On the Investigations of Chip-on-Board Ultra-Violet Sensor by Screen Printing of GaN Powder

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Abstract. In this work, the characteristics of a chip-on-board screen printed GaN UV sensor was investigated. On the sensing element, GaN powders were obtained through ammonolysis of Ga₂O₃ at 1000°C under NH₃ flow. The UV sensor platform was prepared using soft-lithography method, resulted in patterned circuit board. For the screen printing process, GaN powder is mixed with ethylcellulose/ethanol, subsequently deposited on the electrode pairs. The pure GaN sensor exhibited oscillations and change in amplitude upon UV sensing. This could be ascribed to high intrinsic resistance and parasitic capacitance and inductance. To mitigate this effect, rGO fillers were added and showed discern responds. Both sensors (with and without rGO) showed sensitivity at 300 and 30% respectively, while the current magnitude for the latter was 54 times higher than that of former.

1. Introduction

Gallium nitride (GaN) is a direct bandgap (~3.4 eV) semiconductor material that is well-known in the development and manufacturing of light emitting and high power devices [1-5]. With reference to the aforementioned bandgap, GaN could absorb photons with energy around that region. The absorbed energy would be used in the production of electron-hole pairs. This feature enabled GaN to be used as a light sensing element, particularly in the ultra-violet (UV) region [6, 7].

GaN can be synthesized through various processes, e.g. chemical vapour deposition (CVD), molecular beam epitaxy (MBE), hydrothermal ammonolysis, chemical precipitation method, and so on. Among them, CVD was extensively used since high quality thin film GaN can be deposited on suitable substrates that subsequently further processed into various devices [8-13].

Aside from that, the ammonification, or nitridation of Ga₂O₃ can be opted to produce GaN as well [14, 15]. This was done through heating Ga₂O₃ in an ammonia rich environment at 1000°C. This study holds its importance as gallium has a high affinity towards oxidation, while nitridation can only be accomplished under selected environment. Consequently, understanding about the transformation characteristics of Ga₂O₃ to GaN can be accomplished. To date, it is known that Ga₂O₃ possessed monoclinic phase, while that of GaN being hexagonal wurtzite [15, 16]. During nitridation, several chemical reactions occurred which distorted the Ga₂O₃ lattice. The oxygen group would be subsequently replaced by nitrogen, concurrently the rearrangement of Ga- and N- atoms has resulted in a hexagonal wurtzite structure [4]. Coincidentally, a new phase in the form of gallium oxynitride
was revealed by several studies, indicating that such compound would be an intermediate between Ga$_2$O$_3$ and GaN [17, 18]. In extended nitridation condition, gallium oxynitride would ultimately converted into GaN. Although GaN was obtained, however, the corresponded characteristics would be different from that of CVD grown. The resulting GaN powder would be polycrystalline, in some cases residue oxygen could be present within the GaN lattice as defects [15].

Powder based devices can be prepared in several ways, including high pressure compression which resulted in solid pellets, or screen printing technique. The latter eliminate the use of high power instruments, instead, depended on chemistries. In general, powdered material would be dispersed and homogenized in the presence of surfactants to avoid aggregations, also binders that will brought all grains together. In this method, several improvements could be implemented, e.g. addition of conducting fillers to bridge the grains for better electrical conductivity. Nevertheless, having to obtain a dynamic control over several parameters would require extended works to be done.

In this work, powdered GaN was synthesized through nitridation of Ga$_2$O$_3$ powder. Given the scarce literature about applications on GaN powder in the field of optoelectronics, ultra-violet sensor based on powdered GaN would be done. Screen printing method was employed since this allows GaN powder to be deposited on various substrates. For this work, patterned circuit board (PCB) was used as the electrical platform for the sensing element. Direct integration of sensing element towards PCB would enable rapid prototyping of sensory devices to be realized.

2. Methodology

2.1 Fabrication of GaN powder

The fabrication of GaN powder is as follows: 3 g of Ga$_2$O$_3$ powder were placed in a ceramic crucible, subsequently inserted into a tube furnace. The furnace was heated up to 1000°C, concurrently purged with N$_2$ gas. Then, NH$_3$ gas was introduced into the furnace at 200 sccm. This would initiate the nitridation process of Ga$_2$O$_3$. The reaction lasted for 3 hours. After that the NH$_3$ valve was closed, and the growth chamber was purged with N$_2$. The furnace was shut off, and the nitrided Ga$_2$O$_3$ was allowed to cool down prior to retrieval.

2.2 Fabrication of patterned circuit board

The patterned circuit board was fabricated using soft lithography method. Firstly, the pattern was drawn in a computer, subsequently printed on a silicone-coated paper using laser printer. The printed paper was overlaid on a copper cladded board, subsequently passed through a heated roller. Both pressure and heat were applied on them, allowing the toner on the paper to be softened, and then transferred to the copper cladded board. The transferred toner would mask the copper underneath, preventing them from being etched. Etching was performed by immersing the sample into concentrated FeCl$_3$. After etching, the board was thoroughly rinsed with DI water, followed by acetone to remove the toner. For tin plating, the board was immersed in a solution containing mixture of tin chloride and thiourea for 10 seconds. A thin layer of tin has been deposited on the board from this process. The plated board was rinsed and dried prior to next process. A schematic representation of the patterned circuit board is shown in Figure 1.
2.3 Fabrication of UVC sensor

A few drops of ethyl-cellulose/ethanol mixture were drop-wise on GaN powder, forming a thick paste. The paste was screen printed on the PCB platform, guided by two strips of PET tape (≈ 60 μm). The screen printed board was heated on a hotplate at 80°C to drive off the solvents. For GaN-rGO sample, GO was added to the mixture. Upon drying, the sample was quickly heat up to 250°C and cool down rapidly. This will cause the reduction of GO into rGO. A schematic representation of the sample is shown in Figure 2.

![Figure 1. Schematic representation (not in scale) of the patterned circuit board (PCB).](image)

**Figure 1.** Schematic representation (not in scale) of the patterned circuit board (PCB).

2.4 Characterizations

The samples, including Ga₂O₃ and GaN powder, were characterized using FESEM (FEI, Nova NanoSEM 450) to visualize its morphology. For the electrical test, current-voltage (I-V) and current-transient (I-T) profiles were performed using Keithley 2400 source measurement unit in the presence of both dark and UVC (~254 nm) conditions.

![Figure 2. Exploded view of the UVC sensor.](image)

**Figure 2.** Exploded view of the UVC sensor.
3. Results and discussions

(a) Figure 3. (a) digital photographs of Ga$_2$O$_3$ and GaN powders, FESEM images of (b) Ga$_2$O$_3$, (c) GaN, and GaN-rGO composite.

Figure shows the digital images of both Ga$_2$O$_3$ and GaN powder, as well as the electron micrographs of the samples. Ga$_2$O$_3$ powder is white in colour, upon nitridation, it turned yellow, which is a typical colour for GaN. When observed under FESEM, both Ga$_2$O$_3$ and GaN powder shows distinct morphological difference. Compare to Ga$_2$O$_3$, GaN composed of flake like structures. This was likely due to coalescence and recrystallization process, where it can be chemically shown as such:

\[ \text{NH}_3 \rightarrow \text{NH}^* + \text{H}_2 \]  
\[ \text{Ga}_2\text{O}_3 + 2\text{H}_2 \rightarrow \text{Ga}_2\text{O} + 2\text{H}_2\text{O} \]  
\[ \text{Ga}_2\text{O} + 2\text{NH}^* \rightarrow 2\text{GaN} + \text{H}_2\text{O} \]

Initially, NH$_3$ would undergo stepwise decomposition to yield NH radicals and H$_2$. The latter subsequently reduces Ga$_2$O$_3$ into its suboxide, i.e. Ga$_2$O, which exist in vapour phase. At this stage, it can be ascribed that Ga$_2$O$_3$ would be etched by H$_2$. The vapour phase Ga$_2$O reacted with NH radicals, forming GaN in the process. Given that a substantial amount of Ga$_2$O$_3$ was being used, a rich flux of Ga$_2$O would be generated. During GaN formation, minute GaN droplets would coalesce, forming the flake like structure as shown.

Figure 4 shows the I-V and I-T characteristics of the UVC sensor. Both sensors displayed unique sensing characteristics. If the sensor consisted of only GaN powder, significant oscillations were noted on both I-V and I-T profiles. Additionally, the magnitude of the current was in the nanoampere’s range, implying the GaN powder possessed very high resistance. Meanwhile, the oscillating features of the sensor could be attributed to the noise from the measuring instrument, i.e. source measurement unit. However, given that its amplitude responded to UVC illumination, this implied such feature originate from GaN powder itself. The oscillating features of pure GaN based sensor suggesting the significance of parasitic capacitance and inductance. For such oscillations, it can be elucidated from a resistance-capacitance-inductance (RLC) model that located at the GaN-GaN boundary. Initially, as the sensor was biased under dark condition, current flow across it was established. Some charges were stored at the boundary due to parasitic capacitance. Since the resistance was sufficiently high, current flow across the boundaries could be interrupted, resulting in an open circuit condition. Consequently, the parasitic capacitor discharged, briefly bridging the boundaries electrically. Some portion of the energy would be dissipated due to junction resistance, while some returned back to the parasitic capacitor and repeat the process. Upon UVC illumination, electron-hole pairs were generated and the junction resistance was decreased. Given that the significance of parasitic capacitance and resistance, the amplitude of the oscillations increases.

To mitigate the effects of parasitic capacitance and inductance, conducting filler was introduced. The role of such filler was to bridge the GaN-GaN boundaries, while maintaining the sensor’s sensing
characteristics. For that, rGO was sought. In order to prevent the segregation of rGO, GO was used as the starting material, since the latter disperse readily in aqueous solvent. GO in general possessed poor electrical conductivity; however such could be restored through reducing it. In Figure 4(c) and (d), a more distinct UV sensing was noted, additionally reduced oscillations. Interestingly, the oscillations were pronounced in the presence of UV light illumination. This further provides insights towards the behavior of GaN-GaN boundary. Aside from that, the sensitivity for Sn/GaN-rGO sensor was about 30% on average. The sensitivity, $S$, can be calculated using the following equation:

$$S = \frac{I_{UV} - I_{dark}}{I_{dark}} \times 100\%$$

where $I_{UV}$ and $I_{dark}$ are the measured current in the presence/absence of UV light respectively.

![Figure 4.](image)

**Figure 4.** (a, c) I-V characteristics of Sn/GaN and Sn/GaN-rGO; (b, d) transient profile of Sn/GaN and Sn/GaN-rGO.

At the boundaries, the parasitic capacitor could store photogenerated carriers, which would discharges, giving greater oscillation amplitude. Next, the junction resistance for the pure GaN was considerably high, and could be assumed open circuit from time to time. The resistance was high enough to be ignored by the parasitic capacitance-inductance, which leads to undamped oscillations; despite it was being lowered in the presence of UV light. Introducing rGO into the system resulted mitigated the probability of open circuit occurrence since rGO have electrically bridge the boundaries.
Consequently, it acted as a current damper when the parasitic capacitor discharges, leading to exponential decrease of the oscillation amplitude.

![Figure 5](image)

**Figure 5.** Processed transient profile (a) before (b) after.

Figure 5 shows the method of processing the I-T profile of purely GaN based sensor. The notable amplitude change in the presence of UV light was sufficient to suggest its significance, which requires further data processing. From Figure 5(a), the I-T profile approximately symmetry ~25 nA, which is also the linear average current. Since the linear approach unable to distinguish the difference between UV and dark conditions, polynomial approach was adopted. Though a simple mathematical transformation, using the equation below:

\[ I_{after} = \sqrt{I_{before}^2} \]

where the processed current was denoted as \( I_{after} \) while that of as-measured being \( I_{before} \).

The I-T profile at Figure 5(a) was squared, which flips the negative region to that of positive. The square root was necessary to reduce the polynomial order back to one. Next, the oscillations were smoothed out using second order Savitsky-Golay function. This resulted in notable current change upon UV light illumination. Comparing the processed data with that of Sn/GaN-rGO, the latter is still 54% greater than that of former in terms of current magnitude. On the processed data alone, the calculated sensitivity was 10 times higher than that of Sn/GaN-rGO.

4. Conclusions

GaN powder exhibited UV-sensing capabilities, which is demonstrated through screen-printing/patterned circuit board method. The pure GaN and GaN-rGO samples exhibited parasitic capacitance and inductance, additionally higher resistance at the former. This lead to higher occurrence of open circuit conditions where oscillations caused by parasitic capacitance and inductance become discern. The characteristics of such oscillations could be elucidated using RLC model. Through simple signal processing, a definitive signal that illustrates UV sensing for pure GaN sample was obtained. On a side note, the sensitivity of pure GaN (after signal processing) and GaN-rGO samples were 300 and 30% respectively; however, the latter has a higher current magnitude, about 54 times that of the former.
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