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Investigation of etch characteristics of non-polar GaN by wet chemical etching

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ABSTRACT

We characterized the surface defects in a-plane GaN, grown onto r-plane sapphire using a defect-selective etching (DSE) method. The surface morphology of etching pits in a-plane GaN was investigated by using different combination ratios of H_3PO_4 and H_2SO_4 etching media. Different local etching rates between smooth and defect-related surfaces caused variation of the etch pits made by a 1:3 ratio of H_3PO_4/H_2SO_4 etching solution. Analysis results of surface morphology and composition after etching by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) demonstrated that wet chemical etching conditions could show the differences in surface morphology and chemical bonding on the a-plane GaN surface. The etch pits density (EPD) was determined as $3.1 \times 10^8\,cm^{-2}$ by atom force microscopy (AFM).

1. Introduction

Group III-nitride-based materials have many applications in optoelectronic devices [1]. The wurtzite structured nitride material has strong piezoelectric and spontaneous polarization along the *c*-axis, resulting in a clear quantum-confined Stark effect. The non-polar (*a*-/*m*-axis) nitrides have a crystal structure with the *c*-axis lying parallel to the quantum well, and this have attracted considerable interest during the past few years, for their absence of any polarization field [2]. However, non-polar gallium nitride contains high density of threading dislocations (TD) (between 10^9 and $10^{10}\,cm^{-2}$) and stacking faults (SF) ($10^5\,cm^{-1}$) owing to the planar anisotropic nature of its crystal growth. Dislocations limit the lifetimes and performances of nitride-based devices [3].

Therefore, DSE plays an important role in the characterization of crystalline gallium nitride materials. The commonest DSE technique for surface defect investigations is wet chemical etching. Hot phosphoric acid (H_3PO_4), mixed in a H_3PO_4/H_2SO_4 solution, molten potassium hydroxide (KOH), and photo-electrochemical etching (PEC) have been shown to etch pits at defect sites on the GaN c-plane [4]. This method shows promise, because data acquisition is a fast, simple process, and uses inexpensive equipment. Recently, research groups reported the other applications for the DSE technique, such as reducing film dislocations [5] and enhancing the performance of light emitting diodes (LED) [6–8]. There are many reports investigating defects in c-plane GaN using the DSE technique [9,10], but only few investigations of dislocations in a-plane GaN are reported [11]. In this study, we focus on discriminating between surface defects in a-plane GaN, from those in c-plane GaN.

We used the DSE approach to understand surface defects of “non-polar” a-plane GaN layers, grown onto r-plane sapphire by metal organic chemical vapor deposition (MOCVD). We investigated the characteristics of etch pits by changing the etching compound, and evaluated the EPD by exploiting the differing local etching rates of different surface morphologies using specific wet-chemistry. We focused on a comparison of etching behaviors between mixtures of two acids, H_3PO_4 and H_2SO_4 on a-plane GaN with the aim of finding an optimum mixture ratio of the two acids that would best characterize the surface defect types in a-plane GaN samples. Examination of surface morphologies using SEM and XPS showed that different etching solution compositions produced characteristic etching morphologies. An optimal acid mix ratio would allow us to more easily distinguish the types of dislocations that were present prior to etching. Detailed information of surface composition and the electronic structure of GaN layers are essential for understanding the formation of interfaces between layers, and for optimizing device performance.

2. Experiment procedure

All a-plane GaN films were grown on r-plane sapphire (within $\pm 0.5^{\circ}$) using a MOCVD reactor. The precursors were trimethylgal-

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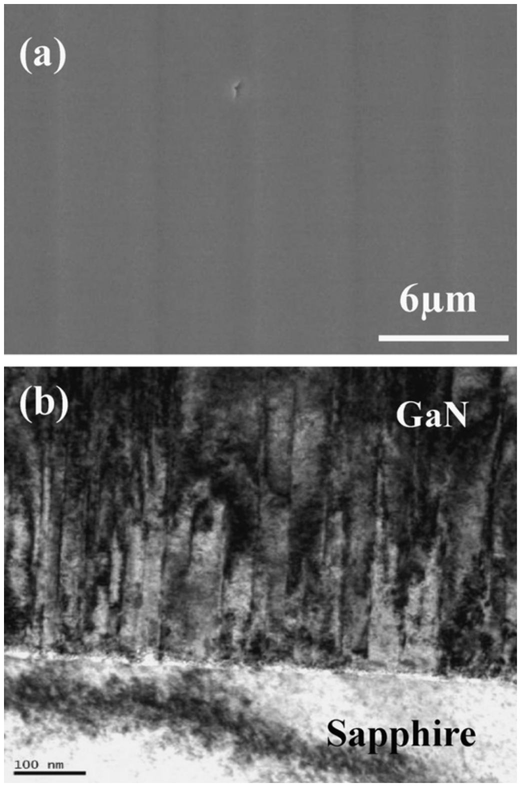

Fig. 1. (a) Plane-view SEM image and (b) XTEM image of as-grown GaN epitaxial layer.

lium (TMGa), ammonia (NH_3), and disilane (Si_2H_6), with hydrogen gas as the carrier gas. The details of growth conditions were mentioned in a previous paper [12]. The SEM image of a-plane GaN shows a smooth, void-free surface (Fig. 1(a)). The high-resolution X-ray diffraction (HR-XRD) omega scan produced a full width at half-maximum height (FWHM) of 788 arcsec. The dislocation density was determined from a cross-sectional transmission electron microscopy (XTEM) image, as shown in Fig. 1(b). The TEM image shows that the dislocation density was still high at 10^{10} cm^{-2}.

Before any wet etching process, all samples underwent organic cleansing. Samples were cleaned in acetone for 10 min then in isopropanol for 10 min with ultrasonic treatment, rinsed in deionized water, and finally, dried in a stream of dry nitrogen gas. During wet chemical etching, a-plane GaN films were etched in hot acid mixtures of H_3PO_4/H_2SO_4 at 160 °C by a series of different etching solutions with H_3PO_4/H_2SO_4 ratios at 1:0, 1:0.5, 1:3, and 0:1. We examined the surface morphologies of etched-GaN films by SEM, and obtained XPS spectra of all etched samples to determine how the composition of the native and processed surfaces altered with the ratio of etching acid components. All the chemical treatments were carried out at 160 °C for 10 min before XPS analysis. XPS offers a highly sensitive surface analysis of the native oxide, probing the topmost 1–10 nm, while providing the information on chemical bonding at the material surface.

3. Results and discussion

Generally, the mechanism of wet chemical etching involves two steps. First, the reactive molecules from the etchant break the bonds (Ga–N) at the surface of epitaxial layer. Then, native oxides (e.g. Ga_2O_3) form at the surface of epitaxial layer, which are subsequently dissolved by the etchant. By selecting an appropriate set of etchants and conditions, the local etch rate at defects is different from that of defect-free regions, thus revealing defects by exploiting different local etching rates. Such DSE produces etch pits or hillocks on a film surface, due to the inhomogeneous nature of defects compared with the crystal matrix. We examined the acid mixture ratio to obtain etch characteristics of a-plane GaN film.

Fig. 2 shows plane-view SEM images of the surface morphologies of a-plane GaN after etching with various ratios of acid mixtures. The temperature (160 °C) and time (20 min) were both fixed. After etching the a-plane GaN layer with H_3PO_4/H_2SO_4 at the ratio of 1:0 (pure H_3PO_4), the shape of the etch pits presented a stripe-like pattern along the *c*-axis. The etched-stripes are composed of two $\{10\bar{1}0\}$ facets and the direction is along the *c*-axis, as shown in Fig. 2(a). The figure shows that a-plane GaN etch pits are very distinct from those of the c-plane GaN reported in previous studies [13]. The c-plane GaN etch pits were formed as nanopipes in hexagonal geometry composed by $\{10\bar{1}0\}$ faceted planes. Compared to c-plane GaN, the etch pits of a-plane GaN are more like nanopipes, which start at the N-facet $\{000\bar{1}\}$ and terminate at the Ga-facet $\{0001\}$, but laid on the surface along the *c*-axis. Thus, pure H_3PO_4 solution etches N-polarity GaN films very quickly, resulting in the complete removal of surface morphology [14]. Li et al. concluded that the different etching characteristics of Ga-polar and N-polar crystals are due to different surface bonding states, and are only dependent on polarities, not on surface morphology, or growth methods [15]. Thus, the surface defects of a-plane GaN etched by pure H_3PO_4 solution are not suitable to calculate the etch pit density (EPD) and obtain the information about various types of dislocations. Furthermore, the etch chemistry should be developed for observing other defect-related etch pits, for example, edge and mixed dislocations. To optimize the etch chemistry for determining the various dislocations present, the ratio of etchants was optimized by mixing the H_3PO_4 and H_2SO_4 [16]. Fig. 2(b) and (c) are the plane-view SEM images of a-plane GaN films, etched by the acid with mixture ratios at 1:0.5 and 1:3. These two figures show that the shape of etch pits are composed of two long $\{10\bar{1}0\}$ facets, as shown in Fig. 2(b). The length of $\{10\bar{1}0\}$ facets is shorter as the proportion of H_2SO_4 in etchant mixtures is increased. When the film is etched by pure H_2SO_4, the shape of etch pits changes to rhombus-like with no $\{10\bar{1}0\}$ facets present, as shown in Fig. 2(d). From these images, it was found that the etch rate of these facets is altered by changing the H_3PO_4/H_2SO_4 ratio. From Fig. 2(c), we see that a different size of etch pit forms when etching with H_3PO_4/H_2SO_4 in a 1:3 ratio. These observations suggest that variation in pit size follows the size of Burgers dislocation vectors in GaN [17]. However, we need to correlate etched pit size and morphology with a-plane GaN dislocation features, as observed by TEM. Based on our experimentation, we recommend the optimal etching solution composition for observing surface defects is H_3PO_4/H_2SO_4 at a 1:3 ratio.

Fig. 3(a) and (b) show the AFM images (3 μm × 3 μm) of a-plane GaN before and after wet-etching for 5 min with a 1:3 H_3PO_4/H_2SO_4 ratio. From the AFM image, it was found that dark spots of post-etched film are more distinct than that of non-etched film. The EPD of etched-GaN surface is approximately 6.1×10^8 cm^{-2}. An EPD value of 10^9 cm^{-2} is far below dislocation density (10^{10}–10^{11} cm^{-2} of the a-plane GaN epilayer grown on r-plane sapphire). In c-plane GaN film, this 2–3 orders of magnitude difference between plan-view TEM and EPD counts is attributed to screw dislocation and to nanopipes, which are not the dominant kind of TDs in GaN film [14]. On contrary, the most common dislocation type for a-plane GaN are threading dislocations, which corresponds to 1–2 orders of magnitude between XTEM and EPD counts.

The surface chemical composition was also investigated by XPS measurements at 45° take-off angle. Fig. 4 shows the XPS spectra of Ga 3d core levels to compare four different surfaces, namely as-grown, pure H_2SO_4, H_3PO_4/H_2SO_4 (1:3), and pure H_3PO_4 treated