

## Article

# A Substrate-Reclamation Technology for GaN-Based Lighting-Emitting Diodes Wafer

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Academic Editor: Jiawang Yan

Received: 20 February 2017; Accepted: 23 March 2017; Published: 27 March 2017

**Abstract:** This study reports on the use of a substrate-reclamation technology for a gallium nitride (GaN)-based lighting-emitting diode (LED) wafer. There are many ways to reclaim sapphire substrates of scrap LED wafers. Compared with a common substrate-reclamation method based on chemical mechanical polishing, this research technology exhibits simple process procedures, without impairing the surface morphology and thickness of the sapphire substrate, as well as the capability of an almost unlimited reclamation cycle. The optical performances of LEDs on non-reclaimed and reclaimed substrates were consistent for 28.37 and 27.69 mcd, respectively.

**Keywords:** GaN-based LEDs; substrate-reclamation; sapphire substrate

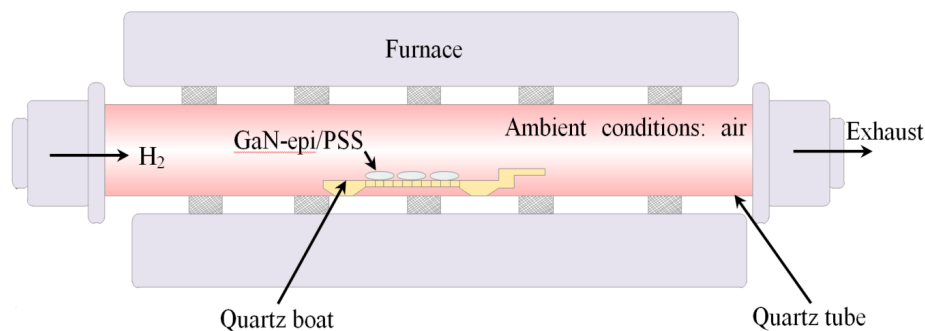
## 1. Introduction

Gallium nitride (GaN) is a direct-bandgap semiconductor. It is commonly used for fabricating light-emitting diodes (LEDs) due to their wide bandgap, chemical stability, and high temperature stability. These LEDs emit from the ultraviolet to the visible range [1–3]. Sapphire ( $\text{Al}_2\text{O}_3$ ) has become a key material for fabricating GaN-based LEDs because it serves as an excellent epitaxial substrate due to its small lattice-constant mismatch with GaN. In particular, patterned sapphire substrates (PSSs) constitute an important epitaxial substrate for GaN-based LEDs because they enhance the light-extraction efficiency and internal quantum efficiency of LEDs [4–6]. The price of a 4 in PSS is approximately \$30–32 USD [7], so PSSs account for about 25% of the total cost of an LED chip. Thus, reclaiming the sapphire substrate for GaN-based LED wafers can significantly reduce the manufacturing cost of LED chips. A chemical mechanical polishing (CMP) method is currently used universally to reclaim substrates [8–10]. However, the disadvantages of CMP include process complexity, surface scrapes, and thinning of the sapphire substrate. Surface scrapes and thinning result in the performance failure of the epitaxial film. Moreover, CMP makes the PSS pattern disappear. In the present work, we study a substrate-reclamation technology to avoid these disadvantages. In a non-vacuum state, we prepare a reclaimed substrate by thermally decomposing a GaN epitaxial film in a furnace system. We also investigate the properties of decomposed GaN on PSSs and the regrown LED epilayers on the reclaimed PSS.

## 2. Experimental Section

The sample consisted of GaN-based LED epilayers grown on a PSS (GaN-epi/PSS), which we fabricated by metalorganic chemical vapor deposition. For the PSS, the cone-pattern diameter, spacing, and height were 4, 2, and 1.4  $\mu\text{m}$ , respectively. GaN-based LEDs epilayers (thickness = 3.5  $\mu\text{m}$ ) were produced by using standard epitaxial procedures. All samples involved similar epilayers and

process procedures, except for the substrate reclaim conditions. The procedures involved in the substrate-reclaim process are as follows: The GaN-epi/PSS was loaded into a furnace, following which  $H_2$  was released into the furnace, as depicted in Figure 1. The process temperature,  $H_2$  flow rate, and process time for the GaN decomposition were varied in a non-vacuum state to determine the initial decomposition parameters. In process I, the GaN-epi/PSS is prepared at temperatures ranging from 800 to 1200 °C and at gas-flow rates of 10 sccm for 30 min. In process II, an operation temperature (1200 °C) is imposed on the GaN-epi/PSS according to the results of process I and the gas-flow rate is 25 sccm for 30, 60, and 90 min. The details of the substrate-reclaim conditions are given in Table 1. The sample is then unloaded and the reaction products on the sample surface are removed by using an alkaline solution to form an exposed PSS. Here the exposed PSS is defined to be reclaimed PSS. Following, GaN-based LEDs epilayers are regrown on reclaimed PSS, and a  $10 \times 24 \text{ mil}^2$  chip is fabricated. This type of LED is called “LED/reclaimed PSS”. The procedure for fabricating chip devices in this study is as follows: An indium tin oxide transparent conductive layer and Cr/Au metal were deposited on the p- and n-type GaN as Ohmic contacts, respectively. Finally, to confirm the properties of the LED/reclaimed PSS device, GaN-based LED epilayers grown on a non-reclaimed PSS were also fabricated. Here, “LED/non-reclaimed PSS” denotes this type of LED.



**Figure 1.** Schematic diagram showing substrate-reclaim setup for GaN-epi/patterned sapphire substrate (PSS) by furnace process in  $H_2$  gas.

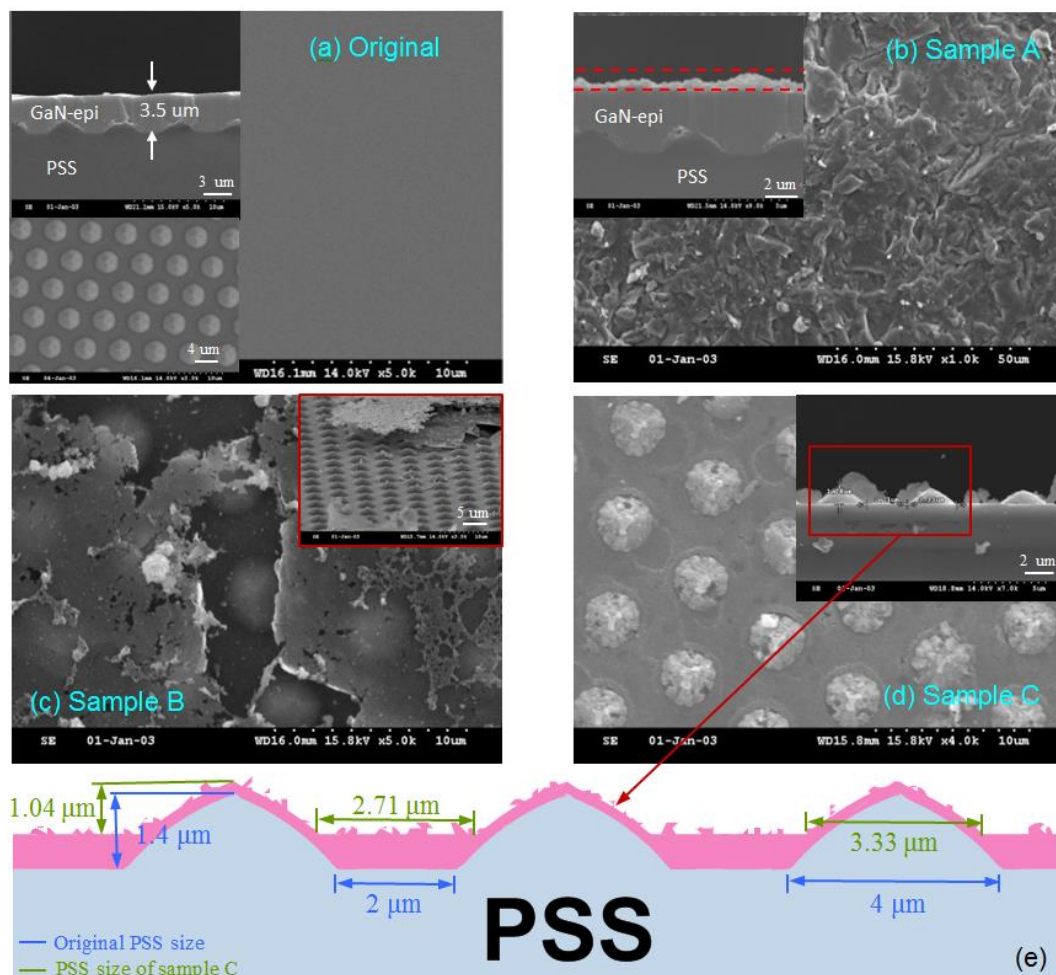
**Table 1.** Substrate-reclaim conditions of GaN-epi/patterned sapphire substrate (PSS).

Sample: GaN-epi/PSSs Experimental Conditions		Temperature/°C	Gas-Flow Rates/sccm	Times/min
I. Processes under different temperatures				
Sample A		800	10	30
Sample B		1000		
Sample C		1200		
II. Processes under different times				
Sample D		1200	25	30
Sample E				60
Sample F				90

### 3. Results and Discussion

Figure 2 shows top-view and cross-section scanning electron microscope (SEM) images of GaN-epi/PSSs both exposed and not exposed to gas-flow rates of 10 sccm for 30 min and at various temperatures (800–1200 °C). Figure 2a shows the surface morphology and cross-section of the GaN-epi/PSSs (i.e., original samples). In addition, the top-view SEM image of the original pristine sapphire substrate is also shown in the inset of Figure 2a. Preparing the GaN-epi/PSSs at 800 °C changed the surface morphology of the GaN-epi film, as shown in Figure 2b. Upon increasing the process temperature to 1000 °C, sheet-shape decomposition began in the GaN epilayers and the substrate cone patterns started to exposed, as shown in Figure 2c. Further increasing the temperature

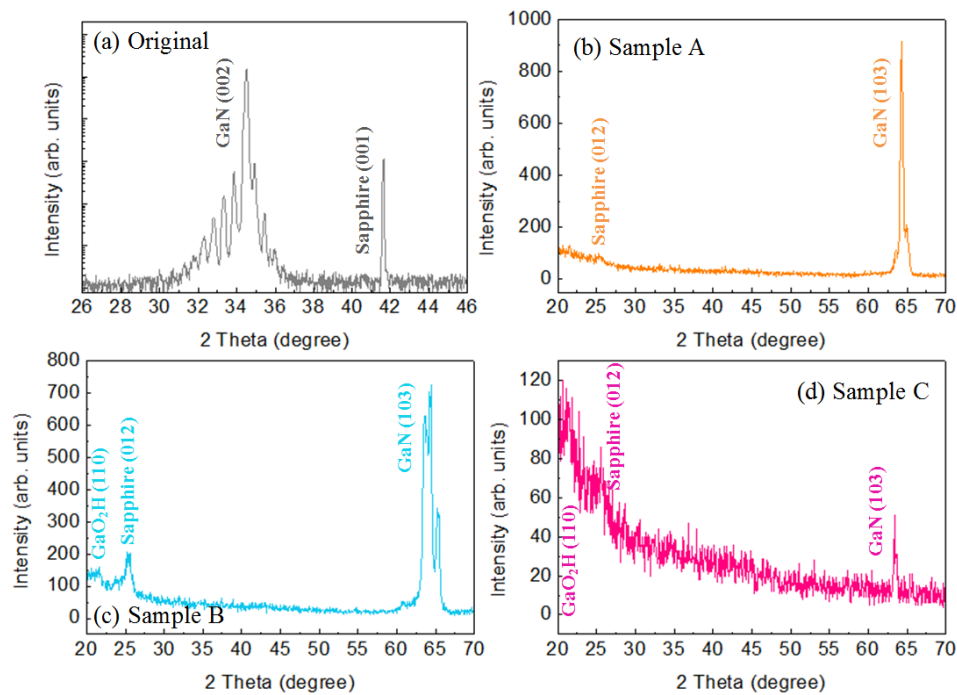
to 1200 °C resulted in cone patterns appearing over the entire sample surface. Figure 2d,e show the top view and cross-section and an enlarged schematic of the PSS after being exposed to a gas-flow rate of 10 sccm for 30 min at 1200 °C. The PSS cone diameter, spacing, and height were 3.33, 2.71, and 1.04  $\mu\text{m}$ , respectively. By comparing them with the original cone pattern, these results indicate that the GaN-epi film still did not completely decompose under these process conditions. In addition, the GaN-epi decomposition reaction correlated positively with the process temperature, which is consistent with the results of Schmid-Fetzer et al. [11].



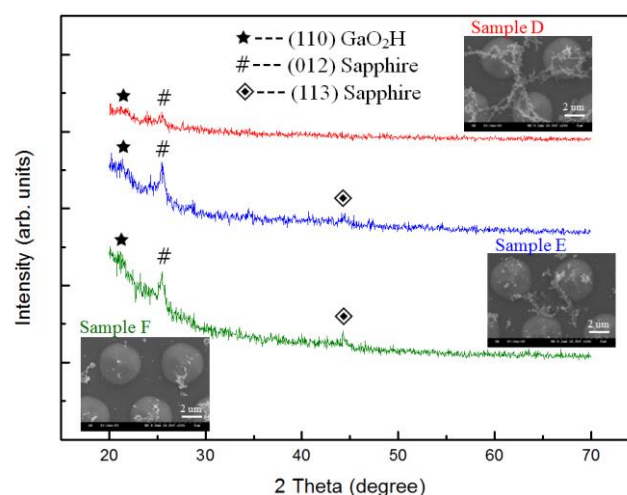
**Figure 2.** Top-view and cross-section scanning electron microscope (SEM) micrographs of GaN-epi/PSSs prepared and not prepared according to substrate-reclamation process I. The enlarged schematic diagram of the PSS in panel (e) depicts the cone pattern size of sample C.

Figure 3 shows the X-ray diffraction (XRD) spectra of the GaN-epi/PSS prepared and not prepared according to substrate-reclamation process I. The diffraction pattern from untreated GaN-epi/PSS has a sharp GaN (002) peak near  $2\theta = 34.6^\circ$ , several satellite peaks from the InGaN/GaN active layers, and a sapphire (001) peak near  $2\theta = 41.6^\circ$ , as shown in Figure 3a. The grazing-angle XRD spectra of samples A, B, and C appear in Figure 3b–d, respectively. The diffraction peaks from the GaN (103) phase near  $2\theta = 63.6^\circ$  gradually began to weaken with increasing the temperature from 800–1200 °C. Moreover, when the operation temperature exceeded 1000 °C, a  $\text{GaO}_2\text{H}$  (110) peak near  $2\theta = 21.47^\circ$  appeared in the diffraction pattern. These results indicate that the GaN-epi film on the PSS begins to transform and to produce a  $\text{GaO}_2\text{H}$  derivative. Note that the GaN-epi film still exists under the conditions of process I. Figure 4 shows the grazing-angle XRD spectra of the GaN-epi/PSS prepared using substrate-reclamation process II. The diffraction pattern reveals a  $\text{GaO}_2\text{H}$  (110) peak at  $2\theta \cong 21.47^\circ$ .

and a sapphire (012) peak at  $2\theta \cong 25.65^\circ$ . As the process time increased from 30 min to above 60 min, the diffraction peaks of the sapphire (113) phase appeared near  $43.47^\circ$ . Comparing these results with those shown in Figure 3 shows that no GaN peak appeared in the GaN-epi/PSS XRD pattern under the conditions of process II. The results indicate that the decomposition reaction of the GaN-epi film on the PSS is increased when the gas-flow rate increases from 10 to 25 sccm, which is consistent with the results of Koleske et al. [12]. Moreover, the exposed pattern morphology is more notable with increasing the process time under a gas-flow rate of 25 sccm, as shown in the SEM image in the inset of Figure 4.



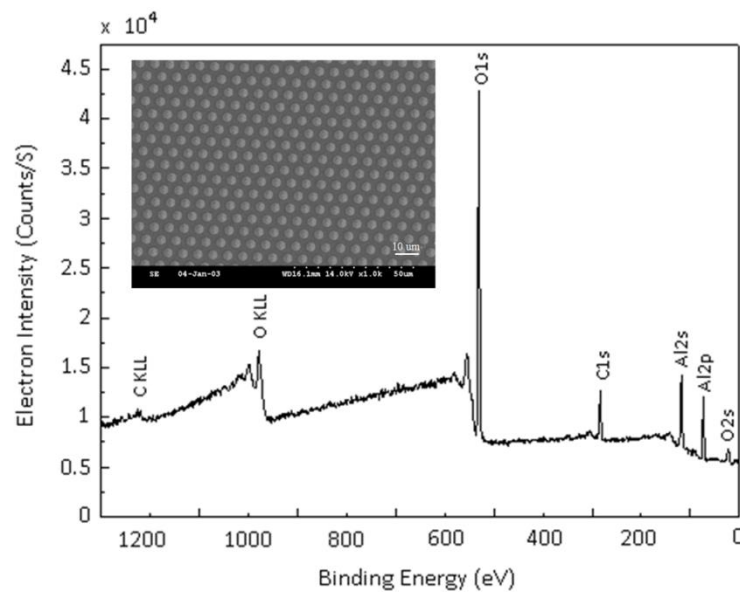
**Figure 3.** X-ray diffraction (XRD) spectra of GaN-epi/PSS with and without using substrate-reclamation process I.



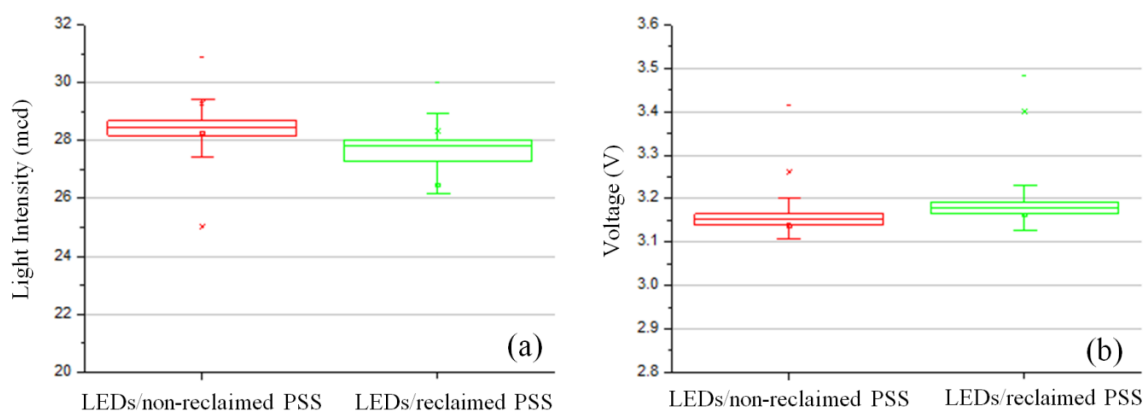
**Figure 4.** XRD spectra of GaN-epi/PSSs prepared by using substrate-reclamation process II.

To ensure the pure surface of the exposed PSS, we analyzed the photoelectron spectrum of the GaN-epi/PSS prepared with a gas-flow rate of 25 sccm for 90 min followed by wet etching (see Figure 5). These results show the Al2p, Al2s, O2s, and O1s peaks located near 74.4, 118, 23,

and 531 eV, respectively. The binding energy of O and Al corresponds to that of O and Al in  $\text{Al}_2\text{O}_3$  (i.e., the sapphire substrate) [13,14]. This result is consistent with an exposed PSS surface without Ga and demonstrates that no  $\text{GaO}_2\text{H}$  is present at the surfaces of the exposed PSS. The C1s peaks are due to the C element adsorbed on the sample surface from the atmosphere ambient. The SEM image in Figure 5 indicates that exposure to a gas-flow rate of 25 sccm for 90 min followed by wet etching results in a pure PSS surface. Figure 6 shows the optical and electrical performances for both LED types with an injection current of 20 mA. The light intensity for the LEDs/non-reclaimed PSS and LED/reclaimed PSS was 28.37 and 27.69 mcd, respectively. The forward voltage for the LED/non-reclaimed PSS and for the LED/reclaimed PSS was 3.16 and 3.18 V, respectively. These results reveal that both types of LEDs have similar optical and electrical characteristics, which indicates that sapphire substrates may be successfully re-used in epi-regrowth of GaN-based LEDs.



**Figure 5.** Photoelectron spectrum of GaN-epi/PSS prepared with a gas-flow rate of 25 sccm for 90 min followed by wet etching.



**Figure 6.** (a) Optical and (b) electrical performance of both LED types with 20 mA injection current.

#### 4. Conclusions

We have demonstrated that a substrate-reclamation technology allows us to achieve a reclamation cycle that is almost unlimited. This technology will help reduce the manufacturing cost of both chips and stock numbers of the scrap wafer in the LED industry. In this research, a GaN-epi/PSS was



found that has a GaO<sub>2</sub>H (110) reactant on the surface of an exposed PSS and a GaN-epi film was completely dissociated after gas-flow rates of 25 sccm for 90 min at 1200 °C. The GaO<sub>2</sub>H (110) reactant was removed to form a pure exposed PSS using an alkaline solution and then the GaN-based LED epilayers were re-grown on reclaimed substrates successfully.

**Acknowledgments:** This study is supported by the National Science Council of the Republic of China under contract No. NSC-101-2218-E-212-001.

**Author Contributions:** Shih-Yung Huang conceived and designed the experimental procedures; Po-Jung Lin contributed the sample measurement results. All authors read and approved the final version of the manuscript to be submitted.

**Conflicts of Interest:** The authors declare no conflict of interest.

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