



Metal-assisted photochemical etching of gallium nitride using electrodeposited noble metal nanoparticles as catalysts



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ABSTRACT

Porous gallium nitride (PGaN) layers were fabricated by metal-assisted photochemical etching (MaPCE) using electrodeposited platinum nanoparticles (PtNPs) or gold nanoparticles (AuNPs) as catalysts. After identification of a suitable negative potential and appropriate cyclic voltammetry (CV) conditions, high-density PtNPs or AuNPs were deposited onto a planar GaN substrate. Based on the concrete numerical values of energy levels, the generation, transfer and consumption of electrons and holes, and the assumption that localized galvanic cells are formed, an etching mechanism was proposed which may provide theoretical guidance for future work on etching of GaN and other semiconductor materials.

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1. Introduction

Porous gallium nitride (PGaN) layers are significant building blocks in light-emitting diodes, surface-enhanced Raman scattering, high sensitivity gas and biochemical sensors, and also provide a suitable substrate for epitaxial growth of III-nitride devices with a low dislocation density [1–5]. Considering the available etching techniques, the plasma-based dry etching technique tends to induce surface damage and lacks selectivity towards morphology, dopant and composition [6]. Photoelectrochemical etching (PECE) has been recognized as one of the most efficient methods, due to the synergetic effect of ultraviolet light and electric field [7–9]. However, the requirement of electrical contact with GaN samples makes this technique unsuitable for large-scale production [10]. By contrast, metal-assisted photochemical etching (MaPCE), an electroless etching technique, may be considered to be a simple and promising alternative to PECE [11–15].

Metal catalysts play a similar role to the platinum electrode in PECE and are an indispensable part of MaPCE. Up to now almost all metal catalysts have been sputter-coated onto GaN substrates as continuous films or through a metal mask with patterns composed of holes of different diameters [16–19]. However, the sputter-coating method requires a special vacuum sputtering system and a custom-built metal mask, and is relatively complex and costly due to the waste of noble metal in the sputtering process. Moreover, although MaPCE has been well studied and used to produce porous silicon layers or silicon

nanowire arrays, its application to GaN is still in the early stages of development [13]. To the best of our knowledge, the role of metal catalysts in the MaPCE process is still unclear, and the detailed etching mechanism is not well understood.

In this work, highly porous GaN layers were prepared by MaPCE through the electrodeposition of high-density platinum nanoparticles (PtNPs) or gold nanoparticles (AuNPs) as metal catalysts. In the light of the concrete numerical values of energy levels, the generation, transfer and consumption of electrons and holes, and the assumption that localized galvanic cells are formed, we propose a detailed reaction mechanism for MaPCE, which can give theoretical guidance for further work on the etching of GaN and other semiconductor materials.

2. Experimental

Single-crystal n-type GaN(0001) films were grown on sapphire(0001) substrates by hydride vapor phase epitaxy (HVPE). The Si-doped GaN layer was 5 μm thick with a carrier concentration of $4.8 \times 10^{18} \text{ cm}^{-3}$. The size of the GaN chips was $1.3 \times 0.3 \text{ cm}$. The GaN chips were cleaned successively with acetone, ethanol and deionized (DI) water, then dipped in aqua regia for 30 min to remove surface contamination. They were then rinsed in DI water and dried with N₂. Schematic diagrams showing the electrodeposition of the metal nanoparticles (MeNPs) and the MaPCE device are given in Fig. 1. The experimental set up used for electrodeposition of the MeNPs is described below. The front side of the GaN chip with an indium point ohmic contact, a platinum wire and Ag/AgCl were used as the working, counter and reference electrodes, respectively. Two cycles of cyclic voltammetry (CV) were carried out over a voltage range from 0.5 to –1.5 V (scan

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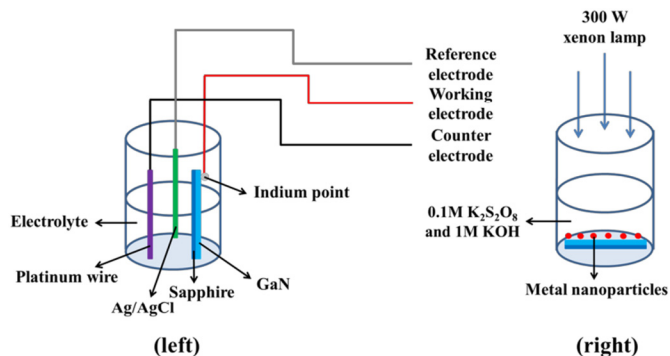


Fig. 1. Schematic diagrams of the equipment used to electrodeposit MeNPs (left) and MaPCE device (right).

rate: 50 mV/s). The electrolyte used to produce the PtNPs consisted of 1 mM H₂PtCl₆ and 0.5 M NaCl, while that used for the AuNPs comprised 1 mM HAuCl₄ and 0.5 M NaCl. The MaPCE process was initiated by immersing the GaN samples into etchants containing 0.1 M K₂S₂O₈ and 1 M KOH for 30 min under 300 W xenon lamp front-side illumination. The surface morphology of the etched GaN samples was characterized by scanning electron microscopy (SEM, Hitachi S-4800).

3. Results and discussion

Fig. 2a shows the surface morphology of bare planar GaN. The surface stripes are crystal steps, which were formed during the single-crystal growth process. Fig. 2b and e show the high-density PtNPs and AuNPs electrodeposited onto the GaN substrate. The particle densities of the PtNPs and AuNPs are 2.5×10^{10} and 2.7×10^{10} per square centimeter, respectively. Histograms showing the particle diameter distribution for the PtNPs and AuNPs are given in Fig. 2c and f. The particle diameter ranges of the PtNPs and the AuNPs are 13–52 and 8–50 nm, respectively. The average particle diameters of the PtNPs and the AuNPs are 24.9 and 26.2 nm, respectively. Cyclic voltammograms for the deposition of the PtNPs and AuNPs are shown in Fig. 2d. Considering the difficulty of preparing highly uniform small metal nanoparticles using an electrodeposition technique compared to a solution-based chemical synthesis method, the formation of high-density PtNPs and AuNPs by

CV in this work can be attributed to two factors. Firstly, instantaneous nucleation of metal particles was observed on the GaN electrode at a low potential [20]. Crystal growth mechanisms suggest that instantaneous nucleation is beneficial to the formation of small particles, so -1.5 V was selected as the negative potential for CV. Secondly, the generation of hydrogen bubbles at the interface of GaN and the electrolyte below -1.2 V efficiently inhibits the aggregation and growth of PtNPs and AuNPs.

Fig. 3a and b show the surface morphology of PGaN fabricated by PtaPCE. The whole etched surface presents a columnar structure, the upper part appearing like round islands, and the lower part showing a highly porous structure. The pore density of the porous structure is up to 8.0×10^8 per square centimeter. The cross-sectional image (Fig. 3c) demonstrates that the surface pores are representative of the underlying porous structure, and the etching rate is 28 nm/min. The pore diameter is between 40 and 180 nm (Fig. 3d). For comparison, the surface morphology of PGaN obtained by AuaPCE is shown in Fig. 3e and f. The entire etched surface presents a gully structure (Fig. 3e), and the edges of the pores are sharper than those of PGaN prepared by PtaPCE (Fig. 3f). The pore density is 4.3×10^8 per square centimeter. The etching rate is 26 nm/min, as shown in Fig. 3g, and the pore diameter is 40–250 nm (Fig. 3h).

Based on the specific numerical values of the energy levels, the generation, transfer and consumption of electrons and holes, and the assumption that localized galvanic cells are formed [21], we propose a detailed etching mechanism as follows, taking Pt as an example. Fig. 4a represents the energy level positions before the contact of GaN and Pt. The Fermi energy level of GaN (E_{F-nGaN}), which is located just below E_{c-nGaN} (-3.28 eV) due to the highly Si-doped characteristic, is higher than the Fermi energy level of Pt, E_{F-Pt} (-5.65 eV). Fig. 4b exhibits the change in energy level positions after contact between GaN and Pt in the dark; the Fermi levels of GaN and Pt become equal at the thermal equilibrium state. Under ultraviolet (UV) light irradiation, Fig. 4c shows that the valence electrons of GaN are excited from the valence band to the conduction band. As the photo-generated carriers continually increase, the generated built-in electric field makes the depletion layer become much thinner. Compared to the dark state, the position of the Fermi level moves upwards, the new pseudo-Fermi level encouraging electrons to transfer from GaN to Pt due to the decrease in the electron transfer barrier. In addition to the thermodynamic driving force, the kinetics of the etching process also increase due to the thinner

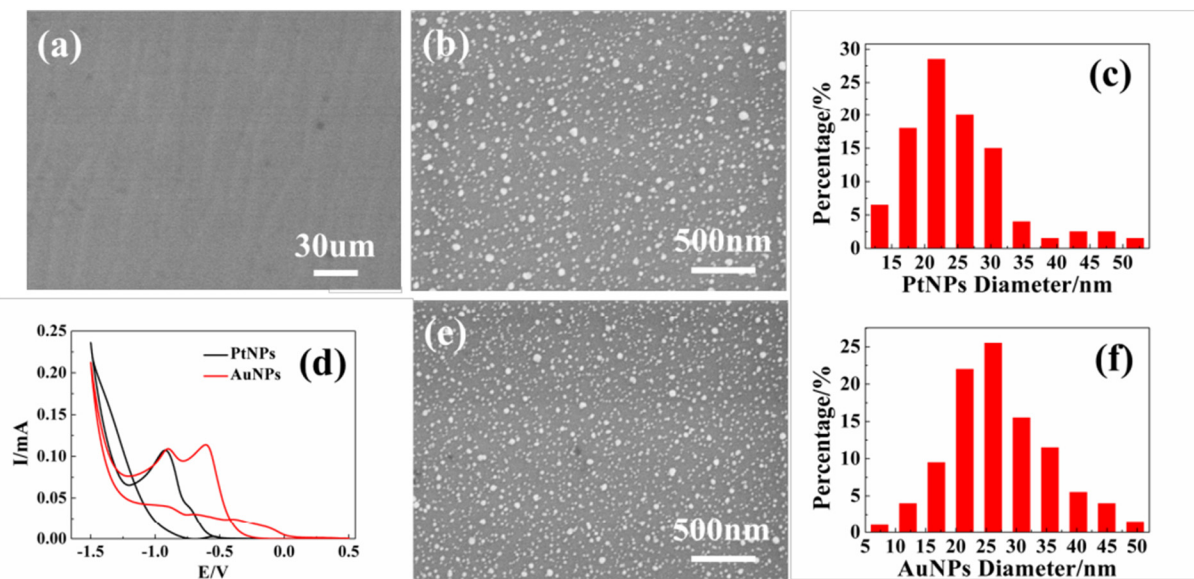


Fig. 2. SEM images of (a) bare planar GaN, (b) PtNPs and (e) AuNPs. (d) Cyclic voltammograms for the deposition of PtNPs and AuNPs. Particle diameter distribution histograms of (c) PtNPs and (f) AuNPs.

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