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Temperature-dependent modification of gallium nitride using vacuum hydrogen plasma

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Abstract

Gallium nitride (GaN) is considered to be one of the most promising materials for applications such as light-emitting diodes, and high-power, high-frequency electronic devices, owing to its excellent mechanical and electrical properties. However, machining GaN poses challenges due to its high hardness and chemical inertness. To achieve high-efficiency and damage-free finishing of GaN, plasma-assisted polishing (PAP), which combines surface modification by hydrogen plasma irradiation and removal of the modified layer using soft abrasives, was proposed. In the PAP process, the modification rate was the crucial limiting factor for the polishing rate. Since substrate temperature significantly influenced the modification process. In this study, the correlation between temperature and modification characteristics of GaN was explored.

Gallium nitride, hydrogen plasma, temperature, modification characteristic

1. Introduction

Due to its superior properties, such as wide bandgap, high thermal conductivity, and high electron mobility, Gallium nitride (GaN) has become increasingly pivotal in the fabrication of high-frequency and high-power electronic devices. To fully harness these excellent characteristics of GaN, a damage-free atomically smooth GaN surface is required. However, GaN is a difficult-to-machine material with high hardness and chemical inertness. For the final finishing of GaN, the commonly used process is chemical mechanical polishing (CMP), using a suspension containing chemicals, such as alkali, known as slurry, along with abrasives [1]. However, when applying the CMP process, which can achieve a high polishing rates for Si substrates, to GaN substrates, the polishing rate was extremely low, typically at 77 nm / h or less. This low polishing rate necessitates a significant improvement. Furthermore, the processing cost and environmental load when purchasing and disposing of the slurry are also large. Additionally, the epitaxial growth GaN film often contains numerous dislocations, leading to the formation of a large number of etch pits on the GaN surface due to the alkaline component in the slurry [2].

For the flattening of some difficult-to-machine materials such as GaN, SiC, and diamond, a dry polishing process named plasma-assisted polishing (PAP), which combines surface modification by plasma irradiation, and removal of modified layer conducted by applying ultra-low polishing pressure or polishing using soft abrasive, was proposed by our research group [3]. In our previous research, it has been demonstrated that PAP, using atmospheric CF_4 plasma, can achieve atomically smooth GaN surfaces with a well-ordered step-terrace structure [4]. However, a primary limitation of PAP, especially when applied to GaN, is its slow modification rate, posing an efficiency challenge in GaN semiconductor manufacturing. To overcome this limitation, the use of vacuum hydrogen plasma to replace atmospheric CF_4 plasma in PAP for GaN was proposed. In the reaction between GaN and hydrogen plasma, the reaction rate of nitrogen (N) with hydrogen (H) radicals, forming NH_3, was faster than that of gallium (Ga) in GaN, leaving Ga on the GaN surface. This selective interaction was crucial for the plasma-assisted modification process. Hydrogen has shown potential for faster reaction rates of GaN compared to traditional reactive gases like CF_4. Nevertheless, even with the adoption of hydrogen plasma, the quest for optimizing the modification speed continues. According to the Arrhenius equation:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

(k is the rate constant; T is the absolute temperature)

It gives the dependence of the rate constant of a chemical reaction on the absolute temperature. So it is concluded that temperature could play a critical role in further enhancing the reaction rate of hydrogen plasma. In this study, plasma modification experiments were conducted under different temperature conditions to explore the relationship between temperature and the modification characteristics of GaN in hydrogen plasma.

2. Experimental setup

Figure 1 shows the experimental setup for plasma modification used in this study. A GaN substrate was fixed on the lower stage, which can be heated up to 500°C. A mixture of Ar and H_2 was supplied from the side of the vacuum chamber, maintaining a constant of 40 torr by controlling the pumping rate with a dry pump. Besides, to control the hydrogen concentration below 4% (burst point), the gas flow rates (Ar: 200 sccm, H_2: 5 sccm) were controlled by mass flow controllers (MFCs). By applying radio frequency (RF) (f=13.56 MHz) power on the upper electrode, plasma was generated in the area between the upper electrode and GaN substrate.

Figure 2 shows the optical emission spectroscopy (OES) spectrum of the Ar-based hydrogen plasma generated during the plasma irradiation. Optical emission from H (656.9 nm) was confirmed from the spectrum.

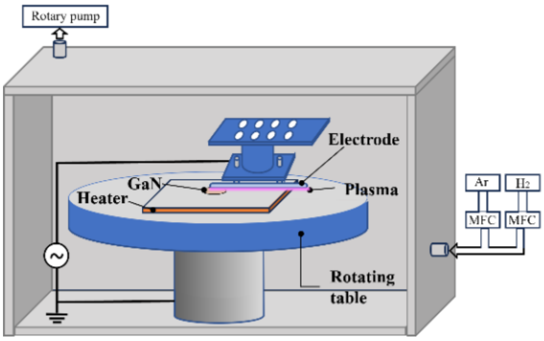

Figure 1. Schematic of the experimental setup.

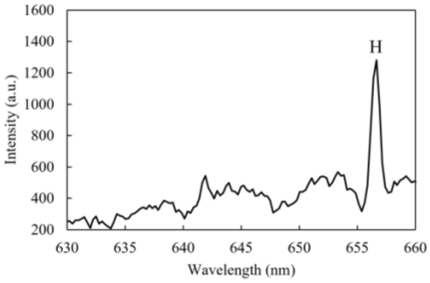

Figure 2. OES spectrum of the Ar-based vacuum hydrogen plasma.

3. Results and discussion

To investigate the impact of substrate temperature on the plasma modification characteristics of GaN in vacuum hydrogen plasma, plasma irradiation experiments were conducted for 30 mins under room temperature, 100°C and 500°C through substrate heating. Before plasma irradiation, GaN substrates were cleaned using SPM & HF solutions. The surface composition change of GaN substrate was analysed by X-ray photoelectron spectroscopy (XPS) before and after hydrogen plasma irradiation. As shown in Fig.3(a), only Ga-N peak was observed in the Ga2p spectrum of the GaN surface before plasma irradiation. After 30 mins of plasma irradiation at room temperature (without heating), a weak peak corresponding to Ga-Ga was observed, as shown in Fig. 3(b). This result suggested that the modification rate at room temperature was very low due to the low density of H radical. Fig. 3(c) shows the Ga2p spectrum of GaN surface after plasma irradiation at 100°C. According to the Arrhenius equation, the modification reaction rate can be increased by raising the temperature, a stronger Ga-Ga peak was observed. However, when the sample temperature was increased to 500°C, the peak of Ga-Ga did not continue to rise; instead, it disappeared. This implies that at 500°C, the modification rate did not follow the equation's increase but rather decreased.

Moreover, the surface morphology changes of GaN substrates before and after plasma irradiation was also measured using scanning electron microscope (SEM). As shown in Fig.4(a) and 4(b), after hydrogen plasma irradiation at 100°C, the surface morphology did not change significantly, while a Ga modification layer was formed. However, as shown in Fig.4(c), after plasma modification at 500 °C, there was a substantial change in the surface morphology, particularly with the observation of numerous hexagonal etching pits. Combining the results from XPS, it can be inferred that in a hydrogen plasma, below a certain temperature, the modification rate on the surface of GaN fellow the Arrhenius equation, where the modification rate increased with the rise in temperature. However, at excessively high temperature (500°C), intense surface thermal motion made it difficult for H radicals to adsorb onto the GaN surface and enhanced desorption from the surface. This led to a decrease rather than an increase in the modification rate. Additionally, the reduction in the adsorption of H radicals caused the preferential reaction of defect sites on the GaN surface, believed to be the reason for the formation of etching pits.

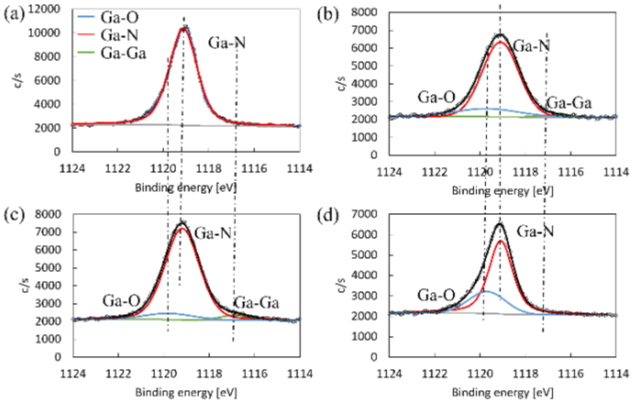

Figure 3. Ga2p XPS spectrum of the GaN surface (a) before plasma irradiation (b) after plasma irradiation under room temperature (c) after plasma irradiation under 100℃ (d) after plasma irradiation under 500℃.

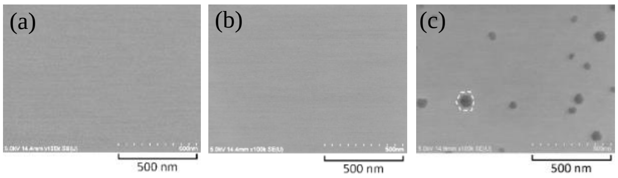

Figure 4. SEM image of GaN surface (a) before plasma irradiation (b) after plasma irradiation under 100℃ (c) after plasma irradiation under 500℃.

4. Conclusions

In this study, the correlation between temperature and modification characteristics of GaN was explored. Within a certain temperature range, raising the substrate temperature can effectively increase the modification rate. However, at excessively high temperature, particularly at 500°C, the modification rate decreased and led to the formation of etching pits on the surface. This result indicated that by optimizing the modification temperature, a high modification rate could be achieved while ensuring surface quality without the formation of etching pits.

Acknowledgements

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