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Full Length Article

Nanostructured N-polar GaN surfaces and their wetting behaviors

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ABSTRACT

We report here the wetting behaviors of nanostructured N-polar GaN wafers. The nanostructured GaN samples were obtained by wet photochemical etching under UV illumination. It is confirmed that the wetting behavior of the nanostructured N-polar GaN surfaces follows the Wenzel model. Both surface roughening and decoration with Au nanoparticles will reduce the contact angle (CA), while modification with lauric acid will increase hydrophobility with CAs that change from 42.1° to 129.5°. Besides, the nanostructured surface shows high contact angle hysteresis due to strong static friction that can reach ~15 mJ/m^2.

1. Introduction

Gallium nitride (GaN) is a direct and wide band gap ($E_g = 3.4$ eV) semiconductor with extensive applications in optoelectronic, high-power and high-frequency devices. Recently, chemical sensors and biosensors based on GaN have attracted great attention [1,2] due to the newly discovered superior biocompatibility [3,4] and the feasibility of covalent functionalization with biomolecular recognition elements [5,6]. As a result, tuning of GaN surface properties, including the wetting behaviors, received some attention due to their potentials for efficient regulation of cell growth [7] and *in vivo* detection of biomolecules. Wurtzite GaN is a typical polar material with two polar surfaces, N-polar face and Ga-polar face, which exhibit distinct chemical properties [8,9]. For example, N-polar GaN sensors exhibit greater responsivities to dilute concentrations of hydrogen [10], water and acetone [11] than Ga-polar devices, while Ga-polar GaN is more suitable for oxygen detection due to the formation of Ga—O bonds [12]. Although the wetting behaviors of Ga-polar GaN have been studied [13,14], similar investigation on N-polar GaN is absent. Moreover, the carbon face of silicon carbide exhibits a water contact angle (CA) greater than that of the silicon face [15] due to polarity induced interaction with polar liquid. As a result, it is necessary to study the wetting behaviors of N-polar GaN due to its potential application as sensor for polar molecules and fluid-controllable devices. In this article, the wetting behavior of nanostructured N-polar GaN was explored. The effects of Au nanoparticles (NPs) and surface modification with lauric acid ($C_{12}H_{24}O_2$) were also studied.

2. Experimental

The *epi*-ready N-polar GaN samples of n-type were purchased from Nanowin, China, with a background carrier concentration of ~10^{17}/cm^3 and a dislocation density of ~10^6/cm^2. The samples were grown by Metal Organic Chemical Vapor Deposition (MOCVD) and were obtained after separated from sapphire substrates by laser lift-off. The size is 5 mm × 5 mm, with a thickness of 0.5 mm. After supersonically washed with acetone, ethanol and deionized water in sequence, each for 15 min the samples were immersed into the etchant that consists of 0.5 M KOH and 0.1 M $K_2S_2O_8$ for 50 min under UV illumination by a 400 W mercury lamp with a power density of 6 mW/cm^2. Au NPs were prepared on the etched samples as a secondary structure by a sputtering post annealing process. The sputtering process was accomplished in an ETD 2000 sputter coating system at ~6 mA for 10 s, 30 s and 50 s, respectively. After that, the samples were annealed at 300 °C for 1 h. The samples were modified by dip coating in 0.01 M lauric ($C_{12}H_{24}O_2$) ethanol solution for 30 min and dried at 60 °C for 8 h. For convenience, the samples before and after etching are named N-blank, N-etched, and the samples coated with Au NPs for 10 s, 30 s and 50 s are named N-Au-I, N-Au-II and N-Au-III, respectively. A blank sample coated with Au NPs for 50 s is called N-blank-Au. In order to ensure the reproducibility of our experiments, each experiment was repeated at least 3 times on 3 identical samples, which show a CA difference less than 5°.

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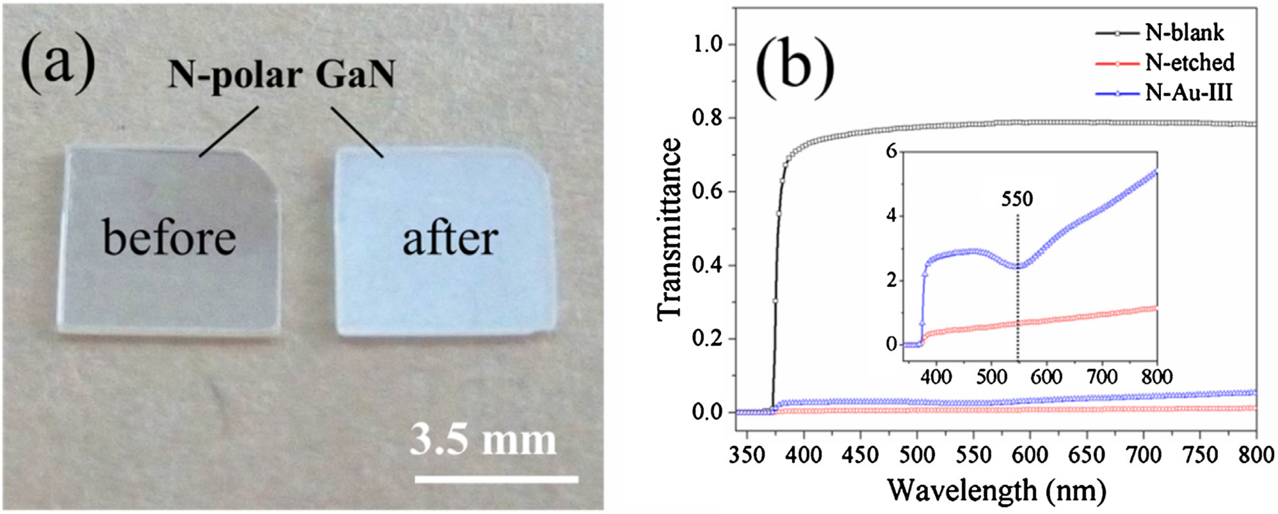

Fig. 1. Optical properties of nanostructured N-polar GaN. (a) Optical images of N-polar GaN before and after wet photochemical etching; (b) the optical transmittance of N-blank, N-etched and N-Au-III. The inset is an enlarged view for N-etched and N-Au-III.

The morphologies of the nanostructured N-polar GaN were examined using a scanning electron microscope (SEM, Hitachi S-4800, Japan). The CAs of sessile water drop (2.5 μL) and the contact angle hysteresis (CAHs) were measured on a CA meter (JY-PHb, China) at ambient temperature. Finally, the CA of a sample is obtained by averaging the values obtained in 5 measurements. The transmission spectra were measured using a spectrophotometer (UV1901PC, China). The roughness of samples were obtained by atomic force microscopy (AFM, Veeco Dimension Icon, USA).

3. Results and discussion

Fig. 1a shows the optical image of N-polar GaN before and after etching. The etching process turns the GaN from transparent to white due to enhanced backward scattering. As shown in Fig. 1b, the etching process greatly reduces the transmittance of N-etched and N-Au-III, in contrast with N-blank characterized by a sharp increase of transmittance for wavelength greater than 365 nm. Note that there is a transmittance minimum at 550 nm for N-Au-III due to excitation of the localized surface plasmon resonances (LSPRs) of Au NPS.

Fig. 2a reveals that photochemical etching results in formation of conical nanostructures with an average cone size of ~600 nm and a density of ~$5.5 \times 10^8/\text{cm}^2$. A magnified image in Fig. 2b shows the smooth conical side wall which is different from the pyramid nanostructures formed in KOH etchant [16]. Fig. 2c shows that Au NPs with average size of ~30 nm were formed after the sputtering post annealing process, resulted from a combination of coalescence and Ostwald ripening [17,18]. Fig. 2d shows a schematic representation for the photochemical etching process [19]. UV illumination excites the valence band electrons to the conduction band to form electron-hole pairs. The holes are highly active and oxidize GaN to form Ga_2O_3 soluble in a basic solution, while the electrons in the conduction band are consumed either directly by $S_2O_8{}^{2-}$ or by radicals ($SO_4{-}^{\bullet}$ and $OH^{\bullet}$) formation after photolysis of $S_2O_8{}^{2-}$. The shape of the conical nanostructures is determined by the ratio of three dissolution rates [20], (1) the etch rate v_n normal to the surface in flat areas free from a hillock, (2) the lateral etch rate v_t parallel to the surface, and (3) the rate v_p that describes the dissolution (or polishing) of the hillock. Both v_n and v_p are determined by temperatures and surface energies of crystallographic planes while v_p is also a function of the composition of the etchant. When $v_{p<} < v_n$, the slope of a hillock is given by v_n/v_t and a pyramid is formed. However, when v_p is large, a conical structure with a slope given by $(v_n - v_p)/v_t$ will be formed.

As the radium of the water drop is much less than the capillary length (cl), which has been determined to be 2.7 mm for water by $\text{cl} = (\gamma_{lv}/\rho g)^{1/2}$, with γ_{lv} being the liquid surface tension and ρ the density, the effect of gravity is negligible [21]. Fig. 3a and d shows the CAs for N-blank before (~68.3°) and after (~95.2°) modification with lauric acid, respectively. The intrinsic CA is smaller than the CA (~83.7°) measured on epitaxial GaN film [22] possibly due to different surface roughness and strong affinity of hydrogen with N-polar surfaces [23]. Modification with lauric acid results in a hydrophobic transition. After preparation of Au NPs, the CAs before and after laruic acid modification are ~62.7° and ~98.8°, respectively. The CA values measured in the case of etched GaN before and after surface modification are of ~53.5° and ~110.4°, respectively. The samples coated with Au NPs exhibit CAs of ~42.1° and ~129.5° before and after surface modification, respectively. The increased CA of N-Au-III results from a combined effect of the conical structures and the Au NPs.

Fig. 4 shows the CAHs of the samples before and after modification with lauric acid. The water droplets adhere to the substrate tightly without slipping when the substrate is vertically placed. The largest difference between the advancing CA and the receding CA can reach 50.0° for the sample coated with Au NPs for 50 s (Fig. 4f). The CAH reflects the surface adhesion. A surface with high CA and CAH is often observed on biological surfaces in nature, such as the Chinese Kaffir lily, red rose and sunflower [24,25]. This kind of surface is suitable to serve as "mechanical hand" in fluid-controllable devices for lossless liquid transfer [26].

The theories commonly used for the wetting behavior of a liquid droplet on a solid substrate are the Wenzel and Cassie models. The Wenzel model [27] assumes that the liquid completely fills the grooves of a rough surface where they contact. The relationship between the apparent CA θ^* and the intrinsic CA θ can be described by $\cos(\theta^*) = \beta \cdot \cos(\theta) = \beta \cdot (\gamma_{sv} - \gamma_{ls})/\gamma_{lv}$, where β is the roughness ratio, γ_{sv}, γ_{ls} and γ_{lv} are the solid–gas, liquid–solid and liquid–gas surface tensions, respectively. As $\beta > 1$, the hydrophilicity or hydrophobicity of a surface that follows the Wenzel model will be amplified. In contrast, a surface that follows the Cassie model [28] will have vapor pockets trapped underneath the liquid. Unlike the Wenzel case, even if the intrinsic CA is <90°, the apparent CA can still be enlarged due to trapped vapor pockets. Notably, the adhesion behaviors for surfaces that follow the Wenzel and