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Photoelectrochemical mechanical polishing method for n-type gallium nitride

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ABSTRACT

A novel polishing method, photoelectrochemical mechanical polishing (PECMP), is proposed for finishing the n-type gallium nitride semiconductor wafers. The method applies the ultraviolet-light irradiation to a wafer surface to generate unpaired electron-holes during a mechanical polishing process. The free-holes facilitate photoelectrochemical oxidation so as to accelerate material removal in the polishing process. The novel method achieves a material removal rate of 1.2 μm/h which is one order of magnitude higher than that of a conventional technique. In addition, the method removes the surface and subsurface damages induced in a previous machining process and obtains an atomically flat and damage-free wafer surface.

1. Introduction

Chemical-mechanical polishing (CMP) has been the only practical technique for preparing the planarization and damage-free semiconductor wafer surfaces. However, the third-generation semiconductors are commonly difficult-to-machine materials with superior thermo-chemical stability and high hardness [1,2]. Application of the conventional CMP technique to the chemically-inert materials, especially the n-type gallium nitride (GaN), inevitably suffers from the low material removal rate (MRR) [3]. As such, in a conventional process of polishing a free-standing GaN wafer, diamond lapping is first used to flatten and thin the wafer, and then CMP is employed to remove the scratches and subsurface damages (SSDs) induced in the diamond lapping process [4].

However, the conventional process is inefficient and time-consuming because of its low MRR of 17 nm/h [4]. To enhance the polishing efficiency for GaN, great efforts have been made in recent years. Although the chemical polishing method allows to achieve the highest MRR of 122 nm/h, the use of the chemicals in a polishing process has been discouraged [5]. Therefore, it is highly desirable to explore a new method for polishing the third-generation semiconductor wafers.

Similar to the other third generation semiconductors, GaN has the superior photoelectric characteristics, due to its wide bandgap (3.4 eV) between the valence band (VB) and the conduction band (CB). In addition, if GaN is used as a photoanode of a photoelectrochemical (PEC) system, its superior photoelectric characteristics facilitate an easy oxidation in the system. Fig. 1(a) describes that an oxide layer is formed on the GaN wafer surface due to the PEC effect of the PEC system and then removed by the subsequent mechanical polishing.

The PEC effect is illustrated as follows. An ultraviolet (UV)-light (wavelength$<$365 nm) is introduced to irradiate GaN in order to excite electrons (e-) from VB to CB, generating electron-hole (h^+) pairs within the UV-penetration layer [6–8]. An electric field is applied to separating the electron-hole pairs through an electrochemical bias voltage (V_{bia}) between the potentials of the GaN photoanode and the cathode (the conductive polishing disc). The CB electrons and the VB holes are forced to flow to the external cathode and the GaN surface, respectively. The wide bandgap provides a VB hole with a high Fermi energy level, such that the oxidative capability of the VB hole is higher than all the chemical oxidants that have been found in nature so far. While the CB electrons are electrochemically consumed by reducing the H^+ cations at the cathode potential (E_{red}), the VB holes of accumulation at the wafer surface may oxidize GaN to generate an amphoteric Ga_2O_3 thin layer [7,8]. Namely, the PEC oxidation of GaN proceeds by the photogenerated free-holes rather than the chemical oxidants [9].

In recent years, the PEC oxidation has been widely used in the wet-etching fabrication of the GaN based devices. It was reported that the

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highest etching rate of 43 nm/min was obtained by rapidly dissolving the amphoteric Ga_2O_3 layer in a proper pH environment [6]. A PEC oxidation layer is much softer than GaN and can be removed in a subsequent mechanical polishing process [9,10]. A synergistic effect of the PEC oxidation and mechanical polishing can thus be expected.

Such a high PEC oxidation rate leads us to a discovery of a novel material removal mechanism of photoelectrochemical mechanical polishing (PECMP) for finishing GaN wafers. This study proposes a PECMP method based on the synergy of PEC and mechanical effects. An apparatus is designed based on the method. The study further investigates the polishing performance of the newly designed apparatus, including the effects of V_{bia} and solution pH on MRR and damage removal, as well as surface morphology. It aims to establish a high-efficiency polishing method for obtaining the atomically flat and damage-free GaN wafers.

2. Experimentation

Fig. 1(b) is a schematic of the newly designed PECMP apparatus. During the PECMP process, a GaN wafer was fixed on the worktable and then rotated at a speed of ω_w. Meanwhile, a stainless steel polishing disc (220-mm-diameter, 15-mm-thickness) glued with an insulative polishing pad (SUBA 800) was rotated at a speed of ω_p in the same direction as the worktable. The polishing disc and polishing pad had the same honeycomb structure configured by a through-hole array. All the through-holes of a size of 11-mm in diameter were evenly distributed in the disc/pad structure. A 350 W Hg arc lamp was adopted to provide 175 mW/cm^2 UV-irradiation with a beam diameter of 50 mm right above the GaN wafer. The wafer surface was thus exposed to the UV-irradiation for the PEC oxidation and subjected to the subsequent mechanical polishing. The duty cycle between the PEC oxidation and mechanical polishing was 1:1.1, calculated from the area ratio between the through-holes and the rest of the polishing disc. The PECMP apparatus was controlled by an electrochemical workstation (CHI 660c, CH Instruments) which was also used to monitor the photocurrent and electric charge quantity (Q_c).

The free-standing single crystal GaN wafers unintentionally doped for this study were of n-type, 1-inch in diameter and 350-μm in thickness (Nanowin Sci. & Tech. Co., Ltd, Suzhou, China,). The Ga-polar (0001) plane of the GaN wafer was identified as the polishing surface in all the experiments. This plane (Fig. 1(a)) had 0.35° off the (0001) plane. The backside of the wafer was glued with a conductive copper adhesive tape and was wired to the electrochemical workstation. The PEC circuit consisted of GaN photoanode, electrolyte (polishing solution) layer within the through-holes, and polishing disc cathode.

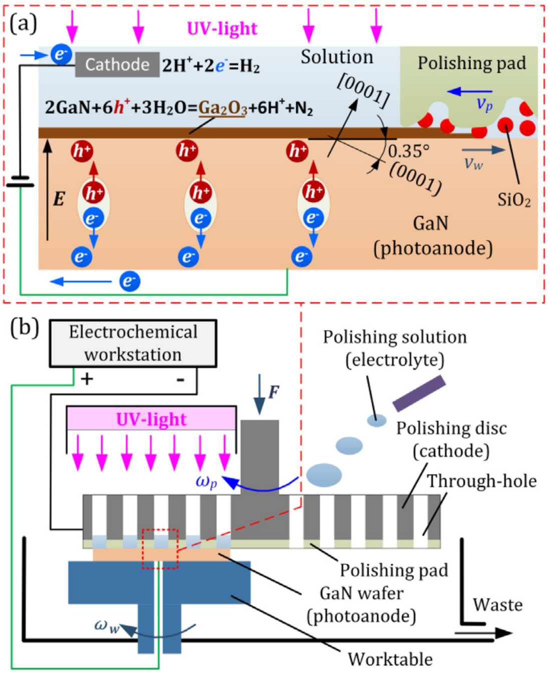

Fig. 1. (a) PEC oxidation and the subsequent mechanical polishing of the oxide layer; (b) Schematic of the PECMP apparatus.

All polishing solutions were freshly prepared with deionized water. Colloidal SiO_2 slurry was diluted into 5 wt.% SiO_2 polishing solution, including 0.1 M K_2SO_4 or 0.05 M H_2SO_4 as the supporting electrolyte. The pH of polishing solution was adjusted by KOH or H_2SO_4. The PECMP parameters are tabulated in Table 1.

Table 1
PECMP parameters.

Parameters	Conditions
Rotational speed of wafer (ω_w)	200 rpm
Rotational speed of polishing pad (ω_p)	200 rpm
Eccentricity	100 mm
The average grain size of SiO_2 abrasives	25 nm
SiO_2 abrasive concentration	5 wt.%
Feed rate of polishing solution	100 mL/min
Applied pressure (F)	6.5 psi
UV–light intensity	175 mW/cm^2

The wafer surfaces were examined using the atomic force microscopy (AFM, Asylum Research Cypher, Oxford instruments) with the taping mode. Damage in a wafer surface was characterized by the cathodoluminescence (CL, LEO 1530). MRR was calculated according to Eq. (1),

$$\mathrm{MRR} = \frac{\Delta m}{\rho \times S \times t} \times 10^7 (\mathrm{nm/h}) \quad (1)$$

The weight loss (Δm, g) was determined using an electronic balance (Sartorius QUINTIX65-1CN) with a readability accuracy of 1.0×10^{-5} g and a repeatability error of 2×10^{-5} g. Symbol ρ represents the GaN density ($\rho = 6.1$ g/cm^3), S is wafer surface area ($S = 5$ cm^2), and t is PECMP time ($t = 2700$ s).

All the experiments were repeated at least three times at room temperature (25 °C) and the relative standard deviation (RSD) was found to be less than 8%.

3. Results and discussion

3.1. PEC responses during PECMP

Under PECMP conditions listed in Table 1, the transient-state linear sweep voltammograms (LSVs) of the GaN wafers were first examined in the different pH polishing solutions. The V_{bia}, referred to E_{red} of H^+ cations at the polishing disc (cathode), was increased from −2.0 to +3.5 V at a scanning rate of 20 mV/s. Because the rotating motion caused the LSV sampling process to tremble, the LSV curves were smoothed and are shown in Fig. 2 with the original

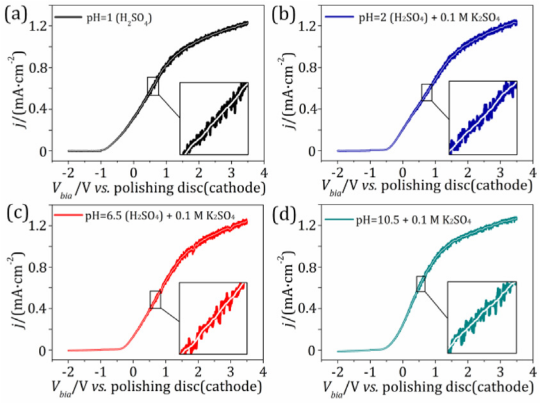

Fig. 2. The LSVs of the GaN wafers during PECMP. Polishing solution pH: (a) 1, (b) 2, (c) 6.5, and (d) 10.5. Scan rate: 20 mV/s.

curves. The photocurrent density is normalized with respect to the exposed area of the GaN wafer, calculated from the duty cycle.

Fig. 2(a) displays the LSVs in the 0.05 M H_2SO_4 polishing solution. The photocurrent started approximately from −0.90 V and then rapidly increased until it passed a turning V_{bia} around +1.0 V beyond which the LSVs show a reduced rate of increment, which is consistent with the PEC responses of the n-type semiconductors. A strengthened electric field due to the increased V_{bia} may suppress the electron-hole recombination which predominately occurs at the defect sites of the crystal and gradually diminishes as V_{bia} is high enough. The PEC responses in Fig. 2 indicate that although there existed 5 wt.% SiO_2 abrasives in the polishing solution, the UV–light intensity that the GaN wafers received was high enough to ensure the continuous PEC oxidation.

When the PECMP of the GaN wafers was carried out in either neutral (Fig. 2(c)) or alkaline (Fig. 2(d)) polishing solution, the LSVs were similar to those observed in Fig. 2(a), except that turning V_{bia} slightly shifted in a narrow range from +0.9 and +1.5 V. These observations revealed that the application of a V_{bia} higher than 1.5 V was sufficient to avoid electron-hole recombination causing the uneven GaN oxidation.

Subsequently, the steady-state photocurrent-time (j–t) responses of GaN wafers were examined using the potentiostatic method. As shown in Fig. 3(a), once the UV–light irradiated the GaN wafer through 0.05 M H_2SO_4 polishing solution layer, the photocurrent rapidly reached a maximum value and then decreased to a plateau value. After the UV–light was shut down, the photocurrent at once decreased to zero, indicating that the GaN breakdown did not occur within the tested V_{bia} range. Furthermore, as the V_{bia} was increased from 1.5 to 1.8, to 2.1, and to 2.5 V, the plateau photocurrent increased from 0.6 to 0.7, to 0.9, and to 1.1 mA/cm^2. That is, a higher V_{bia} generates a higher electric field, so that more VB holes are forced to flow towards the GaN wafer surface to cause more GaN oxidation. Under the same V_{bia}, Fig. 3(b) shows the low photocurrent generated in the alkaline polishing solution, as compared with Fig. 3(a). The plateau photocurrent obtained at 2.5 V was about 0.9 mA/cm^{2,} slightly higher than that at 2.1 V. Thus, in the next experiments, the highest V_{bia} was set at 2.5 V.

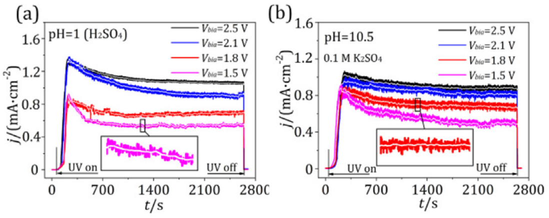

Fig. 3. The *j–t* plots of the GaN wafer at the different V_{bia} in the polishing solution with pH of (a) 1 and (b) 10.5.

Ulteriorly, different from the transient-state LSVs, the steady-state j–t curves represent that a stable oxide layer has been formed on the GaN wafer surface. From the PEC point of view, a thicker oxide layer formed on the semiconductor surface causes a lower photocurrent. These observations suggest that the oxide layer formed in the acidic environment should be thinner than that in the alkaline environment, which in turn reveals that at least in the alkaline environment, the mechanical polishing process does not completely remove the oxide layer before the polished surface is subjected to the subsequent PEC oxidation.

3.2. MRR of the potentiostatic PECMP

Fig. 4 shows MRR of a GaN wafer as a function of V_{bia} of the potentiostatic PECMP conducted in the different pH polishing solutions. The MRR obtained in all the polishing solutions is linearly proportional to V_{bia}. The largest slope of the MRR-V_{bia} plots was observed for the PECMP conducted in the 0.05 M H_2SO_4 polishing solution. Surprisingly, under a V_{bia} of 2.5 V, MRR reached 1.2 μm/h which was one order of magnitude higher than that of a conventional technique. By contrast, in the neutral and alkaline polishing solutions, the highest MRR was approximately 740 nm/h, confirming the results of Fig. 3(b). That is, a thick oxide layer formed in the alkaline environment is unfavorable for promoting MRR. Moreover, the lowest MRR of 121 nm/h was obtained in the polishing solution without the supporting electrolyte, revealing that a poor conductivity of the polishing solution seriously retarded the GaN wafer to be oxidized.

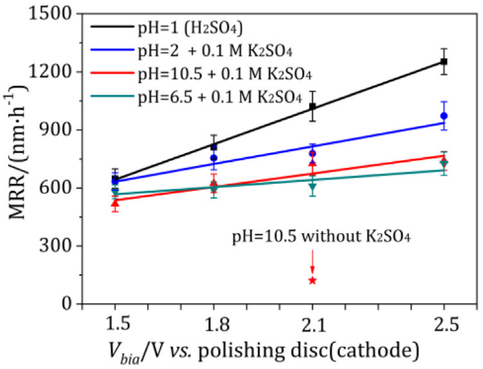

Fig. 4. The MRR of potentiostatic PECMP for the GaN wafer as a function of V_{bia} in polishing solution with different pH.

Furthermore, the electric charge quantity responsible for material removal can be calculated in Eq. (2), assuming that 1-mole GaN oxidation requires 3-mole (n = 3) holes. Polishing efficiency is calculated in Eq. (3),

$$Q_m = \frac{n \times \Delta m \times F}{M} \tag{2}$$

$$\eta = \frac{Q_m}{Q_c} \tag{3}$$

here, GaN molecule weight is $M = 83.7$ g/mol; Faraday constant is F = 96,480 C/mol. The data obtained at three different V_{bia} levels are tabulated in Table 2. Interestingly, the η of PECMP conducted in the acidic polishing solutions is larger than 100%, suggesting that the oxides should have been removed before being oxidized to Ga_2O_3. By contrast, the η obtained in the neutral and alkaline polishing solutions was less than 100%, indicating that the PEC oxidation mechanism in the neutral and alkaline environments is different from that in the acidic. A low η may be due to that the VB holes can also oxidize the H_2O molecules and/or the OH^- anions to generate the oxygen gas. More importantly, these results suggest that the monitored Q_c be used as a parameter to determine the polishing depth (Δh) via Eqs. (4) and (5),

Table 2
Polishing efficiency of potentiostatic PECMP.

Polishing solution	pH	η/%(1.8 V)	η/%(2.1 V)	η/% (2.5 V)
0.05 M H_2SO_4	1.0	118.9 ± 8.5	112.1 ± 5.9	128.6 ± 5.6
H_2SO_4 + 0.1 M K_2SO_4	2.0	130.9 ± 6.0	127.0 ± 7.8	121.5 ± 6.2
0.1 M K_2SO_4	6.5	90.1 ± 5.3	78.3 ± 5.2	83.2 ± 4.2
0.1 M K_2SO_4	10.5	99.8 ± 5.8	98.2 ± 5.9	93.5 ± 4.8

$$\Delta m = \Delta h \times S \times \rho(\mathrm{g}) \tag{4}$$

$$\Delta h = 95 \times Q_c \times \eta(\mathrm{nm}) \tag{5}$$

3.3. Surface morphology and CL analysis

AFM images (Fig. 5(a)) show that the as-received GaN wafer surface had many scratches induced in the previous diamond lapping process with the surface roughness (Ra) of 1.04 nm. After going

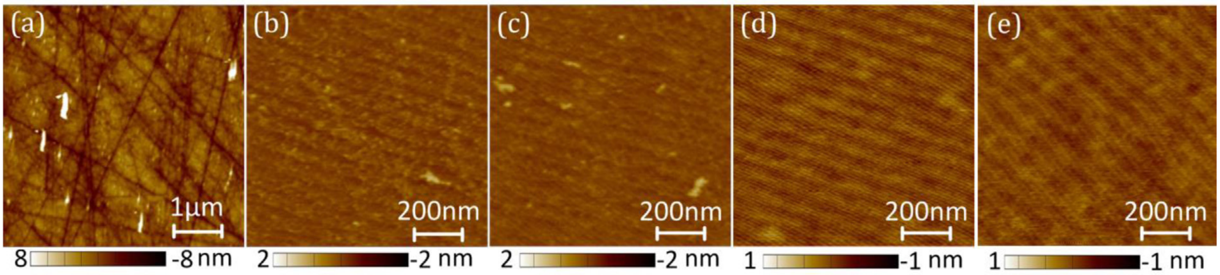

Fig. 5. GaN wafer surface morphologies. (a) as-received wafer, Ra = 1.04 nm, (b) pH = 1, Ra = 0.122 nm, (c) pH = 2, Ra = 0.100 nm, (d) pH = 6.5, Ra = 0.087 nm, (e) pH = 10.5, Ra = 0.067 nm. The potentiostatic PECMP was conducted at 2.5 V for 135 min. The polishing solutions included 0.1 M K_2SO_4, except for the 0.05 M H_2SO_4 polishing solution (pH = 1).

through PECMP at 2.5 V for 135 min, the GaN wafers were immersed in 10 wt.% HF solution to remove the remaining oxides and SiO_2 abrasives. Fig. 5(b) shows that all surface scratches were polished away, while the atomic step-terrace structures of the monocrystalline GaN film appeared. The Ra remarkably decreased to 0.122 nm. After using the same PECMP procedures to polish the wafer in the solution with a pH of 2, as shown in Fig. 5(c), the resulting surface morphology was similar to that observed in Fig. 5(b), except that the Ra further decreased to 0.100 nm.By contrast, a great improvement in the surface morphology was observed after the wafers were polished in either neutral (pH = 6.5) or alkaline (pH = 10.5) polishing solution. As shown in Figs. 5(d) and (e), the resulting surface morphologies had more complete step-terrace structures with their respective Ra 0.087 and 0.067 nm. The latter approaches the theoretical value of 0.0647 nm which is what Ga-polar (0001) plane with 0.35° off can reach for a GaN wafer surface [11]. These observations demonstrate that Ra and MRR simultaneously decrease with an increase in the polishing solution pH. Obviously, a low MRR and a thick oxide layer are favorable for obtaining a perfect wafer surface morphology, although PECMP can generate an atomically flat wafer surface in a wide pH range from 1 to 10.5.

Fig. 6(a) and (b) show the CL mapping and spectra (inset) of GaN wafer before and after PECMP was carried out at 2.5 V for 135 min in the 0.05 M H_2SO_4 polishing solution. The as-received wafer surface was bestrewn with the dark lines, due to nonradiative electron-hole recombination occurring at the scratches, SSDs and dislocations [12]. After PECMP, all dark lines (Fig. 6(b)) disappeared except for the few dark spots with a density of $\sim 8 \times 10^5/\mathrm{cm}^2$, approximating to the inherent dislocation densities ($\sim 5 \times 10^5/\mathrm{cm}^2$) of the as-received GaN wafer. Furthermore, as evidenced by the CL spectra (inset), in comparison with the as-received wafer, the finished GaN wafer gave a remarkably high CL signal, indicating a great improvement in the photoelectric performance. These results confirm that the PECMP method is able to remove all surface scratches and SSDs induced in the diamond lapping processes, resulting in a high quality GaN wafer surface.

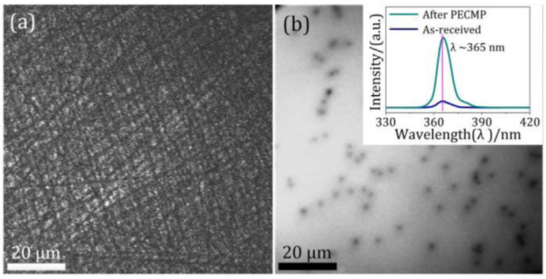

Fig. 6. The CL mapping and the CL spectra (inset) of the GaN wafer (a) as-received; (b) after the PECMP at 2.5 V for 135 min in the 0.05 M H_2SO_4 polishing solution.

4. Conclusions

This study proposes a novel PECMP method for finishing GaN wafers based on the synergistic effect of the PEC oxidation and mechanical polishing. A PECMP apparatus is designed and tested to validate the method. The following results are obtained in the study.

1) The novel PECMP method allows to achieve an MRR of 1.2 μm/h in finishing GaN wafers which is nearly one order of magnitude larger than that obtained by the conventional methods.
2) GaN wafers can be finished by the PECMP method to an atomically smooth surface of roughness Ra 0.067 nm in $1 \times 1\ \mu m^2$.
3) The PECMP method is able to completely remove SSDs that are left from the prior diamond lapping processes.
4) The PECMP method utilizes an electrochemical workstation to control polishing depth through monitoring electric charge quantity.

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