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# Homogeneous transparent conductive ZnO:Ga by ALD for large LED wafers

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ABSTRACT

Highly conductive and uniform Ga doped ZnO (GZO) films were prepared by atomic layer deposition (ALD) as transparent conductive layers for InGaN/GaN LEDs. The optimal Ga doping concentration was found to be 3 at%. Even for 4" wafers, the TCO layer shows excellent homogeneity of film resistivity (0.8 %) according to Eddy current and spectroscopic ellipsometry mapping. This makes ALD a favourable technique over concurrent methods like MBE and PLD where the up-scaling is problematic. In agreement with previous studies, it was found that by an annealing treatment the quality of the GZO/p-GaN interface can be improved, although it causes the degradation of TCO conductivity. Therefore, a two-step ALD deposition technique was proposed and demonstrated: a "buffer layer" deposited and annealed first was followed by a second deposition step to maintain the high conductivity of the top layer.



## 1. Introduction

Transparent conductive oxides are widely used in photovoltaics, thin film transistors and light emitting devices. The most common TCO material is indium doped tin oxide (ITO), but in the past decades the price of indium has been rapidly increasing. One of the most promising replacements, due to its excellent transparency in the visible wavelength range and similar electrical conductivity, is highly n-doped zinc oxide [1]. These layers can be deposited by a number of techniques, such as DC magnetron and reactive sputtering, spray pyrolysis, pulsed laser deposition, molecular beam epitaxy, and atomic layer deposition [2]. Though both Al and Ga doping (AZO and GZO) provide excellent transparency and low resistivity, the latter one has some advantages over AZO, such as higher electrical stability at elevated temperatures [3] and no tendency for dopant segregation at the interface [4]. Moreover, the covalent bond lengths of Ga-O and Zn-O (1.92 Å and 1.97 Å, respectively) are very close to each other as compared to that of Al-O (2.7 Å), thus, the deformation of the ZnO lattice of the same dopant concentration is significantly lower in GZO than in AZO [5]. Therefore, GZO is an ideal candidate for current spreading TCO layer in InGaN/GaN LEDs as demonstrated in several papers [6–8].

Although there are a few reports about GZO resistivities in the upper $10^{-5}$ Ωcm range, such as $8.12 \times 10^{-5}$ Ωcm in [9] and $5.1 \times 10^{-5}$ Ωcm in [10], the published free electron concentrations are surprisingly high. For instance, in [10] a Ga doping concentration of 0.75 at% resulted in a free electron concentration of $n = 2.9 \times 10^{21}$ cm$^{-3}$ which corresponds to a doping efficiency of 9.3 free carriers per Ga atom at an atomic number density of $4.15 \times 10^{22}$ cm$^{-3}$. It cannot be explained by the most widely used substitutional ($Ga_{Zn}$) doping scheme. Moreover, in [9] the reported resistivity ($\rho = 8.12 \times 10^{-5}$ Ωcm), electron mobility ($\mu = 30.96$ cm$^2$/Vs), and carrier concentration ($n = 1.46 \times 10^{22}$ cm$^{-3}$) values do not fulfil the $\rho = (\mu n e)^{-1}$ equation (where $e$ is the electron charge). The best reproducible resistivity values of GZO layers ($1.2–1.3 \times 10^{-4}$ Ωcm) have been published for pulsed laser deposition (PLD) [11] and molecular beam epitaxy (MBE) [12]. These techniques, however, are not really up-scalable to the standard 4" industrial substrate size of e.g. sapphire, 8" Si LED wafers or even for larger solar panels.

On the other hand, at large wafer sizes, atomic layer deposition (ALD) is a promising candidate to produce high quality GZO layers at relatively low temperatures (300 °C) if the achieved resistivities are also comparable to state-of-the-art values. A couple of studies have been published on ALD GZO layers, their resistivity

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values, however, are significantly higher ($1.2 \times 10^{-3}$ Ωcm in [13], $8.0 \times 10^{-4}$ Ωcm in [14], $4 \times 10^{-4}$ Ωcm in [15], and $3.7 \times 10^{-4}$ Ωcm in [16,17]) than the best results obtained by PLD. Since the obtained carrier concentrations for ALD GZO are comparable to the highest values obtained by PLD ($1.4 \times 10^{22}$ cm$^{-3}$) [11], the higher resistivity can be ascribed to the moderate mobility (1.4–11.5 cm$^2$/Vs in [13], 11–29 cm$^2$/Vs in [14], and 11–16 cm$^2$/Vs in [16]). An often experienced problem is that GZO forms a non-ohmic electrical junction on the highly p-type doped GaN top layer of LEDs. This behaviour can be caused by an insufficient doping level in the p-GaN layer, a formation of a $ZnGa_2O_4$ phase at the GZO/p-GaN interface [18], or interfacial electronic defects [16].

By changing the Ga/Zn precursor pulse ratios, an optimal Ga concentration for highly conductive TCOs and an excellent wafer scale uniformity of the ALD GZO layer on 4" wafers could be demonstrated. Besides, in order to combine low specific GZO/p-GaN contact resistance with a relatively high film conductivity despite the reduced GZO thickness of 45 nm, we introduced a two-step ALD deposition method for GZO TCO in standard InGaN/GaN LEDs. The targeted potential replacement of ITO in LED devices by the more abundant GZO without performance degradation also requires the optimization of the LED design for the constraints of this novel TCO. The experimental study below, however, was done on a standard design (layout) optimized for the use of ITO. All the conclusions drawn from the functional performance of the LED with GZO have to take this into consideration.

## 2. Experimental

### 2.1. Sample preparation

GZO layers were deposited in a Picosun SUNALE TM R-100 type ALD reactor. The precursors for Zn and Ga were diethyl-zinc (DEZ), and hexakis(dimethylamino)gallium ($C_{12}H_{36}Ga_2N_6$), respectively. 18 MΩcm purity deionised water was used as an oxidizing agent whereas the carrier and purging gas was 99.999% purity nitrogen. The Zn precursor and the water were kept at room temperature, while the Ga precursor was heated to 130 °C to ensure sufficient vapour pressure. During deposition the pressure in the chamber was kept at 5 hPa and the temperature at 300 °C, at which the precursors are stable, and the ALD growth is possible. The pulse time of the precursors was 0.1 s, and the purging times were 3 s after each metalorganic and 4 s after each water pulse. The Ga doping was performed by periodically applying Ga precursor pulses instead of the Zn ones in every $N^{th}$ deposition cycle. The nominal atomic percent of Ga is thus defined as the cycle ratio of Ga and Zn precursor pulses {[Ga]/([Ga] + [Zn]) = 1/N}. For instance, in the case of 1/33 (~3 at%) nominal doping the applied deposition sequence was (32Zn + 1Ga)x36. These conditions resulted in a growth rate of 0.07 nm/cycle on GaN substrates.

To determine the effect of gallium doping and find the ideal doping level, at first a series of GZO thin films with varying nominal Ga concentration was deposited onto c-sapphire substrates. Homogeneity tests were carried out on a GZO thin film deposited on a 4" glass wafer. The effect of the annealing and the fabricated devices were investigated on GZO layers deposited on a commercial InGaN/GaN LED-wafer. For electrical and electroluminescence tests, fully processed GZO coated LED-chips were used. Prior to ALD, the GaN substrates were etched by HCl in order to eliminate native gallium-oxide layers. Contact pads of Ti/Au (30 nm/70 nm) were prepared by e-beam evaporation both for the transmission line method (TLM) and for the LEDs. Annealing of the samples was performed in an AST SHS 1000 rapid thermal annealing (RTA) system for 5 min in a nitrogen atmosphere.

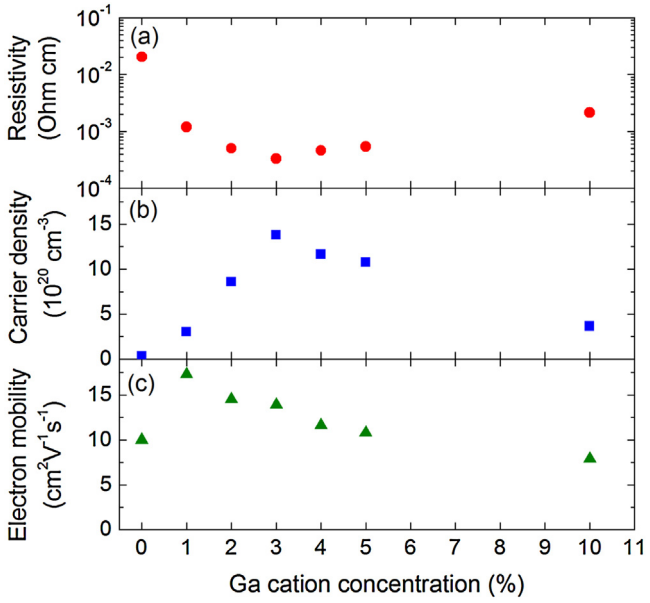


**Fig. 1.** Results of the Hall effect measurements carried out on GZO/sapphire thin films with varying Ga concentration: resistivity (a), free carrier concentration (b), and free electron mobility (c). The optimal doping level is 3 at%.

### 2.2. Characterization methods

The elemental composition of the GZO films was determined with a Bruker Quantax energy dispersive spectrometer (EDS) in a JEOL JSM25 SIII scanning electron microscope (SEM). Hall measurements were carried out at room temperature on square shaped sapphire samples coated with GZO using In contacts in Van der Pauw configuration. The thickness of the films was measured with a Dektak profilometer. The specific resistivities and Hall mobilities were calculated using these measured thickness values. The thickness uniformity of the GZO layer on 4" wafers was studied by a Semilab SE-2000 spectroscopic ellipsometer operating in the 300–1500 nm spectral range [19]. Sheet resistance mapping was carried out with a Semilab WT-2000 system using contactless Eddy-current metrology. For an easy comparison of the obtained thickness and sheet resistance values and to avoid the edge effect in Eddy current measurements both techniques were applied only in the inner 80-mm-diameter region. The high resolution transmission electron microscopy (TEM) observation of the interface was performed by a JEOL JEM-3010HREM instrument. Cross sectional TEM specimens were prepared by ion beam milling [20] in a Technoorg Linda tool using 10 keV $Ar^+$ ions at an incidence angle of 5° with respect to the surface. In the final phase of the milling process, the ion energy was gradually decreased to 0.3 keV in order to minimize ion-induced structural changes in the surface layers.

## 3. Results and discussion

### 3.1. The effect of the doping level

To find the optimal concentration, at first GZO/c-sapphire films with nominal Ga concentrations of 1–5, and 10 at% and thickness of 85 nm were used. The nominal Ga concentrations agreed well with the results of the EDS measurements, no systematic discrepancy between the corresponding values was found. According to Hall measurements (Fig. 1a), at low Ga concentrations, the increasing doping level reduces the specific resistivity of the layers to $\rho = 3.3 \times 10^{-4}$ Ωcm. This trend is reversed at 3 at%, and ρ increases monotonously with increasing doping concentration.