Nanoscale-accuracy transfer printing of ultra-thin AlInGaN light-emitting diodes onto mechanically-flexible substrates

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The transfer printing of 2 μ m-thick AlInGaN micron-size light-emitting diodes with 150 nm (± 14 nm) minimum spacing is reported. The thin AlInGaN structures were assembled onto mechanically-flexible PET/PDMS substrates in a representative 16x16 array format using a modified dip-pen nano-patterning system. Devices in the array were positioned using a pre-calculated set of coordinates to demonstrate an automated transfer printing process. Individual printed array elements showed blue emission centered at 486 nm with a forward-directed optical output power up to 80 μ W (355 mW/cm²) when operated at a current density of 20 A/cm².

Mechanically-flexible and conformable optoelectronics and photonics is an important topic of research, opening up many new scientific and technological opportunities.¹ A recent and attractive approach to flexible photonics is based on the fact that inorganic structures such as semiconductors can be tailored to bend or flex if they are sufficiently thin.² The ‘transfer printing’ of such thin inorganic devices directly onto non-rigid (e.g. polymeric) substrates results in hybrid integration combining the advantageous properties of organic and inorganic materials, offering an optimized flexible photonics platform. This approach has recently enabled the demonstration of mechanically-flexible arrays of inorganic light-emitting diodes (LEDs) and related components with a wide range of applications including conformable displays^{3,4}, image sensors⁵, illumination solutions and biomedical instrumentation^{1,6} as well as optical communication systems.^{6,7,8}

To capitalize fully on the capabilities of inorganic semiconductors for flexible photonics, it will be essential to assemble structures by transfer printing with very high (ideally nano-scale) placement accuracy and preferably also large-area scalability. Indeed, advanced photonic devices often depend on precise spatial combination of micro/nano-structures, either to manipulate the behavior of light (e.g. in micro-resonators, gratings and photonic crystals) or to integrate heterogeneous components

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such as lasers, waveguides and photodetectors.⁹ High accuracy is also critical in order to realize high-density arrays of such devices. To our knowledge, no transfer printing research has so far specifically addressed this issue, and the best reported placement accuracies are ~ 1 to $3\text{ }\mu\text{m}$ ^{10,11}, inadequate to target the aforementioned submicron integration concepts and/or (high fill factor) device arrays. Consequently, there is a need to further enhance the accuracy of transfer printing of thin-film semiconductor structures, without sacrificing fabrication throughput or scalability.

To address this issue, we report here scalable pick-and-place transfer printing of inorganic semiconductor device structures onto mechanically-flexible substrates with, to our knowledge, the highest reported positioning accuracy. The AlInGaN-based devices used were grown on a Si substrate, which is used in a sacrificial manner during the process flow. Transfer printing was realized using a commercial dip-pen nano-patterning system (Nanolnk Inc. NLP2000) converted into a computer-controlled transfer printer.¹² The system uses a 5-axis stage (3 linear and 2 goniometers) combined with high-accuracy optical encoders. The resulting system offers large area coverage ($100\times 100\text{ mm}^2$) while maintaining, manufacturer specified, a positioning accuracy as small as $\pm 25\text{ nm}$. In addition, extensive computer-aided design software allows step-by-step control and automation.¹² To demonstrate the capabilities of our approach, ultra-thin AlInGaN micro-LEDs (each $150\times 150\text{ }\mu\text{m}^2$ in area) were assembled on mechanically-flexible plastic substrates in various configurations including a 16×16 array and with minimum spacing between devices of 150 nm , limited by the roughness of the device-sidewalls. The process is aided by smooth lower surface of GaN-on-Si suspended membranes, which we propose is protected during the aggressive wet etch process used in substrate removal to underetch devices via a thin interfacial SiN_x layer, formed during epitaxial growth.

The LED epitaxial structures used were grown by metal organic vapor phase epitaxy (MOVPE) on Silicon (Si) (111)-oriented wafers¹³ and were processed into $2\text{ }\mu\text{m}$ -thick micron-sized LEDs. A cross-sectional schematic of the epistructure used is given in Figure 1.

Figure 1 - Schematic of the fabrication process for an individual μ LED. The left-hand figure represents (not to scale) the as-grown structure processed as follows: a) Ni/Au current spreading layer deposition and patterning, b) n-GaN exposure and opaque Ti/Au metal pad deposition, c) SiO_2 mask deposition and patterning, d) Deep etching through the epilayers and into the Si substrate, e) Underetching of the Si substrate yielding devices supported by two sacrificial anchors. The grey overlay above e) represents the elastomeric stamp.

The experimental procedures to fabricate arrays of suspended AlInGaN LEDs for transfer printing are also summarized schematically in Figure 1. Device fabrication was initiated with lithographic patterning of semitransparent current-spreading metal (Figure 1a; Ni/Au, thicknesses 12 nm/23 nm) prepared using electron-beam deposition, and subjected to annealing in an air environment to oxidize the Ni component. Inductively coupled plasma etching was used to expose the underlying n-GaN layer of the p-i-n heterostructure (Figure 1b). Metal sputter deposition followed to produce opaque contacts on top of the current-spreading layer and onto the newly exposed n-GaN (Ti/Au, thicknesses 50 nm/180 nm). To define the device lateral dimensions, and allow creation of supporting ‘anchors’, a 1 μm -thick SiO_2 layer was deposited using plasma-enhanced chemical vapor deposition (PECVD) and patterned to protect the devices for deep etching through to the substrate (Figure 1c). Reactive-ion etching (RIE) was then used to continue etching into the Si substrate, thus exposing the Si sidewalls attacked during the following wet etch step (Figure 1d).

To underetch the devices to prepare for their later release from the native substrate, anisotropic wet etching using 60% w/w aqueous potassium hydroxide (KOH) solution at 80°C was used. Anisotropic etching of Si planes (110) perpendicular to patterned supporting anchors were preferentially etched ($\sim 3.5 \mu\text{m}/\text{min}$) while slower-etching (111) planes defined vertical sidewalls. After completion of the underetching, devices were held suspended above an air gap by two diagonally opposed sacrificial anchors.⁶ The total thickness of the devices after removal of the backing substrate is close to 2 μm .

The SiO_2 deposited over the LED current spreading layer and contacts resisted the KOH etching sufficiently to protect the metal layers during the underetching step. Residual SiO_2 was removed after process completion in buffered hydrofluoric acid solution. After standard cleaning, the micro-LEDs were ready to be transfer printed, involving pick-up by an elastomeric stamp and mechanical fracture of the thin anchors (Figure 1e). Stamps¹⁴ were made from polymethylsiloxane (PDMS) by a micromolding technique, and featured pyramidal protrusions at each corner (Figure 1e). Molds were

fabricated from Si (100) wafers – wet etched to create pyramidal recesses – and cells of SU-8 photoresist to define the main body of the stamp (~100 μm thickness). The completed stamps were peeled from their mould and placed on a cover glass. To improve adhesion and avoid lateral play, melted wax was placed around the stamp and the cover glass edges to create a permanent bond with the custom-made stamp support. This support was then mounted on the magnetic transfer arm of the nanolithography system.¹²

Micro-LEDs were transfer printed in a high-throughput parallel assembly (Figure 2a). Each pick-and-place operation can be performed at ~10 seconds per placement, limited only by the operational speed of the translation stages.¹⁵ Multiple device arrays were transfer printed onto PDMS-coated (~100 μm) polyethyleneterephthalate (PET) substrates (~500 μm), with individual, serial or parallel electrical addressing schemes. To achieve this, the PET substrate was patterned in the form of a dummy interconnecting circuit that mimics the final metallization mask for alignment purposes during transfer printing.¹⁶ An adhesion-enhancing layer (PDMS, ~50 μm thick) was coated on top of the dummy circuit. Interconnection of multiple devices by metal tracks requires the devices to be electrically insulated. A low-temperature (100°C) SiO_2 dielectric layer (~350 nm) was deposited by PECVD and patterned by RIE to expose the existing electrodes on each device.¹⁶ A patterning step followed to create metal tracks (Ti/Au, thicknesses 50 nm/280 nm), from which the final interconnecting circuit was defined. Finally, the micro-LED array was encapsulated by another PDMS layer and thus can be operated on the PET substrate or peeled-off as a thin PDMS membrane with embedded micro-LED arrays.¹⁶

Figure 2 - a) Optical micrograph of a 16x16 transfer printed array of LEDs on PET, b) Close-up of devices under operation, c) Colorized SEM image of the backside (i.e. n-side) of an LED on a finished device, d) Detail of the indentation at the upper right corner, resulting from breakage of an anchor, and giving a fracture section through epilayers not exposed to the KOH etch. This higher magnification oblique view shows the overall smoothness of the back surface, and the curved fracture surface.

Sequential transfer printing yielded a 100% complete array (here, by way of example, a 16x16 array), with a horizontal and vertical device spacing of 350 μm and 210 μm respectively (Figure 2a and b). 40 μm wide metal tracks were used to interconnect the elements of the array as seen in (Figure 2b).

Significantly, the backside of underetched devices remains *smooth*, as illustrated by Figure 2c. Atomic force microscopy over $40 \times 40 \mu\text{m}^2$ areas indicated typical 0.8 nm averaged root mean square roughness, approaching closely to the resolution limit of the system used. The well-known polarity-specific etch behavior of KOH and similar solutions would normally be expected to have produced a rough surface, featuring hexagonal micropyramidal protrusions, on direct contact with the III-nitride epilayers¹⁷. It is reasonable to infer here that a thin interfacial SiN_x layer¹⁸ formed during the MOVPE process provided advantageous protection of the III-nitride material from the wet etching.

Figure 3a) shows the current density versus voltage (J - V) characteristics from an individual reference micro-LED pixel at various fabrication stages, acquired using needle probes for the steps before connecting to the metal tracks. The initial turn-on voltage of a typical pixel is approximately 2.8V. With the removal of the supporting Si substrate backplane, yielding a suspended device, this value increased to 3.0V. Transfer-printing of a device onto a PDMS substrate induced another increase on the turn-on voltage to 3.4V. This increase in the turn-on voltage is presumably the result of the increase in specific contact resistance during the successive processing steps. However, the differential resistance above turn-on was not significantly affected by these steps. Once the devices were addressed through metal tracks (i.e. in the final transfer-printed configuration) a change in the slope was observed, resulting from the additional series resistance of the tracks. Turn-on voltage was unaffected compared to the previous processing stage.

Figure 3 a) J - V characteristics throughout several different processing steps and b) L - J performance of a single pixel, with inset displaying the electroluminescent emission spectrum of a pixel driven at 20 A/cm^2 (4.5V).

Figure 3b) shows a typical optical output power versus current density (L - J) characteristic, measured using a power meter with a calibrated Si photodiode detector (0.9cm diameter) placed in close proximity (1.5 cm) to the metal-track addressed LEDs. A Lambertian emission profile was assumed to convert the collected optical power into values quoted for the full forward hemisphere. The LEDs can be driven up to 20 A/cm^2 before thermal roll-over. At this driving current, the total forward optical output power is 80 μW per pixel, corresponding to 355 mW/cm^2 at each device surface. The electroluminescence (EL) spectrum of a single pixel was acquired by an optical fiber-coupled spectrometer (OceanOptics USB4000) aligned with the emitting surface. The emission is centered at

486 nm (~ 37 nm full-width-at-half-maximum) and is composed of two major peaks (*Figure 3c*) which are attributable to the high refractive index contrasts between the thin GaN-based epilayers, air and the PDMS substrate^{13,19}, causing Fabry-Perot interferences which would not be present if roughening of the backside surface during underetching had been severe.

To assess the high-accuracy positioning capabilities of the system used, devices were placed sequentially in a row on a PET/PDMS substrate (*Figure 4a*). These devices were transfer printed individually from the starting 'donor' Si (111) substrate and positioned on the receiving substrate using a pre-calculated set of coordinates in the system control software. These were chosen to give varied target spacings between the devices, starting from 1 μm , and reducing by successive factors of two down to 62.5 nm.

Figure 4 – Colorized SEM imaging of nano-positioned LEDs: a) Strip of positioned devices, with targeted spacings ranging from 1 μm to 150 nm (b,c,d,e)); in b), An example of the measurement lines (green coloured), fitted to the imaged device boundaries over 30-40 μm distances used to estimate the spacing, is shown.

The effective separation between devices was measured in plan-view by a FEI Sirion™ 200 Scanning Electron Microscope (SEM) (*Figure 4*) with a large field detector. Although the device sidewalls do not display perfect verticality, oblique-view imaging confirms the slopes are such that the top surface in this orientation represents the point of closest approach. The microscope's image analysis functions were used to measure device separations, specifically by superimposing best-fit linear boundaries on images acquired over typical lateral distances of 30 to 40 μm . The effective spaces between devices were thus measured and confirmed with a set of close-up image acquisitions (*Figure 4 b,c,d,e*). The measurements as described were repeated on three nominally identical arrays of devices. Numerical results illustrating the high degree of placement accuracy are summarized in Table 1.

Table 1– Comparison between the intended (software input) device spacing and that obtained after the automated transfer positioning, averaged from measurements on three different arrays.

Intended (nm)	Obtained (nm)
1000	1011 ($\pm 62.5\text{nm}$)
500	530 ($\pm 48\text{nm}$)
250	230 ($\pm 28\text{nm}$)
125	150 ($\pm 14\text{nm}$)
62.5	NA

Deviations from the programmed positions were observed and can be expected due to the viscoelastic behavior of the elastomer stamp used to transport the devices. Specifically we suggest that differences

in non-linear relaxation between the four pyramids present on each stamp body, i.e. slightly different retraction rates between pyramids, caused differences in tilt and/or lateral shifts. The minimum 150nm (± 14 nm) spacing attained by our system is presently limited by the side-wall roughness of the LED devices, itself mainly caused by lithography limits and faceting during the exposure to the KOH etch. The peak-to-peak roughness of these side-walls was measured by SEM and found to be higher than the successful minimum placement distance, resulting therefore in devices overlapping each other when attempting to create gaps of 62.5nm.

In summary, transfer printing with 150nm (± 14 nm) minimum spacing of ultra-thin GaN-based micro-LEDs to mechanically-flexible PET/PDMS substrates was demonstrated. The 2 μ m-thick devices were positioned in array configurations by parallel transfer, and were characterized electrically and optically. The devices could be driven up to a current density of 20 A/cm² before reaching thermal roll-over and had a turn-on voltage ~ 3.5 V after transfer. The forward optical output power was up to 80 μ W per device, or 355mW/cm² at the device surface. The nanoscale transfer printing accuracy was obtained by using an adapted commercial nano-patterning system, which was shown to be suited for a high-throughput, automated printing process with large-area scalability. This approach is expected to have wide applicability in nano-accuracy heterogeneous integration.

Acknowledgments

The authors thank Dr P.R. Edwards, University of Strathclyde Department of Physics, for his expert assistance in the SEM imaging and interpretation. This work was supported by EPSRC grants EP/K00042X/1, EP/I029141/1, EP/F05999X/1, EP/I012591/1.

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Supplemental Material

Figure S 1 – (a) Adapted commercial nano-patterning system (NanolInk Inc. NLP2000) used for transfer printing of LEDs. The system is computer-controlled and the CAD software suite used to control the stages is displayed, (b) Close up photograph of the adaptations performed to enable transfer-printing: (1) a supporting stage holds the rigid wafers where the LEDs are patterned, (2) a custom-built magnetic stamp support holds the elastomeric stamps, (3) target substrate deposition area for both rigid/flexible substrates.

Figure S 2 - Flexible device assembly: (a) target substrates are patterned with 'dummy circuits' for alignment and an adhesion-enhancing layer is deposited, (b) LEDs are transfer printed in an array configuration, (c) electrical sidewall insulation of the LEDs and exposure of its electrodes, (d) metal track patterning, (e) device encapsulation terminates the flexible assembly.