activation of Mg Acceptor in Mg-doped GaN by Rapid Thermal Annealing

Thermal activation techniques for the Mg-doped p-GaN layers are one of the most innovative processes that greatly promoted nitride research activities worldwide <sup>[107]</sup>. In MOCVD growth, unintentionally doped hydrogen impurities play important roles to deactivate Mg atoms in the grown nitride films <sup>[108]</sup>. Complex defects consisted by both hydrogen and Mg atom is considered to be the origin of low free carrier concentration in p-GaN and hence such complex defects must be decomposed by desorbing hydrogen for the purpose of obtaining p-type conductivity. Commercial grade nitride optoelectronic devices have been available when Nakamura et al. invented practical way to activate Mg dopants by rapid thermal annealing <sup>[107]</sup>. We also used similar method to activate Mg acceptors to fabricate nitride devices. Activation of Mg acceptor was done by rapid thermal annealing with nitrogen atmosphere. With 5-minute annealing at 1000°C, Mg-doped GaN films grown at 1045°C with Cp<sub>2</sub>Mg flow of 21.6 sccm become p-type, in which approximately  $1 \times 10^{18}$  cm<sup>-3</sup> carriers can be obtained. From systematic analysis on annealing temperature dependence of the carrier density of p-GaN, we have found that annealing at 1000 °C provides acceptable values reproducibly. Carrier concentration was measured by Hall measurements with Van der Pauw geometry using Ni/Au contacts also annealed at 600°C in the oxygen-nitrogen mixture gas (O<sub>2</sub> ~3%). Ni/Au contact exhibits ohmic behavior after the annealing. Despite proposed theories have been controversial, formation of NiO seems to be effective to reduce the contact resistance <sup>[109, 110]</sup>.

### 4.2.2 Fabrication and Characterization of p-Contacts for III-Nitride Vertical-Cavity Surface-Emitting Devices

As is discussed in chapter 3, p-GaN contact issue is critical to fabricate nitride vertical-cavity devices. Commercial nitride-based blue LEDs or LDs utilize Ni/Au ohmic contact as p-type contact material. In the last decade, research efforts have been devoted to search lowest resistance, highly reliable p-contact materials. Ni/Au metal contact has revealed to be improved in terms of both

electrical and optical characteristics by means of oxidized annealing method. When Ni/Au contact on p-GaN is annealed under some proper ration of oxygen presence, both optical transmittance and contact resistance are found to be improved. One possible explanation of this behavior is given that incorporation of oxygen forms transparent NiO and promotes the outdiffusion of Ga atoms from the GaN layer leaving Ga vacancies, which plays a role in increasing the net hole concentration and lowering the Fermi level position. The drastic reduction of contact resistivity by the oxidation annealing could be attributed to the formation of Ga vacancies <sup>[111]</sup>. Although there are other materials such as Pt-, Ti- or Al- contained metal composites (multilayers) used for the p-contact, all of them cannot avoid considerable absorption at around 400 nm. Poor availability of p-AlGaN makes p-type DBRs almost impractical. Combined use of a p-GaN contact layer and a top dielectric mirror provides much realistic way to construct nitride vertical-cavity devices. Because of short lateral diffusion length in p-GaN layers, ring-shaped metallic contact surrounding the dielectric mirror can not efficiently inject holes inside the cavity. To confirm this difficulty, conventional LED structures were fabricated. An Au ring-shaped p-contact was placed at the periphery of the device mesas. Device structure was grown by atmospheric pressure MOCVD as described in chapter 2. InGaN quantum wells were sandwiched by n-GaN and i-InGaN/i-GaN/p-GaN layers. The device mesa structure was lithographically defined and formed by electron cyclotron resonance plasma etching using Cl<sub>2</sub>. Au p-contact was deposited on the mesas, and finally In solder bump was put on the etched n-GaN surface, providing n-contact<sup>†</sup>. Pulsed forward current was applied to the device and the emission images were recorded through the sapphire substrates using microscope setup and liquid nitrogen cooled charge coupled devices (CCD) camera with various shutter speed. Figure 4.1 shows a set of the images of a device. In this specific sample, diameter of inner circle of the ring contact (to guide for eyes, white lines indicating geometrical shape of the ring contact is added) was 140 μm, while width of the contact was 30 μm. Operation conditions were as follows: voltage 8.5 V, current 2.6 mA, frequency 100 kHz, duty 1 %, shutter 30 sec. Obviously, emission was limited just beneath the contact region, and even in that region, some area did not exhibit bright emission, implying incomplete mechanical contact between Au and p-GaN. Almost no diffusion current inside the ring was observed. It is still difficult to estimate hole diffusion length by this observation, but at most several μm was presumably good estimation of the diffusion length.

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<sup>†</sup> The device was fabricated at Prof. Forchel's group in Würzburg University.

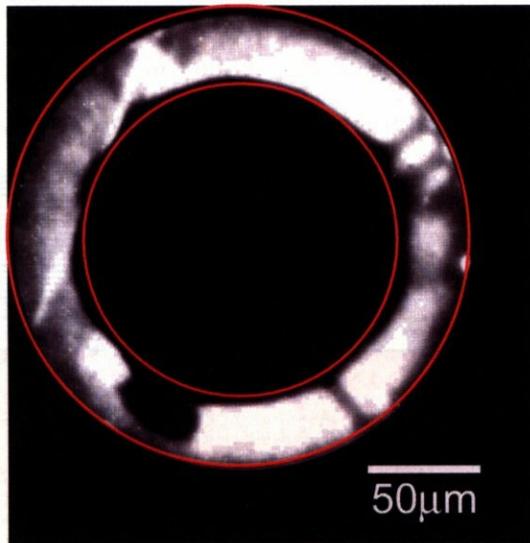
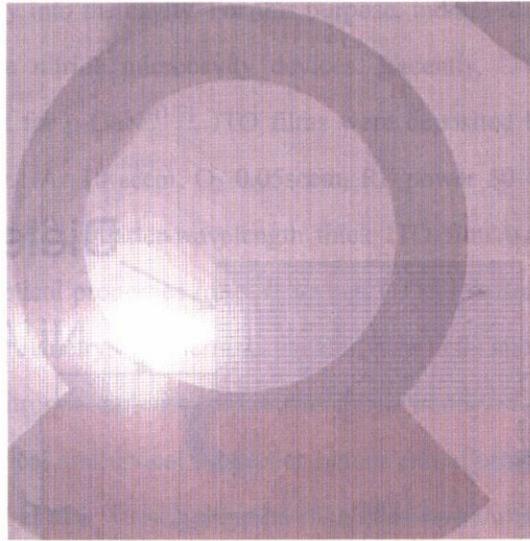


Figure 4.1 Microscopic images of devices with metal ring contact

The problem coming from poor hole diffusion is depicted in Fig. 4.2. As mentioned above, metallic ring contacts are not effective (upper panel in Fig. 4.2). It is also possible to place metal-based ohmic p-contact prior to the deposition of top-dielectric mirror. Dielectric mirror then covers this metal contact, forming so-called intracavity contact. In this structure, a part of problem will be solved with efficient injection into the cavity. However, photons with wavelength of around

400 nm can be easily absorbed by this metal contact, even in the case of very thin, semi-transparent film is used (lower panel in Fig. 4.2).

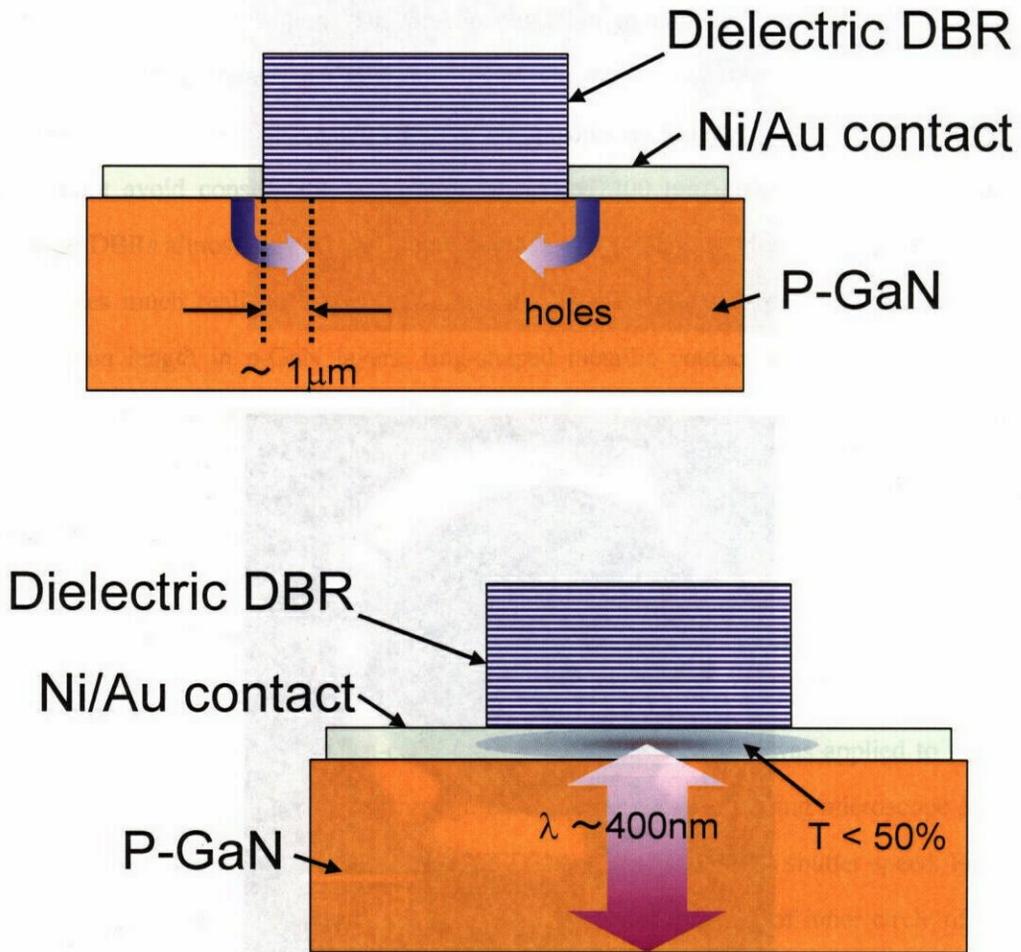


Figure 4.2 Illustrations depicting difficulties concerning hole current injection. Top: ring contact fails sufficient hole supply. Bottom: metal intracavity contact causes severe absorption.

One possible solution for this problem is highly transparent intracavity contact with which we can inject holes effectively into the cavity. For this purpose, indium-tin-oxide (ITO) was applied to the p-contact to fabricate nitride microcavity devices. Recently, ITO films are proposed as a transparent ohmic contact for p-GaN [112]. ITO films were deposited by RF-magnetron sputtering with conditions as follows: Ar 10 sccm, O<sub>2</sub> 0.05sccm, RF power 50 W. Considered its refractive index of approximately 2 [113], quarter-wavelength thick ITO film was used for the microcavity devices. Electrical and Optical properties of as-deposited ITO films are relatively poor due to their crystalline quality or stoichiometry, and thermal annealing is usually applied to improve them. In this study, annealing under nitrogen ambient resulted in much improved properties of ITO films. In figures 4.3 and 4.4, electrical and optical properties before and after the annealing were illustrated. Annealing was performed at 600 °C with duration of 1 min. As can be seen from the figures, both electrical and optical properties were improved by the annealing. To further investigation, atomic force microscopy was used to observe surface structure of the ITO films. Figure 4.5 shows the AFM images of the surface morphologies of both as-deposited and annealed samples. In the annealed sample, enlarged grains with smooth surface can be seen. Probably, the film was polycrystalline as deposited and was crystallized by annealing. ITO is often described as a degenerate n-type semiconductor, and improved crystallinity increases free carrier density. Optical characteristics can be also explained by this increased carrier density, inducing Burstein-Moss shift inside the material.

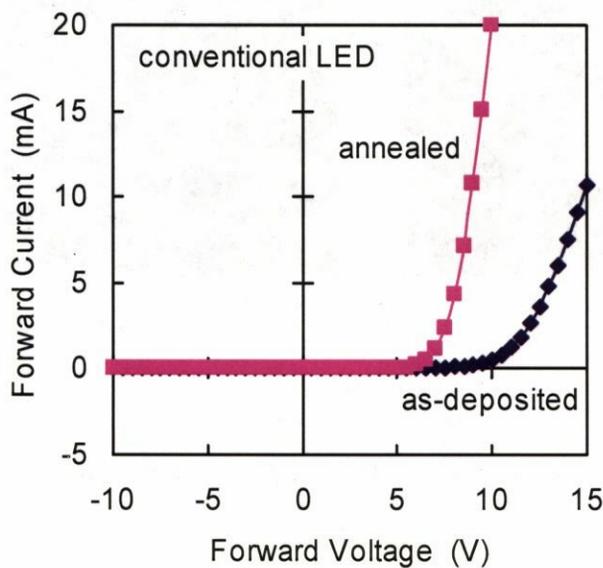


Figure 4.3 Annealing effects of ITO: electrical characteristics

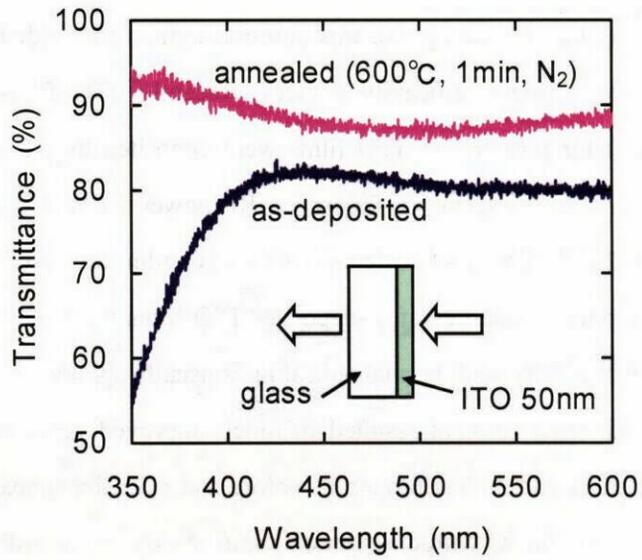


Figure 4.4 Annealing effects of ITO: optical characteristics

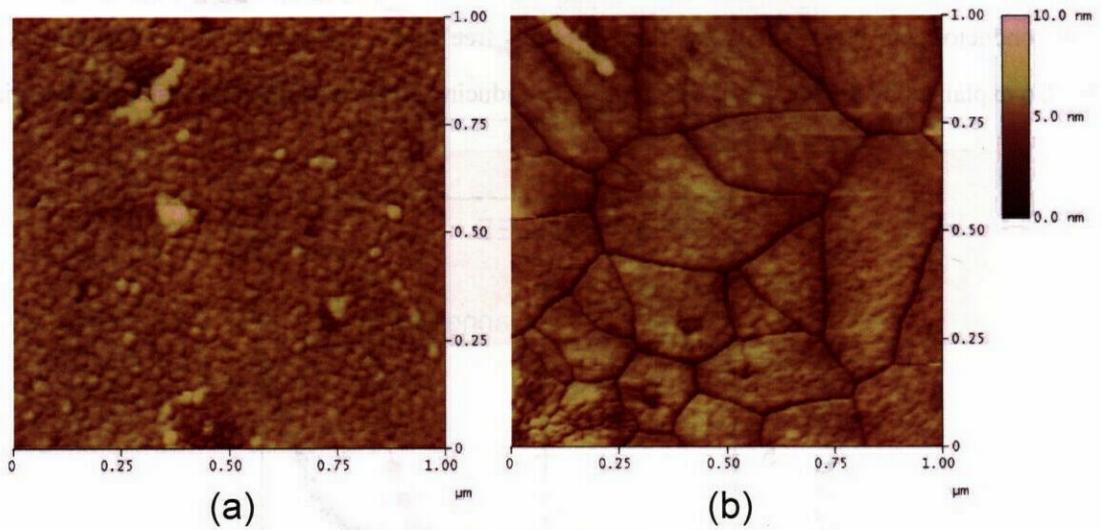


Figure 4.5 AFM images of (a) as-deposited and (b) annealed ITO

Using above-mentioned ITO films, blue InGaN LED was fabricated. Figure 4.6 shows microscope images of the fabricated ITO-LED. Epitaxial layer structure was similar as the devices shown in figure 4.2. First, activation of p-GaN layer was performed and ITO transparent p-contact was deposited and annealed as described previously. Square mesas of  $200 \text{ nm} \times 200 \text{ nm}$  were fabricated by reactive ion etching using  $\text{Cl}_2$  and Xe, using photolithographically patterned Ni masks. After the dry etching, Ni was removed selectively by using commercial Al etchant (phosphoric-acid based solution,  $\text{H}_3\text{PO}_4 : \text{CH}_3\text{COOH} : \text{HNO}_3 : \text{H}_2\text{O} = 72.3 \% : 9.8 \% : 2.0 \% : 15.9 \%$ ). ITO is highly resistant to this etchant at room temperature (etching rate of annealed ITO to the etchant is far below  $10 \text{ nm/hr}$ ), so one can remove only Ni without losing ITO itself. Finally, Al was deposited by thermal evaporation and lifted-off using standard photolithography, and served as an n-contact. In figure 4.6, left probe is an electrode for p-GaN, and right one is that for n-GaN. In contrast to the metal contact shown in figure 4.1, ITO films enabled us to inject current uniformly across the whole area of the device mesa. It should be noted that emission intensity distribution strongly localized to the n-contact side is attributed to the limited carrier diffusion length in the n-GaN layer, rather than p-contact itself. From these results, beneficial aspects of ITO have been confirmed experimentally.

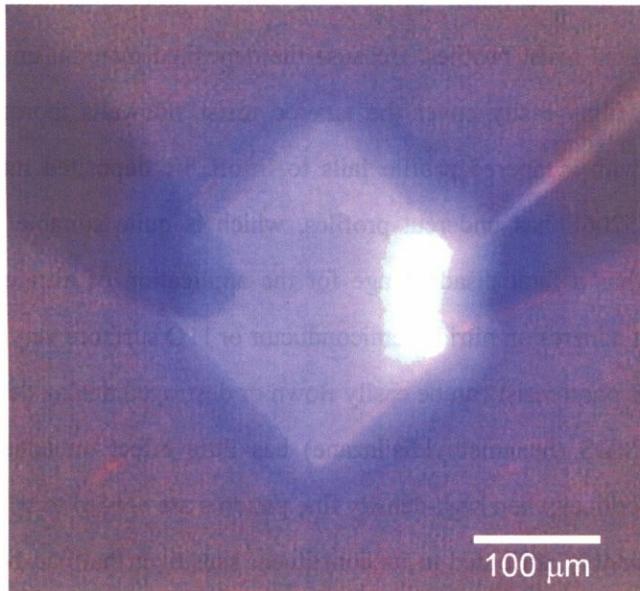


Figure 4.6 Photograph of an ITO-LED

## 4.3 Development of Fabrication Processes especially suitable for III-Nitride Surface Emitting Devices

### 4.3.1 Photolithography Suitable for High Density Nitride Surface Emitting Devices

Photolithographic liftoff process is frequently used in nitride semiconductor device fabrication because wet etching process is limited for the specific cases that etchant does not damage any underlayers. That means wet etching always requires enough etching selectivity between the target material and the others. This criterion is not always fulfilled. Furthermore, wet etching process cannot reproduce mask geometry precisely due to the isotropic nature of the process. Dry etching can be used as an alternative way to obtain anisotropic profiles, but generally the processing species (gases or plasmas) have much worse selectivity than wet etchants. In consequence, liftoff process is quite convenient and usually has enough precision for thin film patterning by photolithography. There are roughly two-types of photoresist used in photolithography; positive-type and negative-type. When exposed through a mask pattern and then developed, the former makes positive patterns, i.e. exposed regions are turned to be soluble into the developer chemical, while the latter does vice versa. Examples of the positive photoresists are AZ1350 or AZ1500, both supplied by AZ Electronic Materials. On the other hand, a positive resist AZ5206E can be used as a negative resist by employing so-called 'image-reversal' procedures. Liftoff process utilizing positive photoresists suffers from non-vertical resist profiles. Because the deposited material uniformly covers over the resist patterns, thick films easily cover the tapered resist sidewalls thoroughly. As a result, the positive photoresist with a tapered profile fails to liftoff the deposited material. In contrast, the 'image-reversed' AZ5206E has undercut profiles, which is quite suitable for the liftoff process. However, AZ5206E has a fatal disadvantage for the application of nitride semiconductor device fabrication. The resist adheres on nitride semiconductor or ITO surfaces very badly. So, fine patterns with simple AZ5206E photoresist can be easily flown or destroyed during development<sup>[114]</sup>. Surface promoter such as HMDS (hexamethyldisilazane) has little effect on adhesion of the resist and substrates. This is so critical when high-density fine patterns are needed to be fabricated. This feature of AZ5206E is presumably attributed to its constituent sensitizer that had been engineered to form catalyst promoting the conversion reaction of diazonaphthoquinone into an insoluble substance during co-called reversal baking step<sup>[115]</sup>. Hydrophilicity (or hydrophobicity) of a photoresist surface is generally determined by the sensitizer, that implies the surface free energy of the resist is also

dependent on the substance. On the contrary, a standard positive photoresist, AZ1500, exhibits good adhesion to nitrides or dielectrics. In order to improve process yield in photolithographic liftoff, new double-layer resist technique is developed. First, positive photoresist for example thin AZ1500 is spun onto the sample and then baked at slightly higher temperature than that used in usual post-bake step. A care was taken not to deposit too-thick resist for the first layer. Secondly, onto this hard-baked AZ1500, AZ5206E is spun, followed by standard image-reversal procedures (detail conditions will be presented in the next chapter). In this way, AZ5206E can be patterned without destroy. AZ1500 works as adhesion layer in this double-layer scheme. The hard-baking temperature should be determined so as not to let the coated AZ1500 immediately dissolve into the successively dropped AZ5206E solution, but to let it eventually dissolve into the developer alkali at the final stage. A 10-minutes baking at 120 °C (on hotplate) was not sufficient, while 150 °C with the same duration was a overbaking condition. We used 135°C and 10 min. as optimum conditions for the process. Figure 4.7 illustrates pattern transfer reproducibility of the double-layer resist (lower panel) and AZ5206E only (middle panel).Both undercut resist profile and good adhesion were simultaneously available with this new method. As a result, High density nitride device arrays can be easily patterned by using this procedure.

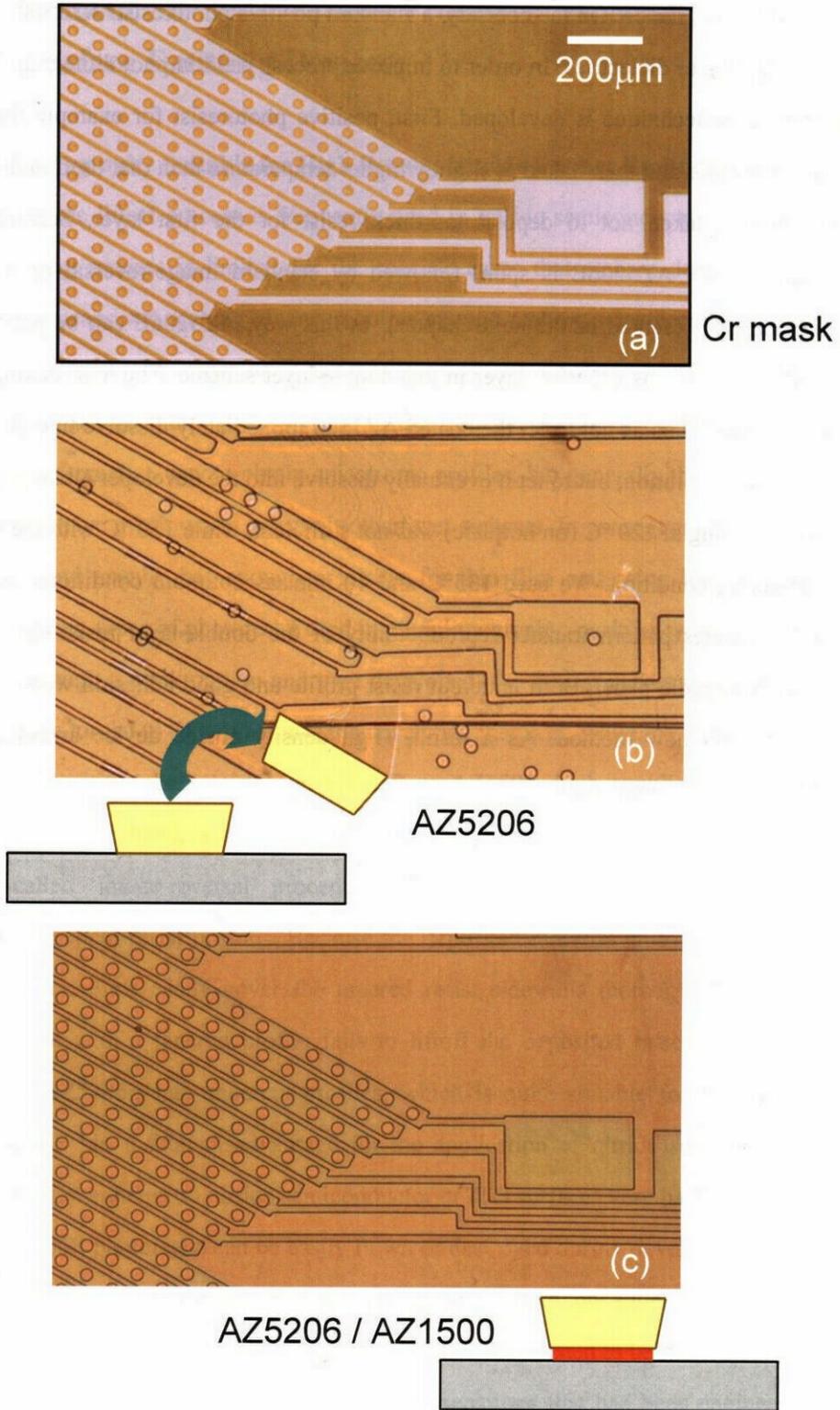


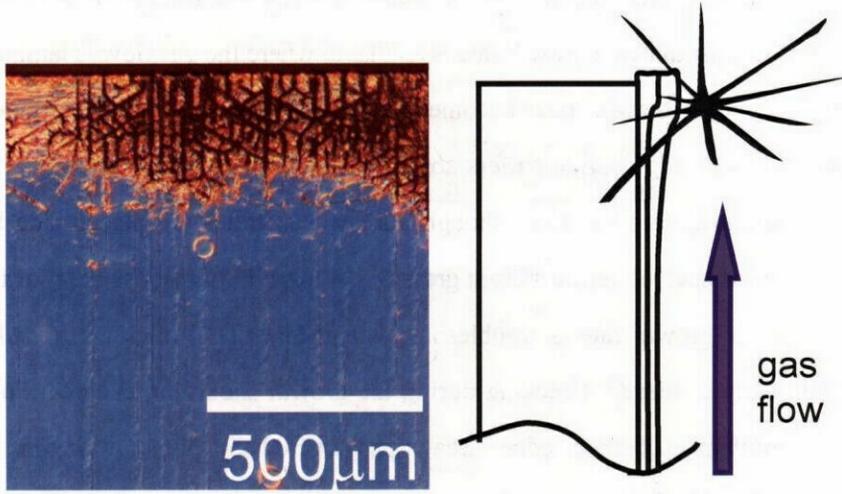
Figure 4.7 Microscope images of photolithography patterns (a) mask pattern, brighter regions corresponds to the Cr masks, developed resist patterns with (b) single layer resist and (c) double-layer resist

### 4.3.2 Substrate Preparation Method for Nitride Surface Emitting Devices with Thick, High Reflectivity DBRs

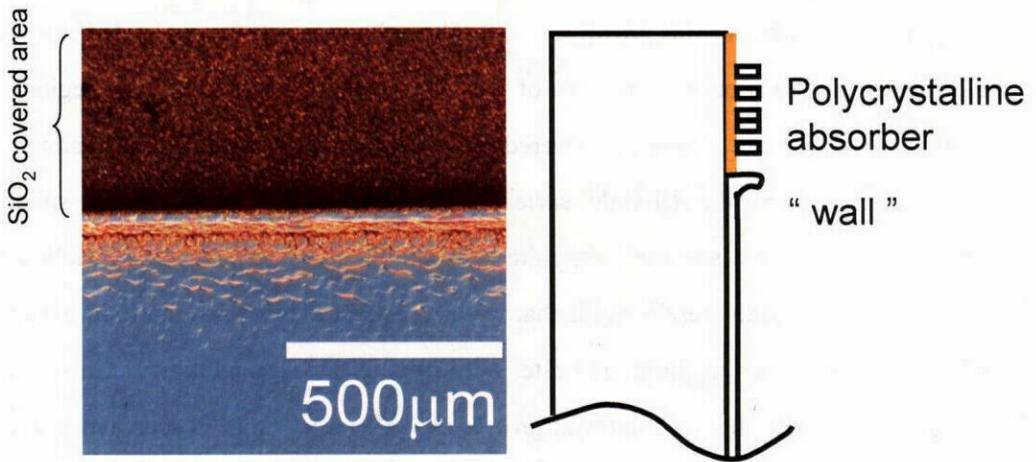
In addition to above-mentioned processes, substrate preparation method to prevent thick AlGaIn/GaN DBR from cracking was also developed. MOCVD has an intrinsic problem with gas flow dynamics. Almost uniform growth rate is available where the gas flow is laminar and stable, but inhomogeneity of the growth rate becomes not negligible where gas turbulence occurs. In consequence, substrate edge region suffers abnormal growth rate due to perturbed flow at the close proximity of the substrate edge. Even though dummy substrates are placed side by side with the substrate to suppress such effects, different growth rate, usually higher than that of the uniform area, is observed. Higher growth rate is troublesome when the critical thickness of AlGaIn/GaN DBR layers can be nearly exceeded. Cracking during the growth should be avoided. For the purpose of solving this problem, substrate edge area was covered by SiO<sub>2</sub> thin film deposited after low-temperature GaN buffer growth. This mask was found to be very effective to control abnormal growth in particular for thicker DBRs.

Epitaxial growth was done with MOCVD, described in the previous chapter. First, the low-temperature GaN buffer was grown as usual. Then, the substrate was unloaded from the reactor to be deposited the SiO<sub>2</sub> on it. Thickness of the SiO<sub>2</sub> was ~10 nm. Wafer edge regions, typically 500~1000 μm wide, were efficiently covered by the SiO<sub>2</sub> films. Note that at this step, no resist organic was coated on the LT-GaN surface to avoid the contamination. In spite of using photolithography, we used a dummy sapphire substrate face to face with the LT-GaN to mask the desired region. Also worth mentioning is that we had tested the other condition, in which SiO<sub>2</sub> was deposited directly on the sapphire substrate, only to find poor wettability of GaN growth cores around the SiO<sub>2</sub> mask. The heteroepitaxial growth of GaN on sapphire is sensitive to the substrate surface. Figure 4.8 shows optical microscope images of edge region of DBRs and schematic drawing of the thickness evolution mechanisms. By laser microscope observations, vertical profile of the grown nitride near the mask edge was revealed to form a wall-like three-dimensional structure. Nitride film thickness was gradually decreased toward the 'wall'. It seems like that excess amount of supplied source species were effectively absorbed by this wall structure and microcrystalline or polycrystalline seeds on the SiO<sub>2</sub> mask. Cracks observed in the conventionally grown sample was may be attributed to the hillock growth within the edge region, where accumulated source species lead higher growth rates. If the growth rate of AlGaIn gets higher than that of GaN in this region, or

if Al content in the hillocks become higher than that in two-dimensionally grown layer, such hillocks will cause cracks due to excess strain. Although more investigations are necessary to understand the mechanisms, these findings are very useful to grow thick, highly strained nitride films.



(a)



(b)

Figure 4.8 Abnormal growths near the substrate edge :  
 (a) conventional growth (b) SiO<sub>2</sub> covered growth

## 4.4 Summary

In this chapter, developments of fabrication processes for nitride surface-emitting devices are presented. Because at least one of cavity mirrors is made by insulating materials in practical nitride vertical microcavity devices, it is reasonable to utilize transparent intracavity contact to overcome design issues concerning efficient hole current injection. For this purpose, indium tin oxide (ITO) is used in this study. Rapid thermal annealing of sputtered ITO films under nitrogen ambient can improve both electrical and optical properties of the films. To improve process yield in photolithographic liftoff, new double-layer resist technique is developed. Undercut resist profile favorable for liftoff as well as good adhesion onto nitride (and ITO) surface is available with this new method. In addition to these developments, substrate preparation method to prevent thick AlGaIn/GaN DBR to crack is established.

