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Wet etching of GaN, AlN, and SiC: a review

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Abstract

The wet etching of GaN, AlN, and SiC is reviewed including conventional etching in aqueous solutions, electrochemical etching in electrolytes and defect-selective chemical etching in molten salts. The mechanism of each etching process is discussed. Etching parameters leading to highly anisotropic etching, dopant-type/bandgap selective etching, defect-selective etching, as well as isotropic etching are discussed. The etch pit shapes and their origins are discussed. The applications of wet etching techniques to characterize crystal polarity and defect density/distribution are reviewed. Additional applications of wet etching for device fabrication, such as producing crystallographic etch profiles, are also reviewed.

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1. Introduction

Single crystalline group III nitride semiconductors have attracted huge research interest during last two decades due to their unique properties and potential applications in short-wavelength light source/detector and high temperature/frequency devices. Taking advantage of the direct wide bandgap of GaN (3.44 eV), blue and green light emitting diodes (LEDs) have been commercialized [1]. The ability of GaN to form solid solutions with AlN and InN, making bandgap engineering possible, is essential for defining the emission wavelength of the LEDs. Ultraviolet (UV), high brightness, and long-life LEDs are under development to replace incandescent bulbs. The high thermal conductivities of GaN (210 W/m K) and AlN (340 W/m K) [2] make them suitable for high power applications, where the heat generated by devices must be efficiently dissipated. Furthermore, the piezoelectric properties of GaN and AlN [2] can be utilized to fabricate high frequency surface acoustic wave (SAW) devices.

SiC is another attractive semiconductor for high temperature, high power, and high frequency electronic devices due to its wide bandgap (3.08 eV for 6H and 3.28 eV for 4H), high breakdown electric field (3×10^6 V/cm), and high electron saturation velocity (2×10^7 cm/s). Though SiC wafers with diameters more than 2 in. (by modified-Lely method [3]) are commercially available, the development of SiC devices is hampered by the high densities of extended defects, such as micropipes and threading dislocations of both screw and edge character. The densities of screw and edge

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dislocations in the sublimation grown SiC are typically in the range of 10^3–10^4 cm^{-2} and 10^4–10^5 cm^{-2}, respectively [4,5].

The group III nitrides and SiC are notable for their excellent chemical stability as characterized by their invulnerabilities to wet etching. Various etchants for GaN, AlN, and SiC have been investigated, including aqueous mineral acid and base solutions, and molten salts. Since the optimum etching parameters are highly dependent on material quality and properties, a systematic review is imperative to help researchers select/optimize an appropriate etching process for specific etching purposes. Wet etches have a variety of applications to wide bandgap semiconductor technology, including defect decoration, polarity and polytype (for SiC) identification by producing characteristic pits or hillocks, and device fabrication on smooth surfaces. These are described in detail below.

First, wet etching techniques are extensively used for defect evaluation due to its merits of low cost, simple experimental procedure, and no requirement of sample geometry. By selecting an appropriate set of etchants and conditions, the local etch rate at a defect can be made different than the defect-free regions, so the defect is revealed. Such defect-selective etching produces etch pits or hillocks on a semiconductor surface due to the inhomogeneous nature of defects (either in composition, physical structure, or both) compared with the crystal matrix. When a new etchant or a new etching system has been carefully calibrated with techniques capable of directly observing defects, e.g. transmission electron microscopy (TEM), atomic force microscopy (AFM), and/or X-ray topography (XRT), one can estimate the defect density in single crystalline materials by measuring the etch pit density (EPD). TEM and AFM are established methods for determining the dislocation density in single crystals, but TEM requires arduous sample preparation and AFM requires a relative large and smooth sample surface. Moreover, for materials with relatively low dislocation densities, locating a dislocation using TEM or AFM is difficult. When the dislocation density is around 10^4 cm^{-2}, for example, theoretically there is only one dislocation present in a 100 μm × 100 μm area.

Second, the crystal polarity can be identified after wet etching since the amount of material removed and the resulting surface morphology is polarity dependent. The group III nitride semiconductors have the hexagonal wurtzite structure consisting of alternating layers of III-N pairs, stacked along the [0 0 0 1] direction in an ABABAB sequence. Thus, the basal plane (i.e. the (0 0 0 1) plane) can be either N- or group III element polar.

The polarity of (0 0 0 1) planes in group III nitrides is conventionally defined as follows [6,7]. As the crystal surface is approached from the bulk along the *c*-direction, if the parallel bond goes from the nitrogen atom to the group III atom, the crystal is nitrogen polar. If instead the parallel bond goes from the group III atom toward the nitrogen atom, the crystal is group III polar. The polarity of the group III nitride affects its surface and bulk properties [8–14], electrical and optical properties [15–20], oxidation rate ([21] and ref. within), and impurity incorporation rate during epitaxy [20,22,23]. For device fabrication, an understanding and control of the crystal polarity in the epitaxial growth is essential as the chemical reactivity and the optimum growth conditions required for high quality epitaxy generally depend on the polarity of the crystals. Due to the experimental difficulties, identifying crystal polarity of GaN was not commonly done before 1998. Thus, wet etching studies, before this date, were performed on materials with uncertain properties.

The polarity of SiC is analogously defined: when the silicon to carbon direction between the bilayers is parallel (anti-parallel) to the growth direction ([0 0 0 1] for α-SiC and [1 1 1] for β-SiC), the growing surface has silicon (carbon) polarity. Thus, the designated silicon faces in α-SiC and β-SiC are (0 0 0 1) and (1 1 1) planes, respectively.

Third, wet etching may also be used to identify the polytypes of SiC. Polytypes of SiC arise from different periodic stacking sequences of the close packed carbon–silicon(0 0 0 1) bilayers. Numerous (more than 200) polytypes have been documented. Among these, 3C-, 4H-, 6H-, and 15R-SiC are the