

# NiO removal of Ni/Au Ohmic contact to p-GaN after annealing\*

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**Abstract:** The Ni/Au contact was treated with oxalic acid after annealing in O<sub>2</sub> ambient, and its *I*-*V* characteristic showed the property of contact has been obviously improved. An Auger electron spectroscopy (AES) depth profile of the contact as-annealed showed that the top layer was highly resistive NiO, while an X-ray photo-electron spectroscopy (XPS) of oxalic acid treated samples indicated that the NiO has been removed effectively. A scanning electron microscope (SEM) was used to observe the surface morphology of the contacts, and it was found that the lacunaris surface right after annealing became quite smooth with lots of small Au exposed areas after oxalic acid treatment. When the test probe or the subsequently deposited Ti/Au was directly in contact with these small Au areas, they worked as low resistive current paths and thus decrease the specific contact resistance.

**Key words:** oxalic acid treatment; specific contact resistance; NiO

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**PACC:** 7430

**EEACC:** 2530D; 2550E

## 1. Introduction

GaN's intrinsic properties such as wide bandgap, high thermal conductivity, high melting temperature, high breakdown voltage, and high saturation velocity<sup>[1]</sup> make it a material of choice for ultraviolet and visible wavelength optoelectronic devices. In the past decade, significant progress in material growth and processing technologies and in new device design has been made. Now the most important and challenging problem is to master the reliability of GaN-based devices. The high Ohmic contact resistance at the metal/GaN interface is a long-standing problem causing poor device performance and reliability. In order to make reliable devices, specific contact resistance must be decreased to under  $10^{-4} \Omega \cdot \text{cm}^2$ . But to p-GaN, due to high activation energy ( $\sim 170$  meV) of the deep Mg acceptor<sup>[2]</sup>, those grown by MOCVD (metalorganic chemical vapor deposition) or MBE (molecular beam epitaxy) can hardly achieve a doping density higher than  $1 \times 10^{18} \text{ cm}^{-3}$ <sup>[3]</sup>, and its work function is very high, so it is still a big challenge to make applicable p-doped Ohmic contacts.

To date, only two Ohmic metallization schemes have been reported achieved specific contact resistances  $R_c$  less than  $10^{-4} \Omega \cdot \text{cm}^2$  on moderately doped p-GaN: one is Ta/Ti, and the other is Ni/Au. Compared with Ta/Ti, Ni/Au is more stable in air, so it is used more widely<sup>[4,5]</sup>. As the reported experiments show, only those Ni/Au contacts annealed in O<sub>2</sub> ambient at certain temperatures can achieve applicable Ohmic contact. There has been no determinate conclusion in the mechanism, but most researchers think it has some relation with the NiO formed at the interface during the process of annealing in O<sub>2</sub><sup>[5-7]</sup>. In these years, HCl, KOH, (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> solutions and aqua regia have been used to remove the oxidation layer on

the p-GaN surface and achieved low specific resistance<sup>[6,8-10]</sup>. Expecting to further improve the property of the contact, we did some post-treatment to the Ni/Au contact to remove the NiO layer formed on the surface during annealing.

## 2. Experiments

The 0.2  $\mu\text{m}$ -thick p-type GaN layer doped with Mg was grown by MOCVD on a (0001) sapphire substrate with a doping density of  $1 \times 10^{17} \text{ cm}^{-3}$ . Followed by rapid thermal annealing at 750 °C for 15 min in N<sub>2</sub> ambient, and then ultrasonically degreased using trichloroethylene, acetone, methanol, ethanol and deionized water for 5 min in each step to remove the organic contaminations on the surface, Ni (5 nm)/Au (5 nm) contacts were deposited using e-beam evaporation, and then annealed at a temperature of 550 °C for 10 min in O<sub>2</sub> ambient. These as-annealed samples were dipped into a 10% oxalic acid solution with a water bath of 70 °C for 15 min and then rinsed with deionized water. The specific contact resistance was measured using circular transmission line method (CTLM) patterns, with an inner dot radius of 200  $\mu\text{m}$  and the spacing between the inner and outer radii varies from 10 to 60  $\mu\text{m}$ . The current-voltage (*I*-*V*) characteristics were obtained by using a Keithley 2400 source meter, the voltage range was -1 to 1 V and the step of measurement was 0.01 V. Auger electron spectroscopy (AES) depth profiles of samples before and after annealing were measured to investigate the NiO forming and distribution after the annealing process, related elements on the surface of as-annealed samples and oxalic acid treated ones were analyzed by X-ray photo-electron spectroscopy (XPS), and the surface conditions of these samples were observed with a scanning electron microscope (SEM).

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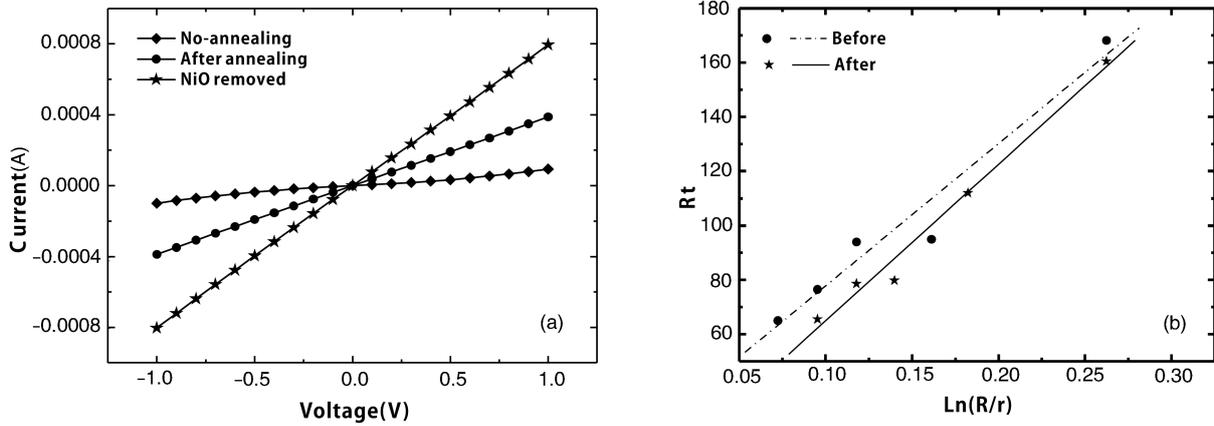


Fig.1. (a)  $I$ - $V$  characteristic of samples; (b)  $R_t$ - $\ln(R/r)$  of the sample before and after NiO removal.

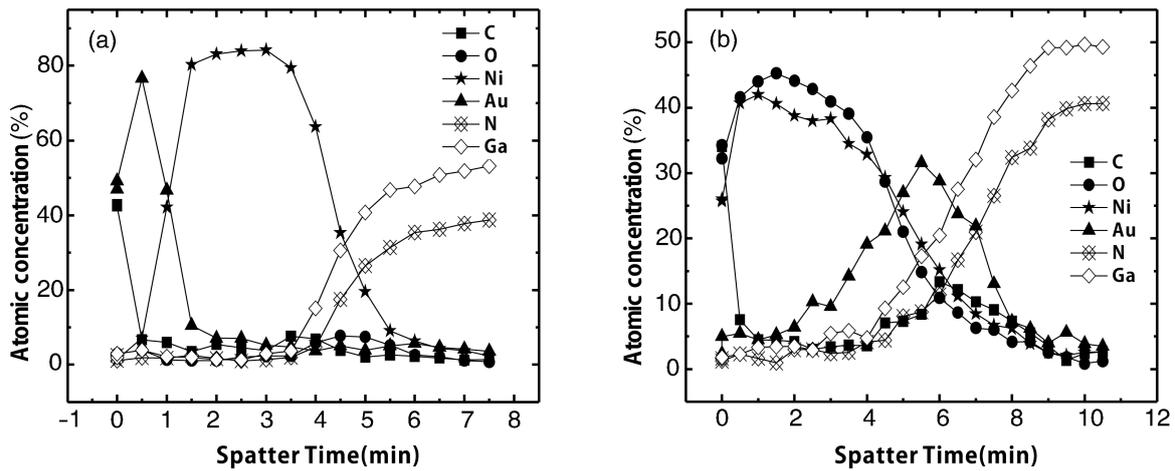


Fig.2. AES depth profile of samples (a) before and (b) after annealing in  $O_2$ .

### 3. Results and discussion

Figure 1 (a) shows the current–voltage characteristics between two pads with  $60\ \mu\text{m}$  gap spacing for different samples. The  $I$ - $V$  curve obtained is nonlinear for the sample without annealing, but linear for both the as-annealed and oxalic acid-treated ones over the whole range of voltages. The current of oxalic acid treated samples at a certain voltage is shown to be obviously larger than that of the as-annealed ones. The specific contact resistance was calculated with the CTLM method as shown in Fig.1 (b), and it decreased from  $7.73 \times 10^{-4}$  to  $2.57 \times 10^{-4}\ \text{cm}^2 \cdot \Omega$  after the oxalic acid treatment. This means that the removal of NiO after annealing can remarkably improve the contact property. What should be pointed out especially is that this increase in current at a certain voltage can only be observed at some testing points, and the reason for this phenomenon will be discussed in detail later.

AES analysis was carried out for samples with and without rapid thermal annealing to investigate the changes of the contacts during the annealing process. The AES depth profile of several elements on the surface of samples with and without annealing in  $O_2$  atmosphere is displayed in Figs.2 (a) and 2 (b). In Fig.2 (a), where the Au layer is on top of the Ni layer on the surface of contact without rapid thermal an-

nealing, there is a clear interface between these two metal layers. During the annealing process, Ni reacted with oxygen that penetrated through the Au layer and NiO was formed. The NiO overturned to the top while the Au fell and was in direct contact with the GaN surface in the condition of high temperature, thus resulting in layer reversal as seen in Fig.2 (b). Although there is no definite interface between the NiO and Au layers, it is affirmative that the NiO is mainly on the top surface. NiO is a p-type semiconductor with a bandgap of 4.0 eV and electron affinity of 1.4 eV<sup>[7]</sup>, so its specific resistance is usually higher than the contact metal. To be convenient for flip-chip bonding to heat sink and final packaging, the p-type contact should be redeposited with another metallic scheme to make it thicker, usually a Ti/Au bilayer was added to it in the following process of device fabrication. Thus when the test probes or the adding Ti/Au bilayer contact with the NiO on the surface, there would be another metal–semiconductor contact resistance or a highly resistive layer connected in series in the path of current, which made the series resistance increase considerably. So in our study, oxalic acid was used to erode the NiO on the contact surface, approximately to the depth of plasma etching of 4 minutes as indicated in Fig.2 (b), which made the bottom metallic Au uncovered and able to contact the test probes or Ti/Au metallic layer directly.

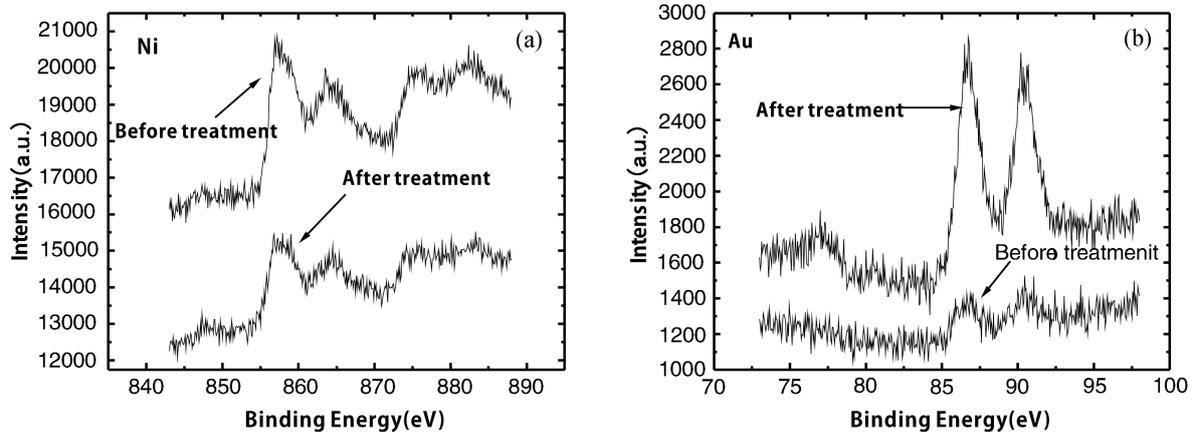


Fig.3. XPS spectra of (a) Ni and (b) Au photoelectrons for samples before and after oxalic acid treatment.

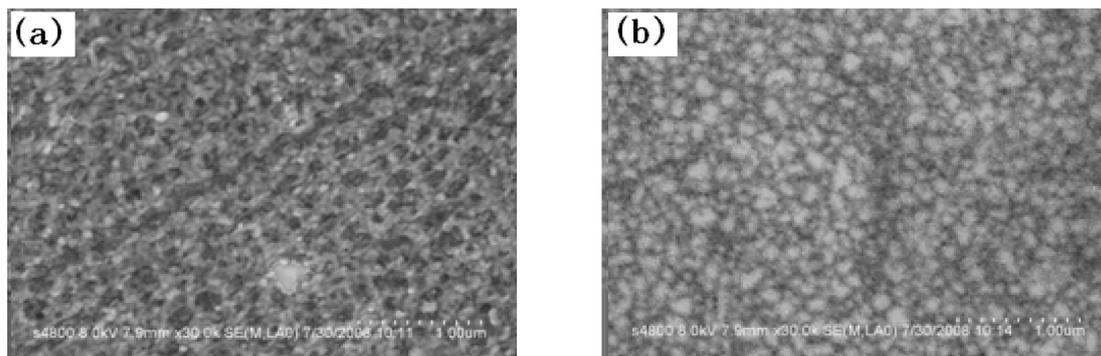


Fig.4. Scanning electron microscopy images: (a) As-annealed without oxalic acid treatment; (b) Oxalic acid treated after annealing.

To confirm that oxalic acid can erode NiO on the surface of the contact, XPS of samples as-annealed in  $O_2$  atmosphere and those followed with an oxalic acid treatment were measured, as shown in Fig.3. Theoretically the range of XPS measurement is within 3 nm, so it can only indicate the states and contents of elements on the surface of the sample. It can be seen from Fig.3 (a) that after oxalic acid treatment the intensity of the Ni signal peak decreased apparently while that of Au increased sharply in Fig.3 (b), which means that the Ni element on the surface was reduced and the Au content increased relatively, indicating the effective removal of most of the resistive NiO by oxalic acid treatment.

Figure 4 displays the surface morphology SEM images of samples as-annealed and with oxalic acid treatment with a magnitude of enlargement of 30 000. The porous texture on the surface of the as-annealed contacts in Fig.4 (a) was formed by the reaction of Ni and oxygen penetrated through the Au layer as well as the coming along layer reversal process. The melting point of Au is as high as  $1064.43^\circ C$ , so the substance with a porous texture on the surface could only be NiO, which can also be testified by Fig.2 (b). After the oxalic acid treatment, most of the NiO on the surface was removed, as can be seen from Fig.4 (b), the surface of contact was quite smooth rather than porous, and many white mottle areas appeared in between. Compared with Fig.4 (a), we presumed the white mottle areas to be uncovered metallic Au. With reference to Fig.2 (b), it could be seen that there was a thick Au–NiO mix-

ing layer existing between the top NiO layer and bottom Au layer, which made it impossible to erode all of the NiO in the contact, so we inferred the dark areas in Fig.4 (b) to be the remaining NiO.

The Au–NiO mixing layer between the top NiO and bottom Au layer after annealing acted as a stop layer, and thus made Au exposed only in some local areas instead of the whole surface. When the test probe made contact with the exposed Au areas in the  $I$ – $V$  characteristic testing, the current at these points would be larger than that of the as-annealed samples, while the probe was in contact with the area with the remaining NiO, the current would be the same. But this does not mean oxalic acid treatment has no practical effect on improving the property of contacts. In the following process of device fabrication, as another metal scheme such as Ti/Au was deposited on the oxalic acid treated surface to make a thicker contact, definitely there would be some local areas where Au is exposed and could make contact with Ti/Au directly. And in the process of device operation, these directly contacted points could act as low resistive current paths and reduce the series resistance effectively.

#### 4. Conclusions

Ni/Au contact annealed in  $O_2$  atmosphere was treated with the oxalic acid solution, and its  $I$ – $V$  characteristic showed that a decrease in contact resistance was achieved in some lo-

cal areas. The AES depth profile of samples annealed in O<sub>2</sub> atmosphere indicated that the substance on the top was mainly NiO, and Au was directly contact with the GaN surface at the bottom, with a NiO-Au mixing layer in between. XPS results showed that oxalic acid could erode most of the NiO on the top, but it was found through the SEM image that the NiO in the NiO-Au mixing layer was not erode thoroughly, leaving only some small Au exposed areas on the surface. Nevertheless, these small exposed areas were enough to improve the property of the contact by contacting with the redeposit metallic layers and acting as low resistive current paths.

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