Strong light extraction enhancement using TiO₂ nanoparticles-based microcone arrays embossed on III-Nitride light emitting diodes

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Strong light extraction enhancement using TiO₂ nanoparticles-based microcone arrays embossed on III-Nitride light emitting diodes

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Colloidal TiO₂ nanoparticles were used for embossing of composite microcone arrays on III-Nitride vertical-thin-film blue light emitting diodes (LEDs) as well as on silicon, glass, gallium arsenide, and gallium nitride surfaces. Ray tracing simulations were performed to optimize the design of microcones for light extraction and to explain the experimental results. An optical power enhancement of ~ 2.08 was measured on III-Nitride blue LEDs embossed with a hexagonal array of TiO₂ microcones of $\sim 1.35 \mu\text{m}$ in height and $\sim 2.6 \mu\text{m}$ in base width, without epoxy encapsulation. A voltage increase in $\sim 70 \text{ mV}$ at an operating current density of $\sim 35 \text{ A/cm}^2$ was measured for the embossed LEDs. The TiO₂ microcone arrays were embossed on functioning LEDs, using low pressures ($\sim 100 \text{ g/cm}^2$) and temperatures $\leq 100^\circ\text{C}$. Published by AIP Publishing.

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Light extraction efficiencies (LEEs) higher than 80% have been reported for blue light emitting diodes (LEDs) using surface patterning¹ and more than 90% using die shaping.² Periodic,^{3–5} quasi periodic,^{6,7} or random^{8–10} surface patterning of the LED surfaces has been extensively investigated, and optical power enhancements (OPE) > 2 have been reported. Patterning the surface of the gallium nitride (GaN) layers on light emitting devices like matrices of micro-LEDs hybridized on CMOS substrates^{11,12} or on thinner InGaN/GaN LEDs is, however, more difficult to implement on a wafer-scale (unless, in the latter case, advanced lattice matched substrates are used).¹³ More recently, add-on patterned layers have been introduced^{14–19} and may help to circumvent this issue. The developed approaches use SiN-based or sol-gel-based photonic crystals, microprisms made from sputtered TiO₂, arrays of microstructures made from polymers with or without high-index TiO₂ nanoparticles (NPs) in it, or grown ZnO wires. Using such methods, OPEs between ~ 1.1 and 2.0 have been reported for III-Nitride LEDs. For add-on patterned layers, the choice of the high index materials,^{15–17} the intimate optical contact of the add-on layer with the III-Nitride surface,¹⁴ and the shape of the patterned structures are the main issues to be addressed since they critically affect extraction of photons emitted with in-plane momentum higher than the superstrate momentum. For example, to improve the OPE, additional recrystallization processes (using temperature around 300°C) were used to reach high effective refractive indices in the deposited metal-oxide material.¹³ Methods requiring lower temperature, e.g., based on polymer embossing, have been reported with significant OPE.¹⁷ However, encapsulation in an epoxy having a refractive index (~ 1.5) similar to the polymer will “screen” the first layer/polymers and no net OPE is expected compared to a simple encapsulation. The addition of higher refractive index materials (e.g., TiO₂ and ZnO nanoparticles)

into polymers has also been investigated as encapsulating materials²⁰ and more recently as light extracting structures.¹⁹ Metal oxide (e.g., TiO₂) nanoparticles are transparent in the visible spectrum and have a refractive index higher than III-Nitrides and are easy to produce. Compared to deposited thin films, nanoparticle assemblies are well suited to avoid mechanical stress linked to differences in thermal expansion coefficients. They also offer more possibilities in designing light extracting structures, especially for three dimensional (3D) structures. Although surface patterns composed of metal-oxide nanoparticles have recently been investigated for light extraction, the OPE was limited to 1.2 .¹⁸

In this study, arrays of microcones made of TiO₂ nanoparticle (NP) assemblies are investigated for light extraction management in GaN-based LEDs. The microcone arrays are embossed using a TiO₂ NP solution dispersed on the target surface and by subsequently pressing a pre-formed mold. Using this procedure, microcone arrays were directly embossed on functioning LEDs without etching or lithography steps. An OPE of 2.08 ± 0.06 was measured for thin film LEDs embossed with the periodic arrays of TiO₂ microcones, without encapsulation in epoxy. Insights into the optical properties of the packed TiO₂ NP layer and into light extraction mechanisms are given. Moreover, the method of embossing microstructures by packing nanoparticles was implemented on different surfaces such as silicon, glass, indium tin oxide (ITO) coated glass, GaAs, and GaN, to illustrate its general applicability. The low temperatures (from room temperature to 100°C) and mechanical pressures as low as 100 g/cm^2 (0.1 bar) used in the embossing procedure make it compatible for micro-LED-based devices hybridized on CMOS devices.

The TiO₂ NP dispersion is composed of a mixture of rutile and anatase phases of crystalline TiO₂ NPs in a water-based solution (33–37 wt. %), commercially available from Sigma-Aldrich, Inc. (see [supplementary material](#)). Both crystalline phases are transparent in the visible range with a

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refractive index higher than GaN. The TiO₂ NPs are roughly spherical with an average diameter of ~ 50 nm. An $\sim 1.9 \mu\text{m}$ -thick layer of TiO₂ NPs was spin-coated on a glass substrate to investigate the optical properties of the composite/porous (TiO₂ NPs-air) material. Total, scattered, and specular reflectivities of these films were measured using a UV-vis spectrophotometer (Perkin Elmer). Quasi specular micro-reflectivity was additionally measured using a homemade setup (spot diameter is $20 \mu\text{m}$ and NA is 0.13) to minimize the effects due to macroscopic thickness variations and optical scattering. Fabry-Perot oscillations (under normal incidence) in the TiO₂ NP-air composite layer were observed in the reflectivity spectra (Fig. 1). The group indices were evaluated from the wavelength positions of the oscillation maxima and fitted using a Bruggeman model.^{21,22} A good agreement was found for wavelengths above ~ 550 nm and for a material fill factor of 0.58 ± 0.05 (corresponding to a refractive index of 1.91 ± 0.08 for a wavelength of 440 nm). This fill factor of 0.58 ± 0.05 remains below the maximum fill factor of a random packing of spherical nanoparticles (0.64).²³ As seen in Fig. 1, the agreement with this effective index model decreases for wavelengths below ~ 550 nm, as the ratio particle size/wavelength increases. A few percent of (Rayleigh) backscattering was measured for wavelengths below ~ 550 nm, reaching 8% at 440 nm (see [supplementary material](#)).

The pattern used to extract guided light consists of a hexagonal array of microcones. Microcone facets can enhance light extraction by shifting the light extraction windows to higher solid angles. Ray tracing simulations were used to investigate the impact of the dimensions of the microcone and its refractive index on the OPE. A vertical thin film GaN LED emitting at 440 nm was considered for the simulations. The dimensions of the LEDs are shown in the inset in Fig. 2. These values were taken from the LEDs used in this work. Reabsorption in the epitaxial layers was neglected. The pitch of the microcone array was $3 \mu\text{m}$, and the refractive index of the microcone was chosen as 1.9 (corresponding to the experimentally determined value for the TiO₂ NP layer). The height (h) and the base width (b) of the microcones were varied in the simulations. The results for an unencapsulated LED are reported in Fig. 2. The calculated OPE was found to reach values above 1.8 for microcone heights in the range of 1.3 – $3.5 \mu\text{m}$ and base widths in the

FIG. 1. (a) Micro-reflectivity spectrum of an $\sim 1.9 \mu\text{m}$ -thick TiO₂ NP layer spincoated on silicon; inset: cross-sectional SEM image. (b) Analysis of Fabry-Perot fringes from a Bruggeman model. Refractive indices of TiO₂ NPs are based on Ref. 22. Error bars represent uncertainty in the thickness of the TiO₂ NP composite layer.

FIG. 2. Optical power enhancement (OPE) for an unencapsulated vertical thin film LED with a hexagonal array of microcones (refractive index of $n=1.9$). A cross section of the geometry is shown in the inset. All the microcones have the same refractive index ($n=1.9$). The mirror reflectivity is 0.8, and the emitting wavelength is 440 nm. Simulations were achieved using Light tools (Ray tracing method).

range of 2 – $3 \mu\text{m}$. The peak value of the OPE (1.95) was obtained for a height of $2.1 \mu\text{m}$ and a base width of $3 \mu\text{m}$. After encapsulation in a medium with a refractive index of 1.5 (see [supplementary material](#)), the OPE increases due to lower refractive index contrast with the outer medium (air). The OPE reaches its maximum value of 3.27 for a microcone base width of $3 \mu\text{m}$ and a height of $1.3 \mu\text{m}$. Moreover, OPE values were above 3.1 for microcone heights in the range of 1 – $2.6 \mu\text{m}$ and base widths in the range of 2 – $3 \mu\text{m}$. The OPE with microcones is therefore increased compared to a flat LED encapsulated with the same material of refractive index 1.5 (OPE = 2.65), pointing out the interest of using materials of higher refractive index in the microcones than the one used in Ref. 17.

Based on these results, a process was developed to fabricate arrays of microcones on flat substrates using TiO₂ NPs. A patterned sapphire substrate from Rubicon Technology Corporation was used as the template to mold Polydimethylsiloxane (PDMS) which was then used as the embossing stamp. On this sapphire substrate (the template), the period of the cone array is $3 \mu\text{m}$; the cone's height and base width were $\sim 1.7 \mu\text{m}$ and $\sim 2.8 \mu\text{m}$, respectively. A drop of TiO₂ NP solution ($20 \mu\text{l}$) was dispersed on the sample and the PDMS stamp was then pressed on the sample with a controlled pressure ($\sim 100 \text{ g/cm}^2$). During this process, the nanoparticles in the dispersion infill the open regions in the PDMS stamp. Retaining the PDMS mold, the sample was then heated at 100°C for 15 min to remove the solvent. Subsequently, the PDMS stamp was withdrawn from the sample (plain substrate or device wafer) leaving behind the pattern formed from composite TiO₂ NPs on the sample. Sample heating was used primarily to decrease the solvent drying time, but by using longer durations, similar results were obtained at room temperature.

A $1 \times 1 \text{ cm}^2$ array of composite TiO₂ NP microcones was embossed on a variety of substrates such as silicon, GaN, GaAs, glass, and ITO coated glass. The representative results on GaN are shown in Fig. 3. More details are given

the [supplementary material](#). Cross sectional scanning electron microscopy (SEM) images show compact nanoparticle assemblies in the microstructure and that the embossed layer is in intimate contact with the substrate, which is a crucial point for the light extraction efficiency. In most cases, the remaining TiO₂ NP buffer layer was found below the microcones [see Fig. 3]. Its thickness varies on the sample and from sample to sample but is typically in the range of a few tens to a couple of hundred nanometers. The period of the embossed TiO₂ NP microcone array was very similar to the sapphire template period (3 μm). The variation of the height and base width of the microcones is below 4%. However, the microcone height and base width showed larger dispersion from one sample to another. Taking this into consideration, the microcone height and base width were determined to be $\sim 1.35 \pm 0.1 \mu\text{m}$ and $\sim 2.6 \pm 0.1 \mu\text{m}$, respectively. These values for the microcone's geometric dimensions were considered for the evaluation of OPE of the samples.

Vertical thin-film (VTF) GaN-based LEDs with and without embossed TiO₂ structures were used to quantify the OPE and the impact on the electrical properties of the LEDs. The investigated LEDs were on the same wafer. The overall thickness of our LEDs is $\sim 1.3 \mu\text{m}$ including a 200 nm-thick p-type layer, a 100 nm-thick heterostructure based on InGaN/GaN quantum wells, and a 1 μm -thick n-type GaN layer. The emission wavelength of the quantum wells is centered on 440 nm. The lateral size of the LEDs is $820 \times 820 \mu\text{m}^2$. The lateral size of the p-type Ag-based mirror used to evaluate the current density is $800 \times 800 \mu\text{m}^2$. A 1 μm thick NiAu-based metallic grid was deposited on the n-type GaN surface for ohmic contact and current spreading. The top view of a fabricated LED is shown in Fig. 4(a).

The TiO₂ microcone arrays were embossed on the LED wafers using the same pattern and process described earlier. The results show that few LEDs were properly embossed. On these LEDs, the microcone array covers almost the entire LED surface, even the contact lines and electrical pads [Fig. 4(b)]. On these areas, the geometric dimensions of the embossed cones were very similar to the ones obtained on flat wafers, typically $\sim 1.3 \mu\text{m}$ in height with a base width of $\sim 2.6 \mu\text{m}$. Here, we note that uniform patterns were not obtained on all embossed LEDs. Some of them showed inhomogeneous surface coverage or variations in dimensions of the embossed microcones. We believe that contact line

FIG. 3. Composite TiO₂ NP-based microcones embossed on a GaN epilayer. Left panel: photo camera image of the embossed sample. Right panel: SEM top and cross-sectional (inset) views of the embossed patterns.

FIG. 4. SEM micrographs of the LED (LED5) surface (a) before and (b) after embossing the TiO₂ NP microcone array (tilted view). The inset shows a more detailed view of the embossed microstructures.

topography affects the spreading of TiO₂ NP solution. This surface topography issue will be absent for thin-film flip-chip (TFFC) LEDs or micro-LED arrays hybridized on CMOS circuits, as both p- and n-type contacts are backside contacts.

Below, we present the morphological and electro-optic results obtained for the 6 LEDs which gave the highest OPE after embossing. These are located on the same $5 \times 5 \text{ mm}^2$ area and close to the unembossed LEDs (located a few mm away from the embossed area). These embossed LEDs are labelled LED1-6 (generically LEDi), and the unembossed LEDs are labelled REF1-5 (generically REFi). LED1-6 were correctly embossed with microcones with only small areas showing missing microcones. The top surface of LED5, after embossing the TiO₂ NP microcone array, is shown in Fig. 4(b). More detailed SEM images of LEDi are reported in the [supplementary material](#).

Electro-optic measurements were performed using a Karl Suss microtech probing station. The electrical probes were used to scrape away the TiO₂ layer on the electrical pads before the measurement. The LEDs have been probed up to 200 mA ($\sim 35 \text{ A/cm}^2$). A silicon photodiode was used to measure the optical power emitted from the top surface into a numerical aperture of 0.2. The main electro-optic results after embossing are reported in Fig. 5 for LEDi and REFi. OPEs were evaluated at an operating current of 200 mA ($\sim 35 \text{ A/cm}^2$) and were obtained by dividing the optical power emitted by the same LED, before and after embossing. This eliminates LED to LED inhomogeneity. An OPE of 2.08 ± 0.06 was found for LEDi (detailed data are reported in the [supplementary material](#)). This value is in reasonable agreement with the value obtained from the ray tracing simulations ($\text{OPE} = 1.85 \pm 0.19$), taking into account the uncertainties in the geometric dimensions and effective refractive index of the microcones. We believe that the scattering property of the remnant buffer TiO₂ NP layer also plays a role in this discrepancy. Indeed, an OPE of ~ 1.25

FIG. 5. Optical power versus current (a) and current versus voltage (b) for LED1-6 (embossed LEDs) and REF1-5 (on the same wafer but not embossed).

(see [supplementary material](#)) was measured from LEDs covered only with a layer of TiO₂ NPs. An anti-reflection effect cannot explain this level of enhancement, suggesting that scattering of guided light at the GaN/TiO₂ NPs or at the TiO₂ NPs/air interface contributes to the light extraction process at the emitting wavelength of 440 nm. This hypothesis is in agreement with the scattered light measured from a thin layer of TiO₂ NPs on silicon at these wavelengths (see [supplementary material](#)). For embossed LEDs, the obtained values for the OPE are significantly higher than those reported with other approaches involving add-on layers made at room temperature¹⁸ and comparable to or higher than the values obtained with approaches which require recrystallization^{2,15} or even GaN patterning.^{6,8,24–26} Further enhancement is also expected after encapsulation, compared to the OPE value reported in Ref. 14.

As far as the electrical properties are concerned, an average increase in the operating voltage of +70 mV (between +40 mV and +100 mV) for $I=200$ mA was noticed for LEDi compared to REFi [see Fig. 5(b)]. This value is similar to the dispersion of operating voltages observed for each group (LEDi and REFi). The reasons for this increase are not clear. Most likely, it is due to remaining NPs between the tips and the contacts since the process temperature (100 °C) is less likely to affect the metal contacts. Further investigations with TFFC LEDs (with both contacts from the back-side) would be necessary to assess if the process affects long term reliability.

In summary, composite microcone arrays based on TiO₂ nanoparticles were embossed at temperatures ≤ 100 °C on functioning GaN-based vertical thin-film LEDs emitting at 440 nm. The effective index of the composite material was estimated to be ~ 1.9 . An optical power enhancement of 2.08 ± 0.06 was measured, without encapsulation in epoxy. This value is in reasonable agreement with the value given by ray tracing simulations (1.85 ± 0.19). Further work is under progress to test other patterns¹⁷ and add other functionalities to the composite photonic layer, like wavelength down conversion. We believe that this study will contribute to the development of heterogeneous integration of micro-photonic functions on optoelectronic devices.

See [supplementary material](#) for more information on TiO₂ nanoparticles, ray tracing simulations, embossed microcone arrays on other substrates (silicon, GaAs, glass, and ITO coated glass), embossing results on LED1-6, properties of a thin film made of TiO₂ NPs, and the impact of microcones on trapped light.

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