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DOPANT-TYPE SELECTIVE ELECTROLESS PHOTOETCHING OF Zn-DIFFUSED InP and InGaAs/InP HETEROSTRUCTURES

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1 Introduction

Visualization of the 2-dimensional p-n junction in III-V semiconductor devices is an important tool for device research, development, and manufacturing. The most common technique uses selective etching of the cleaved edge of an epitaxial layer. After immersion in a dopant selective etch, the junction is revealed on the cleaved edge and can be visualized by optical or scanning electron microscopy. In III-V devices, only a few examples of dopant type selective etching on a cleaved III-V structures have been reported, [1-3]. Of those, only one reports dopant selectivity on a cleaved InP-based structure [3]. That work, unfortunately, requires that a gold layer be deposited on the structure after growth in order to enhance selectivity. Furthermore, it relies on a KFeCN-based etchant, which suffers from poor selectivity and a high dark etch rate.

Ruberto, et. al. [4] have reported dopant-type selective photoetching in InP. They demonstrate an 18 times higher etch rate in n-type InP compared to p-type InP using 544 nm laser light and a weak aqua regia solution. However, this etching difference was demonstrated only on single dopant-type wafers. The work reported here applies the same photoetchant to directly visualize, by dopant-type selective etching of cleaved wafers, the p-n junction in Zn-diffused n^- InP wafers and InGaAs/InP array photodiodes [5].

2 Experiment

The etching system is shown schematically in Fig. 1. The aperture, illuminated by a tungsten halogen bulb, was imaged onto the cleaved wafer edge, which was immersed in the etchant. The weak aqua regia etchant consisted of 1:1:20 HCl:HNO3:H2O. The diameter of the illuminated spot on the wafer was 125 um, and the optical power incident on the surface, as measured by an optical power meter with Si photodiode, was 4 uW/cm^2. The wafer edge was observed by a television camera and displayed on a monitor at approximately 800 times magnification. After approximately 10 minutes, etching of the material was observed on the monitor as either a dark line on the n^- InP
pieces or a darkening of the epitaxial region on the heterostructure devices. After etching, the sample was removed and the diffusion measured using either a microscope or a scanning electron microscope.

For comparison, etching results on the same structures were also performed using a KFeCN-based etchant. This etchant is similar to that previously used to visualize the Zn diffusion in InGaAsP/InP lasers [3]. The KFeCN etchant was made by mixing 10 gm K$_3$Fe(CN)$_6$, 10 gm KOH, and 100 mL of H$_2$O. Typically, Zn-diffused n$^-$ InP wafers were cleaved and held in the etch solution for about 1 minute with plastic tweezers and only room light illumination. (Room light illumination was not found to affect etching when compared to dark etching.) Heterostructures were dipped in the solution for only approximately 5 s to avoid overetching the InGaAs layer. Localized illumination is not required for junction delineation on the n$^-$ InP pieces using the KFeCN-based etchant. However, localized illumination was investigated and results of experiments substituting the KFeCN etchant for the weak aqua regia etchant in the etching system are described below. Localized illumination was not attempted with the heterostructures due to the high etch rate of InGaAs in the KFeCN-based etchant.

The semiconductor-electrolyte interface flat-band voltage for both p and n- type InP in contact with the weak aqua regia solution was measured using a Bio-Rad Laboratories electrochemical C-V profiler. Measurement of the flat band voltage can then be used to determine the depletion width and relative band bending at the interface. Both parameters are essential for understanding the etching results and are discussed below.

3 Results

The photoetched profile of a Zn sheet diffusion into an n- InP sample is shown in Fig. 2. As can be seen from the photo, a distinct ledge is created where the undoped substrate has been etched away. The p-n junction depth is quite easy to measure. The electrochemistry behind this delineation is discussed below.

In comparison, the KFeCN etchant creates a more diffuse p-n junction boundary on the sheet diffused n- InP pieces [Fig. 3]. This is due to a low differential etch rate and high dark etch rate [0.1 um/min] which tends to smear the p-n boundary. Furthermore, the wafer is also etched from the top, thus causing an error in the measurement of the thickness of the diffused layer. These effects are most troublesome when delineating shallow junctions. Fig. 4 shows the result of dark KFeCN etching of a 1 um deep sheet diffusion of Zn into n- InP. The revealed p-n junction is very diffuse. A longer time in the KFeCN etchant creates a deeper, rounder ledge, thus smearing the p-n junction boundary. Also, due to the 0.1 um/min dark etch rate, a longer etch time causes more thinning of the top layer. A shorter time, on the other hand, makes the p-n junction position difficult to discern, but decreases the amount of thinning from the top.

Localized illumination of the cleaved edge immersed in KFeCN etchant creates a more distinct edge similar to that of the weak aqua regia. However, the KFeCN etching technique still causes thinning from the top and, therefore, creates measurement error.
To test the effectiveness of photoetching with the weak aqua regia solution on real heterostructure devices, cleaved cross-sections of InP/InGaAs photodiode arrays are studied. The structure of the two adjacent array diodes is shown in Fig. 5. SEM micrographs of photoetching results on a photodiode array heterostructure are shown in Figs. 6 and 7. In Fig. 6, the illumination is centered on the boundary separating the two array elements. The diffusion depth and lateral spreading of the Zn in the InGaAs layer can be clearly discerned. The delineation shown in Figs. 6 and 7 is caused by the selective removal of the n- InGaAs absorption layer. Interestingly, the mid $10^{17}$ cm$^{-3}$ N type InP layer did not etch. This effect is discussed below.

In contrast, unilluminated KFeCN etching of the photodiode array heterostructure was very difficult due to the high etch rate of the InGaAs. Although this technique did appear to produce dopant-type delineation similar to that of the photoetching in the weak aqua regia solution, the p-n junction delineation was indistinct and irreproducible.

The photoetching technique using the weak aqua regia solution is quite easy and reproducible. The immeasurably low dark etch rate allows one to take time aligning the cleaved edge in the illuminated spot. The etching can be observed directly and easily terminated when the desired amount of etching is accomplished. In comparison, the KFeCN dark etching, since it is unilluminated, can not be observed and variations in etch rate that may occur due to doping and material quality cannot be accounted for in real time. Additionally, illuminated KFeCN etching of heterostructures cannot be done due to the high InGaAs etch rate.

An important feature of the present technique is the use of localized illumination. Some workers [7] have used broad area illumination to enhance photoetching. However, localized illumination creates a higher etch rate due to better carrier separation [8].

4 Discussion

To explain the etching results, one must understand the carrier dynamics near the surface of the semiconductors. Dissolution will take place at those semiconductor surfaces which both have a continuous supply of holes and are in contact with the photoetching solution. The presence or absence of holes at the semiconductor surfaces can be deduced from the band bending at the semiconductor/etchant interface [9]. As shown in Fig. 8, when the cleaved edge is illuminated, electron-hole pairs are formed in the semiconductor. If the bands are bent up, as in n-type material, then holes move toward the surface where they induce dissolution. If the bands are bent down, as in p-type material, holes move away from the surface and dissolution is inhibited. Flat band potential measurements of the semiconductor-electrolyte interface, made using the electrochemical C-V profiler with the weak aqua regia solution as the electrolyte, place the Fermi level of the etch solution at about 0.5 eV above the valence band energy in InP and about 0.1 eV above the valence band in InGaAs. Therefore, the bands are bent up at the surface for n-type.
material and etching occurs upon illumination. Conversely, for p-type material, the bands are bent down and etching is inhibited.

As noted above, the n-type InP top layer of the heterostructure did not etch with illumination while immersed in the weak aqua regia solution. There are several possible explanations for this effect. First, the yield of holes at the n-type InP surface is very small, despite the 1 um absorption depth. The very shallow depletion width [< 0.1 um] sweeps few carriers to the surface, and diffusion from the bulk is minimized due to the short minority carrier lifetime [< 425 nsec] [11]. This is in contrast to the n- InGaAs material, where the depletion width is large [ > 1 um] and the minority carrier lifetime has been reported to be as long as 18 usec [12]. A second possible factor for the lack of etching in the n-type InP cap is the curvature bands near doping or heterointerface interfaces causing a flow of holes across those interfaces. This hole flow competes with hole flow to the surface and decreases etching [13].

A final possible reason for the lack of etching on the n-type InP is the phenomenon of cathodic protection [2]. Cathodic protection is the mechanism wherein the potential of two materials in electrical contact are changed such that etch rate is enhanced in one material and decreased in the other. This is suggested in our structure where the etching of the n' InGaAs appears to be enhanced and the etching of the n-type InP inhibited.

5 Summary

An electroless photoetching technique using a weak aqua-regia solution and white light illumination is demonstrated for visualizing Zn diffusion in InP and InP/InGaAs heterostructures. The technique is superior to dark electroless etching with a KFeCN etch due to low dark etch rate and greater dopant selectivity. This technique is quite simple, inexpensive, quick and reproducible, and should find widespread application in the analysis of 2-dimensional doping profiles.

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7 References


Fig. 1 Electroless Photoetching System
Fig. 2 Photoetched Zn-Diffused n⁺ InP
Fig. 3 Zn-Diffused $n^-$ InP etched in dark with $K_3Fe(CN)_6$
Fig. 4 Shallowly Zn-Diffused n⁻ InP etched in dark with K₃Fe(CN)₆-Based Etchant
Fig. 5 InGaAs/InP Array Cross Section Schematic
Fig. 6 Photoetched Array Heterostructure

SiN  InP: p+ 0.2 μm

InGaAs: p+ 0.2 μm

Zn Diffusion Front

InGaAs: n−
Fig. 7 Photoetched Array Heterostructure: Closeup of Lateral Diffusion under SiN3 Diffusion Barrier
Fig. 8 Photoetch Mechanism