Inkjet printed silver nanoparticle electrodes on GaN-based micro-structured light emitting diodes

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Abstract: Silver nanoparticle ink has been inkjet-printed onto inorganic GaN-based micro-structured light emitting diodes to form narrow conductive tracks with a width down to $\sim 30\mu\text{m}$ and a resistivity value approximating to that of a conventional sputtered metal (Ti/Au) track. These silver tracks serve as “active” electrodes with comparable performance to the deposited metal tracks, demonstrating a new, simple and cost-effective route for the electrode fabrication of GaN based LED devices.

Keywords: silver nanoparticles; inkjet printing; micro-structured light emitting diodes

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1. Introduction

Traditional electrode fabrication in electronic and optoelectronic devices requires high vacuum and complicated photolithographic procedures, which results in high production cost and low production efficiency. During last decade, the inkjet printing technique, especially in the form of drop-on-demand (DOD) inkjet printing, has been intensively investigated as this “add-on” direct writing method can greatly simplify the process, reducing the materials cost and contamination. The DOD system has also extended its applications as a rapid manufacturing tool for electronic devices such as thin film transistors [1, 2], polymer capacitors [3], radio frequency identification (RFID) tags [4] and solar cells [5].

Common conductive inks used in inkjet-printed electronic devices include metallic nanoparticle suspensions and conductive polymers. The former are becoming more popular because of better conductivity performance. For instance, silver nanoparticle ink has been studied extensively for printed electronics in fabricating interconnections and solders [6], electrodes on polymeric substrates [7], circuit boards [8] and solar cells [9]. In previous work, silver nanoparticle ink printed electrodes have been studied mostly on organic substrates, due

to advantages in conductivity and flexibility compared to conventional electrodes such as Indium Tin Oxide (ITO) for the organic devices [10]. However, the electrical properties of these electrodes were barely studied or assessed for current injection during the device operation. Furthermore, to the best of our knowledge, printed conductive microstructures have not been applied to inorganic optoelectronic micro-devices such as GaN-based micro-light emitting diodes (micro-LEDs).

The specific GaN LED devices we use here as demonstrators of the capability of electrode printing are in the form of micro-pixelated arrays. These GaN ‘micro-LEDs’ have found numerous applications in such areas as micro-displays, mask-free photolithography, highly-parallel on-chip fluorescence detection and ‘optogenetic’ neuron stimulation [11]. Unlike ‘conventional chip’ broad-area GaN LEDs (devices of several hundred μm dimension), micro-LEDs have typical pixel diameters of ten to a few tens of microns. Given the small size, specially designed metal tracks of high conductivity are generally required for externally addressing the respective emitters, in arrays that can contain up to a few thousand pixels. These metal tracks are commonly formed by optical lithography and subsequent metal deposition via sputtering or evaporation, which involves complicated procedures and relatively high cost.

In this work, we demonstrate a simpler route to integrate micro-electrode tracks onto the inorganic GaN-based micro-LEDs via inkjet printing. The electrical performance of these printed micro-tracks has been characterized in detail and compared with the traditional metal tracks (Ti/Au) which are fabricated by photolithography. By using a 21.5 μm diameter inkjet nozzle aperture, the printed silver micro-tracks on a reference silicon substrate have a width down to 31 μm which is much narrower than those ($> 100 \mu\text{m}$) reported previously and a resistivity value ($1.54\mu\Omega \text{ cm}$) comparable with Ti/Au tracks ($1.21\mu\Omega \text{ cm}$) deposited on the same substrate. We further demonstrate that these inkjet-printed silver tracks are capable of performing as “active” electrodes for current injection in GaN based LED devices. This

method can greatly simplify the device fabrication and packaging processes without compromising the device performance.

2. Experimental methods

The inkjet printing process was carried out by a commercial inkjet printer (Dimatix DMP-2800). This is equipped with a piezo-driven cartridge delivering 10pL droplets from a 21.5 μ m diameter nozzle, a fiducial camera for alignment and a flat platen which can be heated up to 60°C. The drop spacing for printing the silver ink on different substrates was optimized at 35 μ m for glass, 30 μ m for silicon and 50 μ m for GaN. The trigger electrical pulse length was 11.52 μ s and the frequency was 5kHz, while the drive voltage applied on the nozzle was adjusted to keep the droplet flying speed constant at ~4m/s for the best performance. The platen was heated to 60°C during the printing process to stimulate the solvent evaporation and minimize the spreading of the printed track. All the silver tracks in this work were printed as a single layer on the substrate.

The silver nanoparticle ink used in this work was a commercial formulation (Advanced Nano Products Co., Ltd., Korea). The silver nanoparticles are dispersed in a polar solvent triethylene glycol monoethyl ether (TGME) with a solid metal content of 35.4 wt%. The average size of the silver nanoparticles was ~7 nm, which is sufficiently small compared to the nozzle diameter to avoid clogging. The viscosity and the surface tension of the silver ink are 15.5 cP and 37.1mN/m, respectively, compatible with the requirements for printing. The sintering temperature for the ink is comparatively low, at 200°C according to the supplier.

The devices used in this work were GaN-based flip-chip (i.e. back-contacted, with light extraction through the polished sapphire epitaxial substrate) and what we term ‘planar’ micro-LEDs (see below). The fabrication and characterization of the flip-chip micro-LEDs have been reported previously [12]. Figure 1(a) shows the schematic cross-sectional structure of a flip-chip micro-LED pixel and the inkjet printing process for connecting the LED pixels for matrix addressing. The LED pixel was defined by plasma etching and the pixel diameter and

pitch of the flip-chip micro-LED arrays are 30 μm and 50 μm , respectively. Each pixel has a 10 nm thick Ni/Au layer for current spreading and a 250nm Ti/Au layer served as a mirror electrical contact. The SiO_2 insulation layer on the LED array prevents the pixels from electrical cross-talk. The silver nanoparticle ink was printed directly on the top of each LED pixel and SiO_2 insulation layer to form conductive micro-tracks to connect the pixels.

For the planar micro-LEDs on the other hand, in which light-emitting micro-pixels are defined by selective area electrical passivation using plasma treatment [13], the pixels are addressed by a Ni/Au current spreading pattern formed on the p-type GaN. Lacking the requirement for mesa etching (except for the n-contact) and dielectric deposition, this approach greatly simplifies the device fabrication process. A cross-sectional schematic of the planar LEDs and the associated printing process of silver nanoparticles is shown in Figure 1(b). In this case the printed electrode was formed on the treated p-type GaN surface rather than on a SiO_2 layer.

The printed silver track should have a width comparable to the pixel size and pitch of the micro-LEDs so as to interconnect one single row or column of the pixels. Both theoretical modelling and experimental results indicate that the width of inkjet-printed tracks decreases when the contact angle of printed droplets increases [14, 15]. Thus, in order to increase the contact angle for fabricating narrow silver nanoparticle tracks, we vapour-deposited 1H,1H,2H,2H-perfluorooctyldimethylcholosilane (PFODCS) (ABCR, Karlsruhe, Germany) [16] on glass, silicon and treated p-GaN substrates at room temperature. And it was observed that the contact angle of the silver nanoparticle ink on these substrates was altered. The printed silver tracks were afterwards sintered on a hotplate under ambient air. The electrical resistivity values of the printed silver tracks on different substrates after the sintering process were calculated from the equation below:

$$\rho = R \frac{S}{l} \quad (1)$$

where ρ is the resistivity of the printed silver track; R is track's resistance which was extracted from the measured current-voltage curve by using a two-point method; S is the

cross-sectional area of the printed silver track obtained by numerical integration of a measured profile by stylus profilometry; and l is the length of the printed silver track. In order to make a comparison between the printed silver track and a 'conventional' sputtered metal (Ti/Au) track which is normally used for connecting nitride based LED pixels, the electrical resistance and resistivity value of a sputtered metal (Ti/Au) track on a silicon substrate was also measured and calculated from equation (1).

3. Results and discussion

3.1 The inkjet printed silver tracks

Figure 2(a) is a Scanning Electronic Microscopy (SEM) image of an inkjet printed silver track on a silicon substrate after sintering and the inset is a close-up SEM image showing the sintered silver nanoparticles constituting the track. The cross-section SEM image of the silver track printed on a silica/silicon substrate (a SiO₂ layer on top of silicon substrate, same as the flip-chip micro-LED surface) is shown in Figure 2(b). It is observed that both the printed silver track are well-defined spatially and have smooth surface and edges due to the substrate surface treatment. It is also shown that the silver nanoparticles have been sintered together after the sintering process. Due to the size effect, the silver nanoparticles require lower temperature to contact to each other compared to the bulk material [17]. Under proper sintering temperature and duration, the dispersant (TGME in this case) in the suspension is removed, allowing the nanoparticles to contact with each other and consequently reducing the electrical resistivity [18]. Electrical resistivity is a significant factor affecting the performance of the conductive track. Hence, the resistivity of the inkjet-printed silver tracks on different substrates was studied and compared with the resistivity value of sputtered metal (Ti/Au) reference tracks on a silicon substrate ($\sim 1.21 \mu\Omega \text{ cm}$). Table 1 lists the measured contact angle, track width and the calculated resistivity values of the inkjet-printed silver tracks on glass, silicon and treated p-GaN substrates, respectively, after sintering at 200°C for 60min. In this work, all the silver tracks were sintered at 200°C for 60min in order to obtain sufficient

conductivity. The fact that well-defined silver micro-tracks can be successfully printed on treated p-GaN surfaces demonstrates the possibility of applying this technique to GaN based optoelectronic devices. From the measured resistance, the resistivity of the silver tracks printed on treated p-GaN surface is calculated to be $3.76\mu\Omega\text{ cm}$ which is not much higher than that of the metal (Ti/Au) track. The following work shows that the printed silver tracks can serve well as electrodes for operating GaN-based LED devices. Furthermore, the practical cost of the silver metal track is much lower, since only a few droplets of the silver ink are required.

3.2 Applications of the inkjet printed silver tracks on micro-LEDs

The inkjet-printed silver tracks were applied first to the flip-chip micro-LEDs. Figure 3 shows the Scanning Electron Microscopy (SEM) images of the printed silver tracks running over a representative flip-chip micro-LED pixel. The area between the pixels is covered with a deposited SiO_2 insulation layer, whose surface properties are similar to a glass substrate. Thus the contact angle of the printed ink can be altered by PFODCS treatment [16]. However there was no obvious contact angle alteration observed on the Au surface after the PFODCS treatment due to the different surface properties. It can be seen that the printed silver track has a smooth surface and clean edge, while it spreads uniformly at the top of the pixel as the PFODCS barely has any effect on a Au surface. Besides, unlike the usual printed features on the flat surface of devices, here we demonstrate that it is possible to print the silver ink on the uneven ridged surfaces. The pixel height in the flip-chip micro-LEDs is about $1\mu\text{m}$ which is determined by the plasma etching. Due to this height difference, the conventional thin metal track fabricated by metal deposition may break at the pixel side-wall, resulting in pixel disconnection. The SEM image in Figure 3 shows that the pixel side-wall is sufficiently covered by the printed silver nanoparticles to ensure good electrical connection.

The inset (a) of Figure 4 shows, as an example, that 8 LED pixels are interconnected by the printed silver track. The turned-on device image (Figure 4 inset (b)) demonstrates that the LED pixels have been electrically connected and the light emission from pixel to pixel is

uniform. In order to characterize the performance of the printed silver nanoparticle tracks, we have connected one LED pixel by a Ti/Au track formed by sputtering deposition and another pixel with a printed silver nanoparticle track on the same device. The measured current-voltage (I-V) curves of these LED pixels are shown in Figure 4. It is clear that the I-V curves of the LED pixels connected by the silver track and the Ti/Au track are almost identical, indicating that the electrical performance of the printed silver track is comparable to the Ti/Au track fabricated by the conventional metal deposition and photolithography process. These results also confirm that the performance of the LED pixels is not influenced by the inkjet printing and the sintering processes. For device applications, it is also crucial to study the maximum current the printed silver track can bear, as an overloaded current would break down the printed micro-tracks. We have connected nine pixels by a single printed silver track and our measurement shows the silver track could sustain 100mA current without breaking down. The corresponding current density is approximately $2 \times 10^6 \text{ A/cm}^2$ which is much larger than the usual operating current density required for the nitride based LED devices [12]. Thus, the inkjet-printed silver track is fully applicable as the electrodes for GaN LED devices.

The printed silver track approach has also been applied to the planar LED device for the replacement of the Ti/Au metal track and contact pads, further simplifying the fabrication process of the planar LED device. By printing the silver nanoparticle conductive ink, we fabricated not only conductive tracks for connecting the LED pixels but also conductive pads for wire-bonding. Figure 5 is an optical image of a turned-on planar micro-LED pixel connected to a printed silver track. The printed silver pad was at the end of the track and as shown in the image, metal wires have been successfully bonded to these pads. The key process in the fabrication of the planar device is the plasma treatment of the top p-GaN layer, which passivates the p-GaN surface and thus prevents the current leakage from p-GaN-metal interface. In order to demonstrate the printed silver track and the sintering process do not compromise this electrical passivation of the treated p-GaN surface, silver tracks and pads were inkjet printed on both the plasma treated and non-treated p-GaN surfaces and the n-GaN surface. The I-V curves were measured when the voltage was applied upon the p-GaN and n-

GaN surfaces. Figure 6 shows that the I-V curves of the non-plasma-treated p-GaN surface presents a typical diode characteristic, while the current is extremely low (at the measurement limit of the parameter analyzer) on the treated p-GaN surface.

In the planar device, circular LED pixels with different sizes varying from $2\mu\text{m}$ to $100\mu\text{m}$ in diameter have been fabricated. As the top Ni/Au current spreading layer which defines the planar LED pixel is very thin (10nm), it is difficult to align the printed silver track with the small ($< 20\mu\text{m}$) LED pixels. By using the fiducial camera in the inkjet printer, however, we managed to print the silver track and align it successfully with the $20\mu\text{m}$ and larger LED pixels. The inset images (a) to (d) of Figure 7 show several examples of different sized pixels connected by the silver track, with all these pixels turned-on. To make a proper comparison, we have fabricated a planar LED device chip, on which half of the LED pixels were connected by deposited Ti/Au tracks and another half pixels were connected by the printed silver nanoparticle tracks. Figure 7 shows the I-V curve comparisons between these LED pixels. It can be seen that the I-V characteristics of all the silver track connected pixels of different sizes are similar to those connected by the Ti/Au track, which proves the performance of the printed silver track and demonstrates the feasibility of replacing the metal tracks with printed silver tracks.

The optical output power of corresponding planar LED pixels connected by the printed silver track and the Ti/Au track has also been compared to further prove the capability of the silver track. As a demonstration, Figure 8 plots the optical power versus the driving current of the LED pixels of $70\mu\text{m}$ and $100\mu\text{m}$ in diameter, respectively. It is clear that the optical power from the LED pixel connected by the printed silver track is close to that connected by the Ti/Au track. These results confirm that for the planar LED devices, it is feasible to replace the deposited Ti/Au metal tracks with printed silver tracks for LED pixel connection.

4. Conclusion

In summary, the applications of silver conductive tracks inkjet-printed from silver nanoparticles ink have been explored for the inorganic GaN-based LEDs. As a specific

illustration and challenge to the process, we chose to implement this contacting on a micro-pixelated form of GaN LED. The silver track is as narrow as $\sim 30\mu\text{m}$ with a resistivity value of $\sim 1.1\mu\Omega\text{ cm}$ when printed on a glass substrate. The operation performance of the micro-LEDs pixels connected by inkjet-printed silver track has been characterized. The comparable results to those of pixels connected by the sputtered Ti/Au track prove that inkjet-printed conductive silver tracks are promising substitutes for simple and economical electrical connections fabrication on the micro-LEDs.

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Figure captions

Figure 1 Schematic printing process of the silver nanoparticles ink on the flip-chip (a) and the planar (b) micro-LED pixel respectively.

Figure 2 Oblique SEM images of (a) plane-view of the inkjet printed silver track on silicon substrate and close-by SEM image of the annealed silver nanoparticles in the track; (b) cross-section of the inkjet printed silver track on silica/silicon substrate and close-by SEM image of the annealed silver nanoparticles in the track.

Figure 3 Oblique SEM images of the inkjet printed silver track on the flip-chip micro-LEDs.

Figure 4 Current-voltage curves comparison of the single pixel connected by the sputtered Ti/Au track and the inkjet printed silver track on the flip-chip micro-LEDs; Inset are optical microscope images of 8 pixels interconnected by inkjet printed silver track: (a) under normal white light illumination; (b) turn-on pixels.

Figure 5 Optical microscope image of a turned-on planar micro-LED pixel connected by wire-bonded silver pad.

Figure 6 Current leakage test of the printed silver track on plasma treated and non-treated p-type GaN.

Figure 7 Current-voltage curves comparison between the sputtered Ti/Au track and the inkjet printed silver track connecting 20 μ m and 100 μ m size pixels of the planar micro-LEDs; Inset are optical microscope images of the turn-on pixel connected by inkjet printed silver track: (a) 30 μ m; (b) 50 μ m; (c) 70 μ m; (d) 100 μ m.

Figure 8 Power comparison of 70 μ m and 100 μ m size pixels of the planar micro-LEDs connected by the sputtered Ti/Au track and the inkjet printed silver track.

Table captions

Table 1 Contact angle after surface treatment, track width and resistivity values of the inkjet printed silver track on glass, silicon and treated p-gallium nitride (GaN) substrate after 60min sintering at 200°C respectively.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Table 1

Substrate	Contact angle (°)	Line width (μm)	Resistivity (μΩ·cm)
Glass	~44	~33	~1.1
Silicon	~35	~31	~1.54
Treated p-GaN	~31	~54	~3.76