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# GaInN/GaN solar cells made without p-type material using oxidized Ni/Au Schottky electrodes

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ABSTRACT

GaInN/GaN solar cells made without p-type material are demonstrated using an oxidized Ni/Au Schottky barrier design to collect photo-generated carriers. The best devices exhibit a short-circuit current density of 0.065 mA/cm$^2$ with an open-circuit voltage of 0.4 V under AM0 (1-Sun) illumination. Preliminary computer simulations are in reasonable agreement with experimental results, giving a pathway to improve device performance via iterative redesign and testing.



## 1. Introduction

GaInN semiconductor alloys cover an unusually wide energy range ($0.7 \le E_g \le 3.4$ eV) and have optical absorption coefficients approaching $10^5$ cm$^{-1}$ at energies just above their bandgaps [1]; making this material system a good candidate for developing multi-junction, thin-film solar cells [2]. Most GaInN/GaN solar cell designs evaluated to date contain some form of *p-n* doping profile to enable collection of photo-generated carriers [3–6]. The difficulty of making *p-type* GaN and $Ga_{1-x}In_xN$ ($x \le 0.2$) of good electronic quality has been well documented in the literature on GaInN/GaN LEDs and laser diodes [7–8]. Moreover, there have been only a few reports of *p-type* GaInN with higher indium content [9–10]; which is necessary to make *p-n* GaInN solar cells with band gaps in the range 1.9–1.0 eV.

It was demonstrated long ago that solar cells could be made from material of one doping type (n *or* p) by employing a metal/semiconductor Schottky barrier to collect photo-generated carriers [11–12]. Recently, this concept was applied to make GaInN/GaN solar cells *using only n-type material* [13–14]. An oxidized Ni/Au composite film was employed as the *transparent* Schottky electrode. This choice was motivated by the knowledge that oxidized Ni/Au films make ohmic contacts to *p-type* GaN [15], and thus should form rectifying junctions when in contact with *n-type* GaN.

In this paper, the potential of such GaInN/GaN Schottky solar cells is evaluated further by characterizing the optical and electrical properties of the Schottky electrode, as well as the electronic behavior of its rectifying interface with n-type GaN, and by fabricating devices and comparing their photovoltaic response to results obtained via numerical simulation.

## 2. Experimental methods

The GaInN/GaN solar cell material employed in this study was grown by OMVPE on a c-plane sapphire substrate. The structure consists of a 4 μm n$^+$ GaN layer, followed by a 15-pair MQW absorber region (2.5 nm $Ga_{0.9}In_{0.1}N$ wells/12 nm GaN barriers), and capped by a 40 nm GaN layer. The GaInN/GaN MQW absorber and GaN capping layer were not intentionally doped but have n-type conductivity owing to residual donors. A layer schematic is shown in Fig. 1 for a fully processed device. The *oxidized* Ni/Au composite material forms a “broad-area” Schottky barrier with respect to the GaN capping layer.

A different n$^-$/n$^+$ GaN layer structure was used for preparation of Schottky diodes. It was grown under similar conditions to the solar cell material, but the n$^-$layer is lightly doped with silicon

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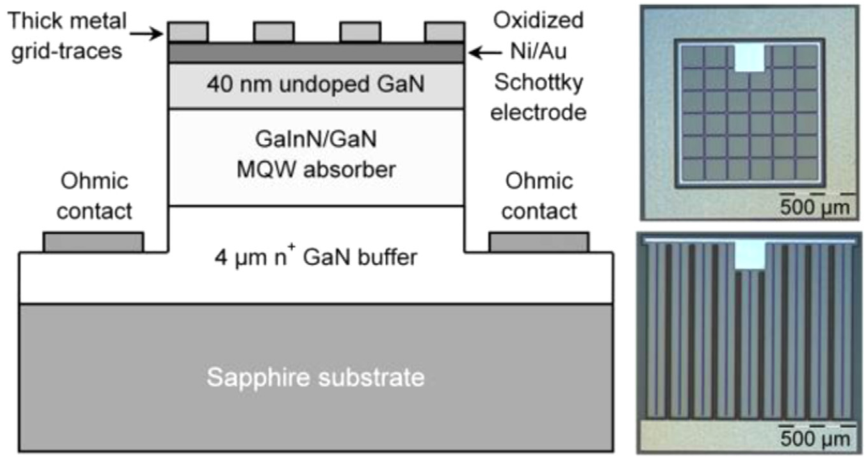


**Fig. 1.** Layer schematic (cross-section) and optical images (plan-view) of fabricated GaInN/GaN – Ni/Au TCO Schottky solar cells.

($[N_d - N_a] = 9 \times 10^{16}\ \mathrm{cm}^{-3}$ from C-V measurements at 300 K). The MQW region was omitted to avoid the possibility of stress relaxation in the GaInN layers, which is typically accompanied by an increase in threading dislocation density. These structural defects give rise to additional leakage current paths, making it more difficult to obtain reliable Schottky barrier parameters.

All material test structures, Schottky diodes, and solar cells were made using conventional photolithography, dry etching, and metal deposition techniques. In each case, the Schottky electrode material was formed by depositing, via e-beam evaporation, a thin layer of Ni followed by a thin layer of Au, and then annealing at 500 °C for 10 min in air to form a transparent conducting oxide (TCO). Three different layer structures were evaluated with the following construction: one period of Ni (5 nm)/Au (5 nm), two periods of the same bilayer, and one period of Ni (10 nm)/Au (10 nm). These three Schottky electrode materials are referred to hereafter as Ni/Au (5/5), Ni/Au/Ni/Au (5/5/5/5), and Ni/Au (10/10), respectively.

Schottky diodes were fabricated in a planar architecture, i.e., without mesa etching, having circular Schottky (inner) electrodes ranging from 200 to 450 μm in diameter and ohmic (outer) contacts of much larger area. Ohmic contacts were made first by depositing Ti (30 nm)/Al (200 nm)/Ni (50 nm)/Ag (400 nm) and annealing at 600 °C for 5 min in forming gas. Transparent Ni/Au (5/5) Schottky electrodes were formed next, as described above, and then coated with Ni (50 nm)/Ag (400 nm) without further annealing. This thick Ni/Ag pad metallization creates an equipotential plane across the entire Schottky electrode and protects the thin TCO film from damage during probing.

Test samples for evaluating optical transparency and sheet resistance were prepared on double-side polished sapphire wafers. In the latter case, a Ni (50 nm)/Ag (400 nm) metal bilayer was deposited on top of the Schottky electrode material and patterned to form isolated probe contacts with pad dimensions of 390 μm (width) × 150 μm (length). The separation between adjacent probe contacts increases from 7 to 25 μm (along the pad length direction). The Ni/Au film was removed from the area outside this "TLM ladder" to prevent undesired fringe current flow.

Solar cells were made using similar methods, with the addition of an ICP etching step ($BCl_3/Cl_2$ chemistry) to define the active mesa and expose the $n^+$ GaN for ohmic contact formation. Both *grid* and *finger* style devices were fabricated, each with two pitch values (150 and 75 μm) for grid spacing and finger separation. In the latter case, adjacent mesa fingers were isolated by dry etching down to the $n^+$ GaN layer to form interleaving ohmic contacts. Optical images are shown in Fig. 1, grid (upper) and finger (lower), for devices with 150 μm pitch. The total device area is $1.4 \times 1.4\ \mathrm{mm}^2$ in all cases, but the "illuminated area" (active mesa *minus* opaque top metal) ranges from 0.76 to 1.24 $\mathrm{mm}^2$ among the four configurations.

## 3. Results and discussion

The nature of the potential barrier between Ni/Au TCO films and n-type GaN was evaluated by making I-V measurements (at 300 K in the dark) on Schottky diodes. Raw current values were converted to current density by dividing out the area of the Schottky contact pad. A representative set of J-V curves is shown in Fig. 2 for diodes with Ni/Au (5/5) Schottky electrodes. Under forward bias, current scales with junction area, as evidenced by overlapping J-V curves for devices ranging in size from $3.1 \times 10^{-4}$ to $1.6 \times 10^{-3}\ \mathrm{cm}^2$. At low reverse bias, diode currents are below the detection limit ($\approx 10$ pA) giving rise to noisy signals with no voltage dependence. At higher reverse bias (beyond $-2$ V), current increases with voltage but it is not proportional to junction area. The behavior of these devices is consistent with that of conventional metal/GaN Schottky diodes, prepared via heteroepitaxy, with threading dislocation densities $\geq 10^9\ \mathrm{cm}^{-2}$.

The forward bias portions of these J-V curves (i.e., linear regions between +0.4 and +0.8 V) were fitted using Eq. (1), along with a Richardson constant, $R$, of 24 A $\mathrm{cm}^{-2}\ \mathrm{K}^{-2}$ ($m_e^* = 0.2 m_e$), to find Schottky barrier heights, $\phi_b$, and diode ideality factors, $n$. Least-squares curve fitting gives $\phi_b = 1.12 \pm 0.04$ eV with $n = 1.29 \pm 0.07$.

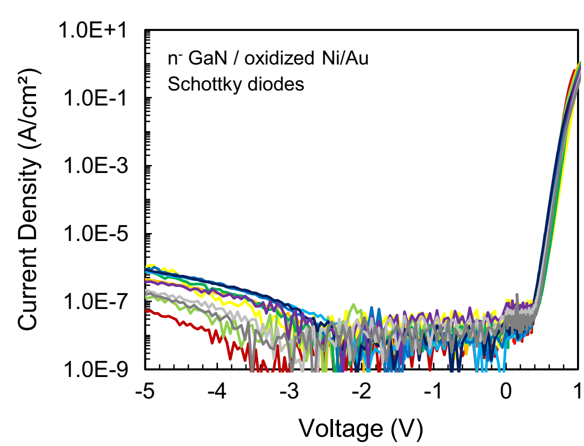


**Fig. 2.** J-V characteristics for Schottky diodes consisting of Ni/Au (5/5) Schottky electrodes on an $n^-/n^+$ GaN epitaxial layer.

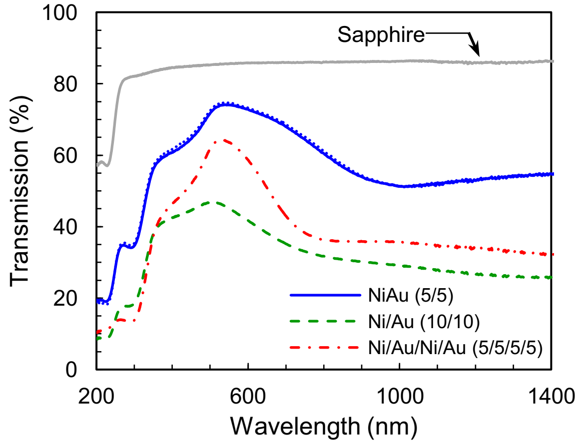


**Fig. 3.** Optical transmission spectra (raw data) for oxidized Ni/Au Schottky electrode materials.

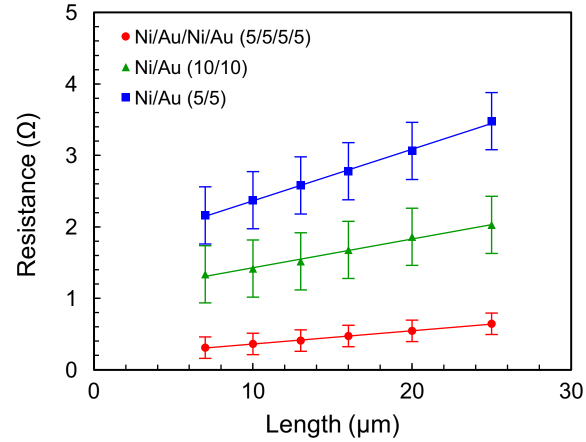


**Fig. 4.** Electrical resistance vs. contact spacing for oxidized Ni/Au Schottky electrode materials.

$$J = RT^2 e^{-q\phi_b/kT}(e^{qV/nkT} - 1) \quad (1)$$

Direct comparison to literature values is not possible because there are no reports of *oxidized* Ni/Au Schottky barriers on *n-type* GaN. There is, however, evidence that reverse leakage current in AlGaN/GaN HFETs can be suppressed by oxidizing the Ni/Au Schottky gate [16]. In this case, the Ni/Au film was in direct contact with a 5 nm GaN cap layer, and the authors reported similar Schottky barrier parameters ($1.1 \le \phi_b \le 1.3$ eV, $1.5 \le n \le 1.9$).

The optical transparency, $\tau$ of Ni/Au Schottky electrode materials was determined using a Filmetrics F20-UVX instrument. The raw transmission spectra (300 K), shown in Fig. 3, reflect the optical response of the film/substrate composite. Photons with $\lambda \le 440$ nm will be absorbed by the GaInN/GaN MQW; hence, this wavelength range is of particular interest. After normalizing out the contribution from sapphire, the Ni/Au (5/5) composite has a maximum transparency of 86.6% at $\lambda = 540$ nm; however, $\tau$ is only 74.7% at 440 nm and it decreases to 70.1% at 370 nm. There are actually two spectra plotted in Fig. 3 for Ni/Au (5/5), corresponding to measurements about 1 cm apart on a $2 \times 2$ cm$^2$ sample. These curves (solid vs. dotted) are nearly indistinguishable, demonstrating good process uniformity. By comparison, others found $\tau = 73\%$ at 440 nm (68% at 370 nm) for a Ni/Au sample with identical layer thicknesses made using similar processing conditions [17].

It is not surprising that $\tau$ for Ni/Au (10/10) is significantly lower than that of Ni/Au (5/5), given a doubling of Ni and Au layer thicknesses. It is interesting, however, that Ni/Au/Ni/Au (5/5/5/5) exhibits higher transparency than Ni/Au (10/10) despite the same overall thickness. This suggests that oxidation gives rise to different volume ratios of “transparent” (NiO) and “opaque” (Au) materials in these composite films.

The sheet resistance, $R_{sh}$, of Ni/Au Schottky electrode materials was obtained from multiple I-V sweeps (recorded at 300 K) using a Keithley 2400 SMU. Measurements were taken from eight TLM ladders at different locations across $1 \times 1$ cm$^2$ samples. All three data sets plotted in Fig. 4 exhibit a linear relationship between resistance and contact spacing. This behavior is consistent with Eq. (2),

$$R_t = 2R_c + R_{sh}(L/W) \quad (2)$$

where $R_t$ is the total resistance (obtained via measurement), $R_c$ is the contact resistance, $L$ is the (variable) contact separation, and $W$ is the (fixed) contact width. Data analysis yields a sheet resistance of $28.1 \pm 3.9$ $\Omega/\square$ for the Ni/Au (5/5) case, in good agreement with previous work ($R_{sh} = 32.1$ $\Omega/\square$ [17]).

The Schottky electrode thickness was increased in an effort to reduce sheet resistance. If Ni/Au (10/10) had the same material resistivity as Ni/Au (5/5) then $R_{sh}$ should decrease by ½ owing to a doubling of overall film thickness. The extracted value for Ni/Au (10/10), $R_{sh} = 12.1 \pm 2.5$ $\Omega/\square$, is consistent with this expectation. Unfortunately, the improvement in $R_{sh}$ comes at the expense of much lower optical transparency compared to Ni/Au (5/5). A more promising result was obtained for Ni/Au/Ni/Au (5/5/5/5), with a fitted value of $R_{sh} = 3.9 \pm 1.5$ $\Omega/\square$ accompanied by enhanced transparency relative to Ni/Au (10/10). Others have shown that oxidized Ni/Au films exhibit a non-homogenous structure with Au nanoparticles embedded in a NiO matrix [18]. Perhaps the smaller Ni layer thickness leads to narrower NiO regions between adjacent Au islands, which should increase the rate of electron tunneling and thereby decrease the effective sheet resistance.

The effective bandgaps of contemporary group III nitride solar cell designs [3–6] are too large to realize single-junction devices with short-circuit current densities, $J_{sc}$, approaching those of solar cells made from GaAs or Si – *the GaInN/GaN MQW absorber employed herein is no exception*. This situation places a premium on optical transparency of the Schottky electrode, so a decision was made to use oxidized Ni/Au (5/5) material in our initial solar cell designs.

Preliminary electrical screening was done using an LED emitting at 398 nm with an intensity of 13 mW/cm$^2$. Devices with distorted I-V curves, indicative of localized areas of poor quality material or of processing related defects, were excluded from

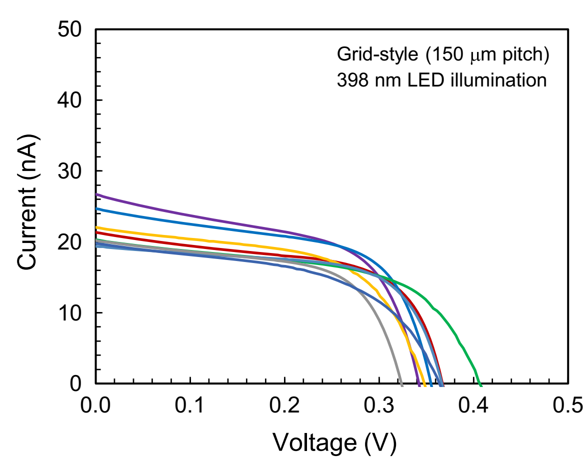


**Fig. 5.** I-V curves for GaInN/GaN – Ni/Au TCO Schottky solar cells (grid-style, 150 µm pitch) under 398 nm LED illumination.

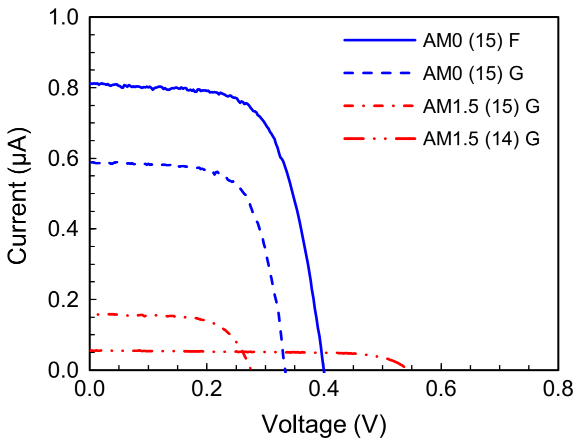


**Fig. 6.** I-V curves under AM0 (1-Sun) and AM1.5 (1-Sun) illumination for GaInN/GaN – Ni/Au TCO Schottky solar cells. Data is shown for both grid (G) and finger (F) devices with 150 μm pitch, and for measurements taken roughly one year apart, (14) vs. (15).

further consideration. A representative set of data is shown in Fig. 5. These I-V curves provide direct evidence of a photo-response from the GaInN quantum wells, as the surrounding GaN does not absorb 398 nm photons. These data also give a sense of the variability among devices. Solar cells having the best fill-factors under LED excitation were selected for additional testing.

Electrical testing under calibrated solar radiation was performed using Newport AM0 and AM1.5 solar spectrum simulators at 1-Sun intensity (verified using a Newport solar intensity power meter and a reference Si solar cell). I-V curves are shown in Fig. 6 for "best-in-class" devices having different geometries and/or illumination conditions. Normalizing measured currents by illuminated mesa areas gives $J_{sc}$ values of 0.065 and 0.073 mA/cm$^2$ for finger and grid devices, respectively (under an AM0 spectrum). Applying the same procedure to the grid-style solar cell measured under AM1.5 illumination yields a significantly lower value of $J_{sc}=0.019$ mA/cm$^2$.

Numerical simulation of the GaInN/GaN MQW structure only, using APSYS software from Crosslight, gives $J_{sc}=0.084$ mA/cm$^2$ under AM0 (1-Sun) illumination. This value is reduced further to 0.057 mA/cm$^2$ by accounting for optical losses in the Ni/Au (5/5) Schottky electrode. The same numerical calculations yield $J_{sc}=0.032$ mA/cm$^2$ under AM1.5 illumination (including optical losses in the Schottky electrode). The agreement between theory and experiment is reasonable given the approximate nature of the analysis (polarization charges and quantum-confinement effects were ignored in the calculations and no attempt was made to correct measured I-V curves for optical losses from surface reflection).

The open-circuit voltage, $V_{oc}$, of a Schottky solar cell should be smaller than that for a *p-n* junction device because it scales with Schottky barrier height instead of semiconductor bandgap [19]. Nevertheless, the $V_{oc}$ values associated with the I-V curves in Fig. 6 are lower than expected for a barrier height in excess of 1 eV. Numerical simulation gives $V_{oc} \approx 0.5$ eV, under both AM0 and AM1.5 illumination, when assuming an ideal Schottky barrier with $\phi_b = 1.08$ eV.

Additional insight on $V_{oc}$ may be found by comparing the two I-V curves taken under AM1.5 illumination. These data are from the exact same device, with the first I-V curve measured one year ago (14) and the second recorded within the past month (15). The reduction in $V_{oc}$ over time is not unique to this particular solar cell; similar behavior has been observed in many devices. The Schottky electrodes in these solar cells are only 10 nm thick, and they were not encapsulated by a protective coating (as was done for Schottky diodes used to extract $\phi_b$). Consequently, the electronic nature of the Ni/Au–GaN interface may be sensitive to moisture or other chemical impurities in the environment. Such contamination may give rise to lower initial Schottky barrier heights, and could also explain the reduction in $V_{oc}$ with time.

## 4. Summary and conclusions

The viability of GaInN/GaN solar cells *without p-type doping* has been demonstrated using an oxidized Ni/Au Schottky barrier design to collect photo-generated carriers. Considerable work remains to be done to bring $J_{sc}$ and $V_{oc}$ for these Schottky solar cells in line with the best GaInN/GaN *p-n* junction devices. There have been two other reports on GaInN Schottky solar cells [20,21]. These devices were made using pure metal films as Schottky electrodes (Pt [20], Ni [21]). It is not possible to directly compare $J_{sc}$ and $V_{oc}$ values because this prior work did not employ calibrated solar illumination for device testing.

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## References

[1] J. Wu, W. Walukiewicz, Band gaps of InN and group III nitride alloys, Superlattices Microstruct. 34 (2003) 63–75.
[2] J. Wu, W. Walukiewicz, K.M. Yu, W. Shan, J.W. Ager III, E.E. Haller, H. Lu, W. Schaff, W.K. Metzger, S. Kurtz, Superior radiation resistance of $In_{1-x}Ga_xN$ alloys: full-solar-spectrum photovoltaic material system, J. Appl. Phys. 94 (2003) 6477–6482.
[3] O. Jani, I. Ferguson, C. Honsberg, S. Kurtz, Design and characterization of GaN/InGaN solar cells, Appl. Phys. Lett. 91 (2007) 132117.
[4] C.J. Neufeld, N.G. Toledo, S.C. Cruz, M. Iza, S.P. DenBaars, U.K. Mishra, High quantum efficiency InGaN/GaN solar cells with 2.95 eV band gap, Appl. Phys. Lett. 93 (2008) 143502.
[5] R. Dahal, J. Li, K. Aryal, J.Y. Lin, H.X. Jiang, InGaN/GaN multiple quantum well concentrator solar cells, Appl. Phys. Lett. 97 (2010) 073115.
[6] Y. Kuwahara, T. Fujii, T. Sugiyama, D. Iida, Y. Isobe, Y. Fujiyaa, Y. Morita, M. Iwaya, T. Takeuchi, S. Kamiyama, I. Akasaki, H. Amano, GaInN-based solar cells using strained-layer GaInN/GaInN superlattice active layer on a free-standing GaN substrate, Appl. Phys. Express 4 (2011) 021001.
[7] K. Kumakura, T. Makimoto, N. Kobayashi, Activation energy and electrical activity of Mg in Mg-doped $In_xGa_{1-x}N$ ($x<0.2$), Jpn. J. Appl. Phys. 39 (2000) L337–L339.
[8] P.-C. Chen, C.-H. Chen, S.-J. Chang, Y.-K. Su, P.-C. Chang, B.-R. Huang, High hole concentration of p-type InGaN epitaxial layers grown by MOCVD, Thin Solid Films 498 (2006) 113–117.
[9] C.-A. Chang, T.-Y. Tang, P.-H. Chang, N.-C. Chen, C.-T. Liang, Magnesium doping of In-rich InGaN, Jpn. J. Appl. Phys. 46 (2007) 2840–2843.
[10] L. Sang, M. Takeguchi, W. Lee, Y. Nakayama, M. Lozac'h, T. Sekiguchi, M. Sumiya, Phase separation resulting from Mg doping in p-InGaN film grown on GaN/Sapphire template, Appl. Phys. Express 3 (2010) 111004.
[11] E. Ahalstrom, W.W. Gartner, Silicon surface-barrier photocells, J. Appl. Phys. 33 (1962) 2602–2606.
[12] W.A. Anderson, A.E. Delahoy, Schottky barrier diodes for solar energy conversion, Proc. IEEE 60 (1972) 1457–1458.
[13] Kevin T. Chern, Louis J. Guido, Timothy A. Ciarkowski, Noah P. Allen, Oleg A. Laboutin, Roger E. Welser, Victor C. Elarde, GaInN/GaN – Ni/Au transparent conducting oxide Schottky barrier solar cells, In: Proceedings of the 40th IEEE Photovoltaic Specialists Conference, 2014, pp. 1139–1142.
[14] Kevin T. Chern, GaInN/GaN Schottky barrier solar cells, Ph.D. Thesis, Virginia Tech, 2015.
[15] J.-K. Ho, C.-S. Jong, C.C. Chiu, C.-N. Huang, C.-Y. Chen, K.-K. Shih, Low-resistance ohmic contacts to p-type GaN achieved by the oxidation of Ni/Au films, J. Appl. Phys. 86 (1999) 4491–4497.

[16] S.-C. Lee, M.-W. Ha, J.-Y. Lim, J.-C. Her, K.-S. Seo, M.-K. Han, Suppression of leakage current of Ni/Au Schottky barrier diode fabricated on AlGaN/GaN heterostructure by oxidation, Jpn. J. Appl. Phys. 45 (2006) 3398–3400.

[17] W.C. Chong, K.M. Lau, Comparison of Ni/Au, ITO, and ATO-based current spreading layers for near-ultraviolet light-emitting diodes, Phys. Status Solidi C 4 (2007) 2646–2649.

[18] L.-C. Chien, F.-R. Chen, J.-J. Kai, L. Chang, J.-K. Ho, C.-S. Jong, C.C. Chiu, C.-N. Huang, C.-Y. Chen, K.-K. Shih, Microstructural investigation of oxidized Ni/Au ohmic contacts to p-type GaN, J. Appl. Phys. 86 (1999) 4491–4497.

[19] R.F. McQuat, D.L. Pulfrey, A model for Schottky-barrier solar cell analysis, J. Appl. Phys. 47 (1976) 2113–2119.

[20] J.-J. Xue, D.-J. Chen, B. Liu, Z.-L. Xie, R.-L. Jiang, R. Zhang, Y.-D. Zheng, Au/Pt/InGaN/GaN heterostructure Schottky prototype solar cell, Chin. Phys. Lett. 26 (2009) 098102.

[21] S. Lin, B.P. Zhang, S.W. Zeng, X.M. Cai, J.Y. Zhang, S.X. Wu, A.K. Ling, G.E. Weng, Preparation and properties of Ni/InGaN/GaN Schottky barrier photovoltaic cells, Sol. St. Electron 63 (2011) 105–109.