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Effect of photocatalytic oxidation technology on GaN CMP

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ABSTRACT

GaN is so hard and so chemically inert that it is difficult to obtain a high material removal rate (MRR) in the chemical mechanical polishing (CMP) process. This paper discusses the application of photocatalytic oxidation technology in GaN planarization. Three N-type semiconductor particles (TiO_2, SnO_2, and Fe_2O_3) are used as catalysts and added to the H_2O_2–SiO_2-based slurry. By optical excitation, highly reactive photoinduced holes are produced on the surface of the particles, which can oxidize OH^- and H_2O absorbed on the surface of the catalysts; therefore, more OH^* will be generated. As a result, GaN MRRs in an H_2O_2–SiO_2-based polishing system combined with catalysts are improved significantly, especially when using TiO_2, the MRR of which is 122 nm/h. The X-ray photoelectron spectroscopy (XPS) analysis shows the variation trend of chemical composition on the GaN surface after polishing, revealing the planarization process. Besides, the effect of pH on photocatalytic oxidation combined with TiO_2 is analyzed deeply. Furthermore, the physical model of GaN CMP combined with photocatalytic oxidation technology is proposed to describe the removal mechanism of GaN.

1. Introduction

Gallium nitride (GaN), composed of the III-group element Ga and V-group element N, is the third generation of semiconductor material, following the first-generation Ge and Si, and the second-generation GaAs and InP [1–6]. It is widely used in optoelectronics, high-temperature and high-power devices, and high-frequency microwave devices, because of its wide direct band gap, strong atomic bond, high thermal conductivity, good chemical stability, and strong anti-irradiation ability [7–12].

GaN is a hard material with a high melting point, 1700 °C. At atmospheric pressure, the structure of GaN crystal is six wurtzite. The material growth is carried out as (1) by metal-organic chemical vapor deposition (MOCVD) [13,14].

$$Ga(CH_3)_3 + NH_3 \rightarrow GaN + 3CH_4 \quad (1)$$

Light-emitting diodes (LEDs), working as the fourth-generation light source, have the advantages of safety, energy efficiency, environmental protection, and longer life. The recombination of electrons and holes in the LED's PN junction produces fluorescence of spontaneous emission, which is the luminous principle. The lattice dislocation between GaN film and the substrate material causes biaxial compressive strain in GaN thin films, which easily results in various defects such as holes and stress, thereby reducing the device's luminous efficiency. As a homogeneous substrate material, GaN greatly reduces the defect density and becomes the optimal substrate material. The processing technology of the substrate surface is one of the important factors that determine the device quality; thus, an atomically smooth surface of the GaN substrate is needed for epitaxial layer growth of GaN-based LEDs [15,16].

Chemical mechanical polishing (CMP) is practically the only surface fine-machining technology that can realize global planarization. Because GaN is a hard and chemically inert material, the material removal rate (MRR) of GaN in a CMP process is much lower than that of sapphire and silicon carbide (SiC) [17–24]. Therefore, improving the MRR of GaN to realize efficient removal is a difficult problem to be solved.

Photocatalytic oxidation technology uses an N-type semiconductor particle as the catalyst in the oxidation process. By optical excitation, the electrons (e^-) in the valence band of the catalyst are excited into the conduction band, as a result, highly reactive electron-hole pairs will be produced on the surface of the particles [25–31]. The highly reactive photoinduced holes have a strong oxidation ability, and therefore can oxidize OH^- and H_2O that are absorbed on the surface of the semiconductor particles, the radical OH^* is then generated. Up to now, photocatalytic oxidation technology with N-type semiconductor particles has not been used in GaN CMP process, considering the strong oxidability advantage of this method, it was adopted in this study.

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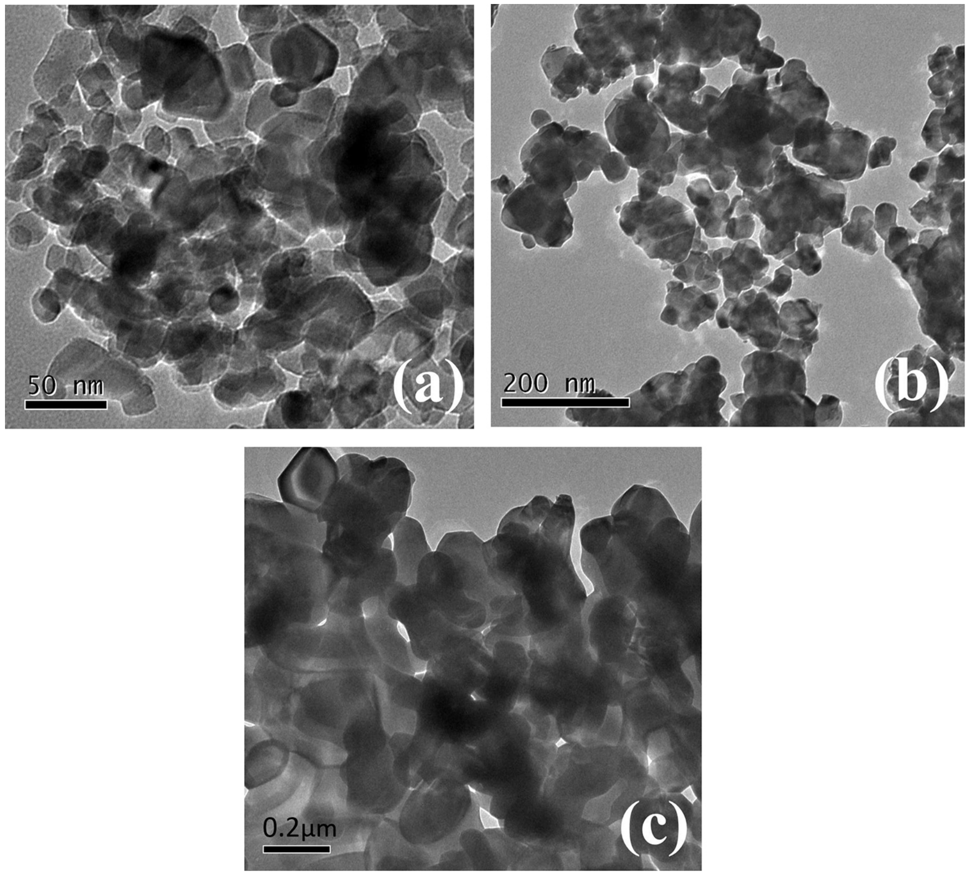

Fig. 1. TEM images of catalysts: (a) TiO_2 particles, (b) SnO_2 particles, and (c) Fe_2O_3 particles.

2. Experiment

N-type GaN (0 0 0 1) templates, deposited on 2-inch-diameter sapphire, were used to perform CMP experiments. The film thickness was 30 μm. In order to perform X-ray photoelectron spectroscopy (XPS) characterization, square GaN templates were used in this work, the dimensions of which were 1 cm × 1 cm. H_2O_2–SiO_2-based slurries (pH 9) were prepared for GaN CMP experiments on a CETR CP4 machine, the secondary particle size of SiO_2 in which is 92.9 nm. Three kinds of N-type semiconductor particles (TiO_2, SnO_2, and Fe_2O_3) were added as catalysts to the slurries. Before CMP experiment, Zetasizer Nano ZS was used to test the particle size distribution of SiO_2 and N-type semiconductor particles. After the wafer was cleaned ultrasonically for 10 min and blow-dried with pure N_2, the material removal rate (MRR) of GaN was calculated by weight loss using (2), which is the average of at least three polishing runs for 15 min each. Sartorius ME36S was used to test the weight loss after CMP experiments, the measurement accuracy of which is 0.001 mg, thus the measurement accuracy of the material removal rate by the weight loss calculation is 0.321 nm/h. Phase Shift MicroXAM-3D was used to observe the surface morphology of GaN after polishing, so as to test the polishing effect. In addition, other detailed conditions of the GaN CMP process are summarized in Table 1.

$$\mathrm{MRR} = \frac{\Delta m}{\rho \times s \times t} = \frac{10^7 \times 4 \times \Delta m}{6.15 \times 2.54^2 \times \pi} \tag{2}$$

Here, Δm/g is the weight loss after CMP process, ρ/(g cm^{-3}) is the density of GaN wafer, s/cm^2 is the area of the wafer, t/h is the polishing time of each run, and MRR/(nm/h) is the corresponding removal rate of GaN.

Table 1
GaN CMP process conditions.

Name	Unit	Quantity
Platen rotation speed	r/min	160
Carrier rotation speed	r/min	120
Applied pressure	kg/cm^2	0.28
Diameter of platen	mm	250
Polishing pad type		Non-woven fabric type
Abrasive particle		Silica
Particle concentration	%	4
Oxidant concentration	%	3
Catalyst concentration	%	1
Feed rate of the slurry	ml/min	150
Polishing time	min	15

3. Results and discussion

3.1. Structure and morphology of catalysts

Degussa AEROXIDE TiO_2 P25, adopted in this work, is a kind of mixed crystal, in which the weight ratio between anatase (A type) and rutile (R type) is approximately 80/20. Because the mixture of two structures increases the defect density and carrier concentration of TiO_2, the number of electrons and holes increases, which allows it to capture the solution component on its surface more easily.

SnO_2 is a yellowish powder, with a tetragonal rutile structure. Fe_2O_3 is a rufous powder, which has an α-type crystal structure. Because the nanoparticle sizes are too small for other types of imaging, the morphology of TiO_2, SnO_2, and Fe_2O_3 are observed by transmission electron microscope (TEM) as shown in Fig. 1.