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Electrochemical potentiostatic activation for improvement of internal quantum efficiency of 385-nm ultraviolet light-emitting diodes

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ABSTRACT

The electrochemical potentiostatic activation (EPA) method is proven to effectively improve the internal quantum efficiency (IQE) of 385-nm ultraviolet light-emitting diodes (UV-LEDs). UV-LEDs wafers were immersed into 1.0 M HCl solution, and an electric voltage of 3.0 V was applied to the p-type GaN layer in order to increase the hole concentration by breaking the Mg—H complex. Secondary ion mass spectroscopy analysis clearly indicates the successful removal of hydrogen atoms by the EPA process, which is a ~35% reduction of the hydrogen concentration compared to the conventional N_2 annealing. The light-output power was enhanced by ~20% at an input current of 50 mA, which originated from an improvement of the IQE by ~20%. The reverse leakage current was also lowered by about one order after the EPA process.

1. Introduction

Recently, GaN-based light-emitting diodes (LEDs) have become a core technology for solid-state lighting. In the near future, it is expected that GaN-based LEDs will account for most of the general lighting market [1]. The low-cost fabrication of high-efficiency LED chips is considered as a fundamental requirement for GaN-based solid-state lighting. Many approaches have been studied in order to meet these requirements, such as epitaxial growth on large-area silicon substrates, the use of non-polar sapphire substrates, and advanced chip designs, like vertical chips [2–6]. Poor quality of the p-type GaN layer is one of the main obstacles that hinder the achievement of high efficiency. Typically, n-type GaN layers exhibit a sufficient electron concentration of about 5×10^{18} cm^{-3}. The hole concentration of the p-type GaN layer should be similar to the electron concentration, but at only $\sim 1 \times 10^{18}$ cm^{-3}, it is half an order of magnitude lower than necessary, despite technological developments over the past decade. Moreover, the hole mobility in p-GaN is just 10–20 cm^2/V s, which is much lower than the electron mobility of 200–300 cm^2/V s in an n-GaN layer [7].

A p-GaN layer is grown by metal-organic chemical vapor deposition (MOCVD) with Mg doping. Such Mg-doped GaN layers are electrically passivated, because the Mg atoms are bonded to the H atoms to form Mg—H complexes during the MOCVD process. An activation process is needed to break the Mg—H bond, and to drive out the H atoms from the p-GaN [8]. In 1991, Amano et al. first succeeded in activating the Mg-doped GaN to p-GaN using a low-energy electron-beam irradiation technique [9]. Since then, several activation methods have been studied to increase the hole concentration in the p-GaN layer. In 1992, Nakamura et al. suggested a thermal annealing method above 700 °C [10], which is currently adopted by most chip makers to activate p-GaN layers. Since then, several modified methods have been suggested, such as KrF excimer-laser activation [11–13], multiple-step annealing [14], thermal annealing in an oxygen gas mixture [15], utilization of hydrogen-storage metal electrodes [16], and annealing with minority carrier injection [17,18]. Little achievement in hole concentration has been achieved by these methods, but these have basically not been suitable for mass production. In an earlier report, we demonstrated that the electrochemical method can break the Mg—H complex and improve the hole carrier concentration in a p-GaN layer [19]. This electrochemical potentiostatic activation (EPA) method was employed for 385-nm ultraviolet (UV)-LEDs, and its

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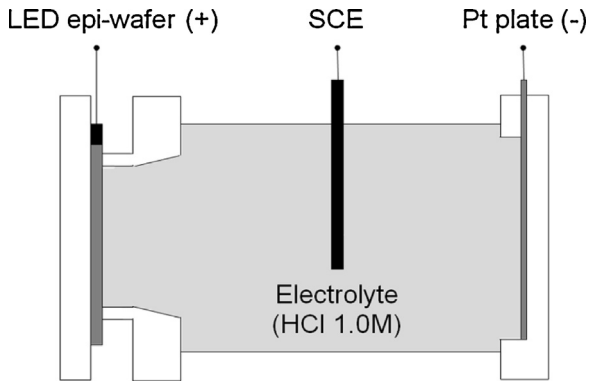

Fig. 1. Schematic view of experimental system for EPA process. Working electrode (cathode): LED epi-wafer; counter electrode (anode): Pt sheet; reference electrode: standard calomel electrode. Electrolyte: 1.0 M HCl solution in H_2O.

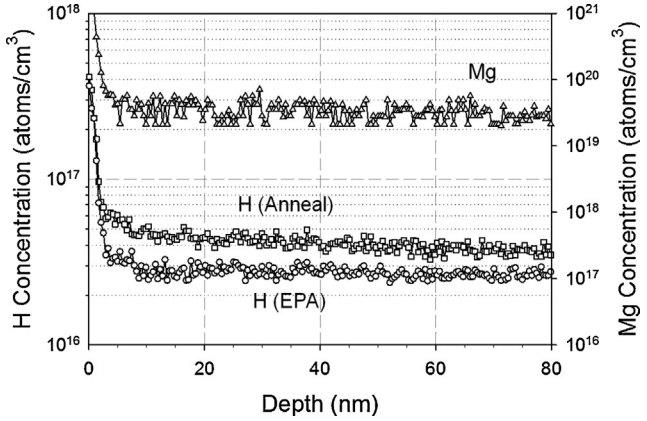

Fig. 2. SIMS depth profile of hydrogen concentration in LED epi-wafers. p-GaN layer was activated by the conventional N_2 annealing (□) and EPA (○) at 3 V.

effect was evaluated in terms of the electrical and optical performance of LED devices.

2. Experimental

The experimental system for the EPA process was modified to avoid undesirable parasitic effects by exposing only the p-GaN surface to the electrolyte, as shown in Fig. 1. In an earlier experimental system, not only p-GaN but also n-GaN and multi-quantum-wells (MQWs) were exposed to the electrochemical solution, in which the current level was unstable under potentiostatic conditions. The flat-zone regions of UV-LED wafers were soldered with indium for the formation of electrical contacts, and the surface of the p-GaN layer was exposed to 1.0 M HCl solution. An In-soldered wafer was used as the working electrode (WE, anode), and a Pt sheet was utilized as a counter electrode (CE, cathode). A standard calomel electrode (SCE) was used as the reference electrode (RE). The EPA process is carried out by applying a forward voltage of 3 V for 5 min.

The UV-LED structures used in this study were grown by a showerhead-type MOCVD reactor on a 2-in. *c*-plane sapphire substrate. An undoped-GaN buffer layer with a thickness of 30 nm was deposited at 550 °C, and then a 1.5-μm-thick undoped GaN layer and a 2-μm-thick Si-doped n-GaN layer were grown at 1050 °C. For MQWs, five pairs of 2-nm-thick $In_{0.04}Ga_{0.96}N$ quantum wells and 12-nm-thick $Al_{0.08}Ga_{0.92}N$ barrier layers were grown at 800 °C. Finally, an Mg-doped p-$Al_{0.25}Ga_{0.75}N$ electron blocking layer with a thickness of 25 nm and 100-nm-thick p-GaN layer were deposited at 1040 °C. LED chips were fabricated with a size of 500 × 500 μm^2. The details of the fabrication process can be found in Ref. [20]. Light output–current–voltage (*L–I–V*) characteristics were measured by a Keathley 236 and an Ecopia LED tester after SMD-type packaging. The internal quantum efficiency (IQE) values were monitored by an Etamax DOSA-IQE measurement system after TO-can packaging. Also, the hydrogen atom concentration in the p-GaN layer was monitored by secondary ion mass spectroscopy (SIMS).

3. Results and discussion

Hydrogen is a complicated and uncontrollable element in the growing and doping of GaN films. It bonds with Mg acceptors to form neutral Mg—H complexes, which is considered to be the main reason for poor p-GaN conductivity. In order to break these Mg—H bonds, we have suggested an EPA method, and proved that hydrogen atoms could be successfully removed using p-GaN layers grown on an Al_2O_3 wafer [19]. However, when we performed the EPA process with an LED epitaxial structure, the current level was very unstable under potentiostatic conditions, unlike EPA with just a simple p-GaN layer. When an LED epi-wafer is immersed in electrolyte, the electric voltage can be applied to not only the p-GaN layer, but also the n-GaN layer and multi-quantum-wells (MQW). The current flow through n-GaN and MQW can act as a parasitic path that deteriorates the EPA process performance and repeatability. In order to avoid this undesirable current path, we have modified the EPA system, as shown in Fig. 1. Only the p-GaN surface was exposed to the electrolyte, so that the EPA process could be performed with reliability. The electrolyte was switched from KOH solution to HCl solution, because HCl has lower chemical reactivity against GaN material, such that the surface of the p-GaN layer was not damaged by the electrolyte, even when a voltage above 10 V is applied. Surface roughness value was maintained less than 1.0 nm after EPA process. Details about the effect of the major process parameters in EPA, such as the voltage, time, and electrolyte, will be reported separately in another article.

After the EPA process, the concentration of hydrogen atoms inside the p-GaN was monitored by the SIMS profile. As shown in Fig. 2, this process could successfully remove nearly 35% more hydrogen atoms compared to the conventional annealing. A large area of the peripheral region of the LED epi-wafer was not exposed to the HCl solution for the EPA, but displayed the same hydrogen SIMS profile as the solution contacted area. It seems that hydrogen diffusivity is high enough that Mg—H bonds could be broken almost evenly by the electric voltage all around the wafer, regardless of the contact to the electrolyte [21]. It is assumed that hydrogen would take the form of a positive charge (proton) after the Mg—H bond breaking, because a positive current is applied to the LED epi-wafer. A proton could drift very quickly from the inside of the p-GaN layer to the surface, such that the contact with the HCl solution is not an important issue at all. After the UV-LED fabrication, the *L–I–V* characteristics of LEDs do not show any differences either, depending on the contact with the solution. In contrast, the p-GaN surface where the electrolyte was exposed was slightly oxidized during the EPA process. This is easily confirmed by surface analyses such as X-ray photoelectron spectroscopy and SIMS, which are not shown here. The oxidized film thickness is so thin that it can be easily eliminated by simple dipping in buffered oxide etchant (BOE) for 5 min. If a p-contact electrode is deposited without this surface cleaning, the operation voltage of UV-LEDs increases by 0.1–0.2 V. In conventional annealing in N_2 atmosphere, hydrogen atoms diffuse out to the p-GaN surface and combine with other hydrogen atoms to form H_2 gas. This is simplified the activation mechanism of the p-GaN layer by thermal annealing. In the EPA process, hydrogen atoms, rather than protons, drift to the p-GaN surface by the electric field, and combine with chemical species in solution (Eq. (1)). One important issue to be considered is that there exists a