Mass Transfer of Microscale Light-Emitting Diodes to Unusual Substrates by Spontaneously Formed Vertical Tethers During Chemical Lift-Off

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Abstract: A much simplified method for transferring Gallium nitride (GaN) light emitting diodes (LEDs) to an unusual substrate, such as glass, Si, polyethylene terephthalate, or polyurethane, was demonstrated with spontaneously formed vertical tethers during chemical lift-off (CLO), without requiring a sacrificial layer or extra process steps. The LED arrays resided on a stamp that was coated with an adhesive layer. After the layer with the LEDs was transferred to the new substrates, the stamp was removed by acetone to complete the preparation. Over 3 × 3 cm² LED arrays transferred to various substrates without any damage and misorientation. We also found that the optical and electrical characteristics improved after transfer due to decrease in built-in stress. This simple and practical method is expected to greatly facilitate the development of transferrable full color GaN microLEDs on various substrates with either greatly reduced or no damage.

Keywords: GaN; light emitting diode; chemical lift-off; transfer

1. Introduction

Large-scale and flexible electronic and optoelectronic devices have recently attracted much attention for use in wearable displays, solar cells, sensors, and biomedical devices [1,2]. For flexible, bendable, and wearable devices, organic films have been widely employed because of their excellent scalability and flexibility. Compared to inorganic materials, however, organic films have drawbacks such as a short lifetime, low efficiency, low brightness, difficulty in enlarging, and low stability in humid environments. Gallium nitride (GaN)-based microscale light-emitting diodes (microLEDs) have attracted substantial attention in recent years as they have the potential to replace conventional organic light-emitting diodes (OLEDs) for flexible and bendable displays [3,4].

Conventional routes to these devices involve epitaxial growth of active materials followed by chip fabrication, wafer dicing, and pick-and-place robotic manipulation into individually packaged components for interconnection by bulk wire-bonding. However, dicing becomes more difficult as the chip size decreases beyond 100 µm × 100 µm, and integrating them on flexible and bendable substrates also becomes a challenge. Therefore, another route has been suggested for the manufacture of electronic devices, and it involves chip fabrication, the separation of chips from the mother substrate, and transfer of separated chips to devices. There are two ways to separate chips from a substrate, namely laser lift off (LLO) and chemical lift off (CLO) [5]. Generally, separating GaN LEDs from a sapphire substrate by LLO is an expensive process because it requires the use of a deep ultraviolet excimer laser [6–8]. In addition, the current LLO process requires a series of complicated steps to transfer-print the GaN
LED structure onto a flexible substrate, including bonding the structure to a hard substrate before LLO, selective removal of the bonding layer after LLO, transferring the flexible substrate using an elastomeric stamp, another round of transfer-printing if a flip transfer is necessary, and a long process time [5,9].

The transfer of GaN films to receptor substrates results in a considerable release of stresses, which originate from the large lattice and thermal mismatch between the GaN-based layers and sapphire substrate. The released stresses may result in structural defects and even cracks in the epitaxial layers that degrade device performance [10]. Therefore, there is a strong need to develop a simplified method for higher-yield transfer while preserving the original layout of the GaN LEDs. Recently, Trindade et al. reported the scalable pick-and-place transfer-printing of GaN LEDs fabricated on silicon onto a mechanically flexible substrate through CLO, using a horizontal tether as the sacrificial layer and anchor to hold the isolated LED chips [11]. For thin-film LEDs, the device-processing steps for GaN LEDs fabricated on a Si substrate are almost identical to those for GaN LEDs on a sapphire substrate, except that the former requires the host substrate to be removed in a simple chemical mechanical process, while the latter uses an LLO process. Therefore, this method has the advantage of a short process time, simple steps, and low damage of the epilayer without using a high-power UV laser during the LLO process. In addition, with the significant improvements in growth and fabrication techniques, the current external quantum efficiency of GaN LEDs on a silicon substrate represents an improvement of 65% and is comparable to that of GaN LEDs on sapphire [12]. GaN LEDs can be grown on large-scale Si wafers, e.g., Si(111) substrates with diameters of up to 200 mm, which are cheaper than sapphire wafers. The GaN-on-silicon approach also benefits from the use of existing equipment for silicon manufacturing [13]. However, the pick-and-place transfer-printing method requires expensive equipment, a long process time, and a sacrificial layer. In addition, the characteristics related to wavelength shift and efficiency before and after transfer of the LEDs are not well known.

Here, we suggest a simplified transfer-printing method for GaN LEDs grown on a silicon wafer through spontaneously formed vertical tethers during the CLO process. This method does not require an additional sacrificial layer or extra process steps such as the fabrication of an anchor that would allow the development of mass transfer for flexible devices. The optical characteristics of the GaN LEDs, before and after transfer, were studied by Raman, microphotoluminescence (microPL), and electroluminescence (EL) spectroscopy.

2. Experimental

Figure 1a shows a schematic diagram of GaN-based LEDs on a Si substrate. The GaN-based LED structure (operating at a dominant emission peak of 450 nm) was grown on an Si(111) substrate using metal-organic chemical vapor deposition. The LEDs consisted of the following layers: a Si-doped n-GaN layer that was 2 µm thick, a molecular quantum well (MQW) active layer consisting of five periods of un-doped InGaN wells and un-doped GaN barriers, and a Mg-doped p-GaN layer with thickness of 0.15 µm and a hole concentration of $3 \times 10^{17}$ cm$^{-3}$. In order to fabricate the LEDs, which were 100 × 100 µm$^2$ in size, the p-GaN layer was etched using an inductively coupled plasma (ICP) that utilized Cl$_2$ and BCl$_3$ source gases until the n-GaN layer was exposed for n-type contact. After mesa etching, the GaN LEDs were isolated to separate them from the Si substrate by using an ICP that utilized Cl$_2$ and BCl$_3$ source gases until the surface of the Si substrate was exposed. The LEDs were then fabricated using an indium–tin oxide (ITO) layer that was 200 nm thick as a transparent current-spreading layer as the n- and p-pad electrodes, respectively.

To prepare the devices for their later release from the native substrate, they were underetched by anisotropic wet etching with a 60 wt% aqueous potassium hydroxide (KOH) solution at 80 °C. The etch rate in the (110) direction was faster than that in the (111) direction. As a result, the Si(110) plane was preferentially etched in the lateral direction. Upon completion of the underetching, the LEDs were suspended above the Si substrate, resting on small hexagonal pillars that could spontaneously serve as vertical tethers, as shown in Figure 1. Next, the isolated microLED arrays were coated with poly(methyl
methacrylate) (PMMA), and the remaining pillars were removed by wet etching with KOH, as shown Figure 1b–d. The LED arrays with the PMMA stamp were moved to unusual substrates such as Si, glass, polyethylene terephthalate (PET), or stretchable polyurethane (PU). Finally, the PMMA was removed by acetone, as shown in Figure 1e.

Figure 1. Schematic illustrations and images corresponding to steps for the transfer of Gallium nitride (GaN) light emitting diodes (LEDs): (a) isolated microLED arrays, (b) Isolated GaN micro LED arrays with spontaneously formed vertical tether, (c) deposition of PMMA and removal of remaining pillars, and (d) transfer of microLED arrays to unusual substrate. (e) MicroLED arrays on an unusual substrate.

3. Results and Discussion

Figure 2 shows optical microscope images and field-emission scanning electron microscope (FE-SEM) images before and after the CLO process. To detach the LED arrays from the Si substrate, we used spontaneously formed vertical tethers during the CLO process. Supplementary Figure S1 shows that Si was etched anisotropically with increasing etching time, where the Si(110) plane is defined as the lateral direction. Figure 2a,b shows that the cross-sectional area of the spontaneously formed vertical Si tethers was 52 × 21 \( \mu \text{m}^2 \) and the height was 710 nm before the deposition of PMMA. These vertical Si tethers were removed by additional etching with KOH. The PMMA stamp holding the microLED arrays was moved to the glass substrate, and the PMMA was removed by acetone to expose the microLED arrays. Figure 2c,d shows the PL mapping images of GaN LED before and after transfer to glass substrate. It clearly shows that there was no degradation of optical properties and a shift in spacing between the LEDs. These results demonstrate that, unlike LLO, CLO is a damage-free process. Figure 2e shows the emission images of GaN LEDs on various transparent, flexible, or rigid substrates. Figure 2f shows an area measuring 3 × 3 cm\(^2\) that was transferred to a glass substrate. These results show that the CLO approach is not dependent on the size of the transfer area.
hexagonal GaN is located at 567.4 cm$^{-1}$ [14]. The relationship between the E$_2$ mode Raman peak shift ($\Delta \omega_y$) and the in-plane biaxial stress ($\sigma_{\chi \chi}$) can be expressed as [14,15]:

$$\sigma_{\chi \chi} = \frac{\Delta \omega_y}{K_y}$$

where $\sigma_{\chi \chi}$ is the stress in GPa, $\Delta \omega_y$ is the Raman peak shift in cm$^{-1}$, and $K_y$ is the stress coefficient (4.3 cm$^{-1}$ GPa$^{-1}$). The stress on the GaN surface before transfer was estimated to be 0.465 GPa, which means that the GaN epilayer on the Si substrate had high tensile stress. The E$_2$ Raman peak in the spectra obtained for the GaN LEDs on Si, glass, and PET substrates after transfer is shifted to 567.1 cm$^{-1}$. The stress on the GaN surface was estimated to be 0.07 GPa after transfer, indicating that the tensile strain was fully released. Since tensile stress can blue shift an emission peak and reduce the efficiency.

Figure 2. (a) Optical microscope image of GaN LED array with vertical tethers. (b) FE-SEM image of a GaN LED with a spontaneously formed vertical tether. PL mapping image of GaN LED (c) before transfer and (d) after transfer. (e) Images of light emission from GaN LEDs transferred onto various substrates. FE-SEM image of GaN LEDs on a silicon substrate after transfer. (f) Optical microscope image of a GaN LED array (3 x 3 cm$^2$) on a glass substrate after transfer.

Figure 3 shows Raman spectra of the three samples measured at room temperature. In the spectrum of the GaN LEDs before transfer, the peak at 565.4 cm$^{-1}$ corresponds to the E$_2$ mode of the GaN hexagonal phase. It has been previously shown that the E$_2$ mode Raman peak of unstrained hexagonal GaN is located at 567.4 cm$^{-1}$ [14]. The relationship between the E$_2$ mode Raman peak shift ($\Delta \omega_y$) and the in-plane biaxial stress ($\sigma_{\chi \chi}$) can be expressed as [14,15]:

$$\sigma_{\chi \chi} = \frac{\Delta \omega_y}{K_y}$$

where $\sigma_{\chi \chi}$ is the stress in GPa, $\Delta \omega_y$ is the Raman peak shift in cm$^{-1}$, and $K_y$ is the stress coefficient (4.3 cm$^{-1}$ GPa$^{-1}$). The stress on the GaN surface before transfer was estimated to be 0.465 GPa, which means that the GaN epilayer on the Si substrate had high tensile stress. The E$_2$ Raman peak in the spectra obtained for the GaN LEDs on Si, glass, and PET substrates after transfer is shifted to 567.1 cm$^{-1}$. The stress on the GaN surface was estimated to be 0.07 GPa after transfer, indicating that the tensile strain was fully released. Since tensile stress can blue shift an emission peak and reduce the efficiency.
of a device, a red-shift of the emission peak and improvement in the LED efficiency are expected in the spectrum obtained after transfer.

Figure 3. Raman spectra of GaN LEDs before and after transfer onto various substrates.

The strain of the MQW layer is more effectively released after transfer to Si, which is proven by X-ray reciprocal space mapping (RSM) of the (105) reflector for sample before and after transfer to Si (Supplementary Figure S2). The vertical solid line represents the fully strained axis. As shown in Supplementary Figure S2a,b, a larger horizontal shift of the InGaN peak with respect to the GaN peak is observed for the sample after transfer to Si, indicating a higher strain relaxation in the MQW layer. This result is identical to strain relaxation in the Raman spectra after transfer.

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Figure 4 shows the PL spectra, measured at room temperature, of the InGaN/GaN MQW LED structures before and after transfer onto various substrates. In the spectrum obtained before transfer, the LED emission peak at about 441 nm typically corresponds to the MQWs. However, in the spectrum obtained after transfer, the PL peak of GaN LEDs on Si, glass, and PET substrates is red-shifted to 442.4, 443.5, and 443.2 nm, respectively, because the tensile stress in the top GaN was reduced by the transfer via stress redistribution, as shown in Figure 3. The compressive strain of the InGaN QW material was also reduced in this regard. Two main effects could play important roles in the PL emission wavelength of the MQWs: One was the quantum-confined Stark effect (QCSE), which is related to the piezoelectric field, and the other was the bandgap shrinkage of InGaN within the MQWs. The first effect caused a blue shift while the latter caused a red shift in the PL emission when the compressive strain was reduced in the MQWs; their compensations led to the small red shift observed in the PL emissions. The small red shift of wavelength of LEDs on the glass and PET substrates resulted from an increase in joule heating when compared to the LEDs on the Si substrate. However, the reduced QCES would increase the spatial overlaps between the wave functions of electrons and holes within the QWs which could, in turn, significantly enhance the electron-hole recombination efficiency of the InGaN/GaN MQWs LEDs [16].
Figure 4. PL spectra of GaN LEDs before and after transfer onto various substrates.

Figure 5a,b display the current–voltage (I–V) curves of GaN LEDs before and after transfer onto various substrates. To confirm that the reflection at the interface between the GaN LED and substrate was negligible, we compared the LEDs before and after transfer onto the Si substrate. Figure 5a shows that the electrical properties of the LEDs are not changed after transfer. This result shows that CLO is a damage-free process without degradation in the contact metal or formation of structural defects and cracks. Figure 5b displays the light output power of the InGaN/GaN LEDs before and after transfer. The light output intensity (at an injection current of 20 mA) of the LED after transfer was 33% higher than the output intensity of the LED before transfer. This improvement can be attributed to the enhancement of the electron-hole recombination efficiency with the decrease in QCSE by strain relaxation.

Figure 5. (a) I–V curves and (b) optical output power of GaN LEDs before and after transfer onto the Si substrate.
4. Summary

In this work, we demonstrated a simple transfer method with spontaneously formed vertical Si tethers during the CLO process for GaN LEDs onto flexible substrates. This method allows for the mass transfer of GaN LEDs and reduces the process time. After transfer, the tensile stress was significantly decreased, resulting in a red shift of the emission peak and improvement of the efficiency of GaN LEDs. The results reported here suggest that state-of-the-art GaN LEDs on Si substrates can be manipulated in the form of microLEDs in applications that would be difficult with conventional LED technologies.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/9/20/4243/s1,
Figure S1: Spontaneous formation of vertical tethers. Figure S2: RSM of X-ray diffraction intensity around the (105) reflector for micro LED (a) before and (b) after transfer to Si substrate.


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References


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