94

N91-30208

GROOVED SURFACES ON InP

Sheila G. Bailey
NASA Lewis Research Center, Cleveland, Ohio, 44142

Navid S. Fatemi and Geoffrey A. Landis,
Sverdrup Technology, Inc., Brookpark, Ohio, 44135

Phillip P. Jenkins
Cleveland State University, Space Photovoltaic Research Center,
Cleveland, Ohio

INTRODUCTION

Formation of a textured or grooved front surface on a solar cell can increase the efficiency in several ways, including enhanced absorption and light trapping. Anisotropic etching techniques have been little used on indium phosphide (InP), principally because anisotropic etching in the III-Vs is more complicated than on silicon. In III-V materials the (111) plane is chemically different from the $(\overline{1}\overline{1}\overline{1})$ plane, and both etching and epitaxial deposition behave differently on these surfaces [Ref. 1]. This paper summarizes the current state of profile etching in InP and includes data on novel geometries attainable as a function of etchant temperature and composition, substrate orientation and carrier concentration, and the oxide thickness between the substrate and the photoresist. Depending on dopant concentration, the same etchant can produce either anisotropic or isotropic grooves. V-grooved solar cells have been manufactured on InP, and the improved optical absorption demonstrated [Ref. 2]. Preferred parameters for various applications are listed and discussed.

ANISOTROPIC ETCHING

Reduction of surface reflection, as shown in figure 1, can be achieved by use of a grooved surface. The groove walls are (111) In crystal planes. The grooves are defined by a photoresist pattern, and an anisotropic etchant is used to etch the groove profile through the open stripes in the photoresist. Reflection is minimum when the groove top and bottom surfaces are sharp, with minimum or no flat area. For the (111) grooves on a (100) InP wafer, the photoresist stripes must be aligned along the $[01\overline{1}]$ direction. (As discussed, alignment in the perpendicular direction will produce other groove shapes.) Figure 2 shows the flat orientation for a (100) InP wafer. Note that the Japanese and European standard for the primary and secondary flat is different from the SEMI standard.

An etchant composed of 10:1:1 proportions of HBr, H_2O_2, and HCl, respectively, will produce V-grooves on InP. Each component is precooled to -20°C prior to mixing and carefully maintained at -20°C during the required etching time to achieve the desired geometry. This time varies with the chosen geometry and the substrate doping concentration. For doping concentrations less than 1E18 cm^{-3}, a complete sawtooth structure of 8 micron periodicity takes approximately six minutes, when the photoresist is applied over a native oxide layer.

The effect of the etchant used can be seen in Figures 3 and 4, which are views of InP wafers that have been cleaved after etching but before removal of the photoresist stripes to show the cross section of the grooves produced. The photoresist is visible at the top of the grooves. Figure 3 shows an InP wafer etched in HCl. The HCl etchant reveals low-angle (311) planes. Figure 4 shows an identical wafer etched with the $HBr:H_2O_2:HCl$ etchant discussed above. The planes revealed by the etching are (111) surfaces. It should be noted that the etching shown here was done in ambient "room light," and is believed to be unenhanced by photoetching [Ref. 3].

We have found that producing the desired sharp groove-tops is dependant on the surface treatment of the InP wafer. Initial oxidation has been found to be rapid in InP [Ref. 4]. A "native" oxide layer formed in room air of variable humidity can be expected to be approximately 3 nm thick. Removal of this oxide layer prior to photoresist application has a dramatic effect on the lateral etch rate, as can be seen by comparing Figures 5 and 6. Nearly sharp groove peaks are produced by undercutting on InP wafers with an oxide layer, while almost no undercutting, resulting in flat groove tops, is produced on InP wafers where the oxide layer has been stripped. Deliberate growth of anodic oxides was found to slightly increase the rate of lateral etching, but yielded the same final structure. Previous authors have found differences in etch rates and profiles using SiO_2 and standard photoresist [Ref. 5].

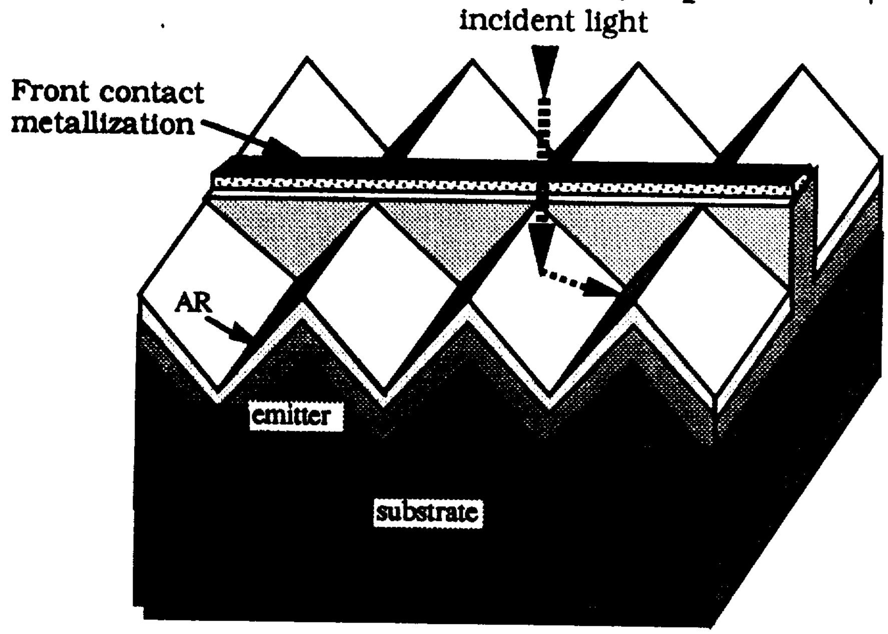

Figure 1. V-Grooved InP Solar Cell.

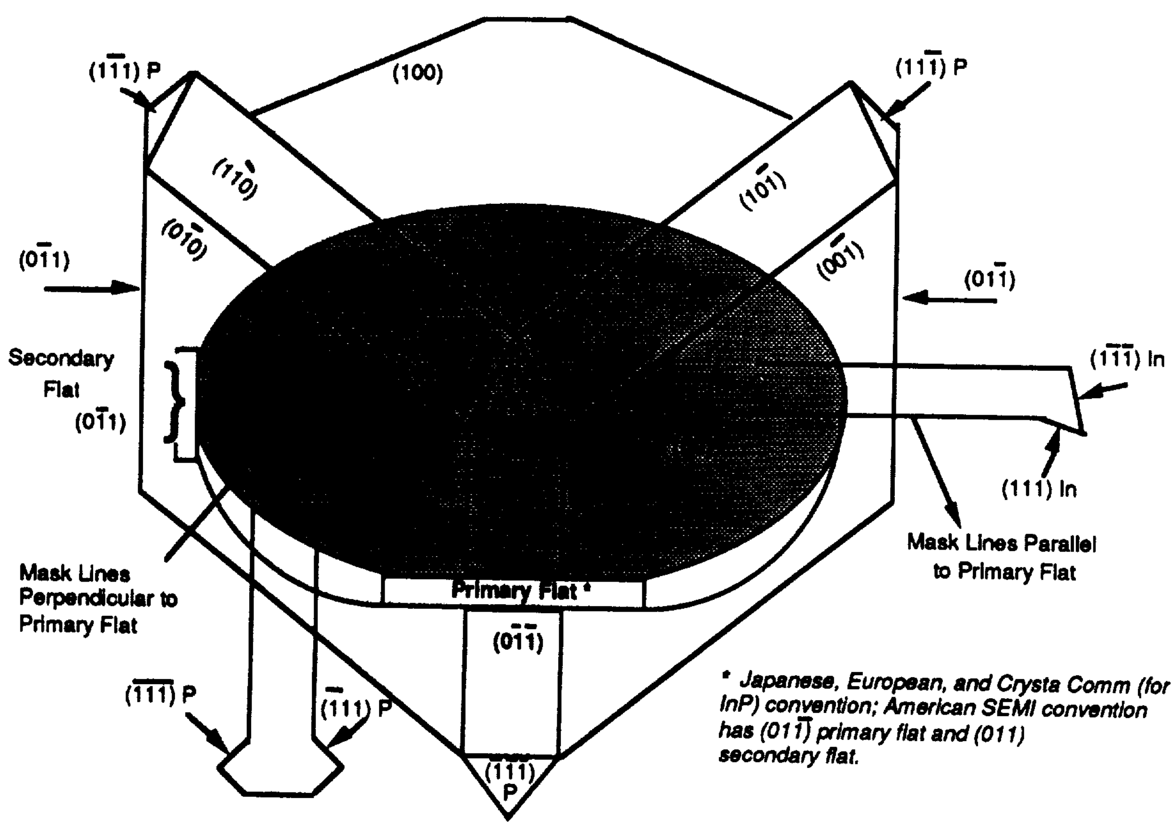

Figure 2. Orientation of InP wafer and mask lines for desired geometries

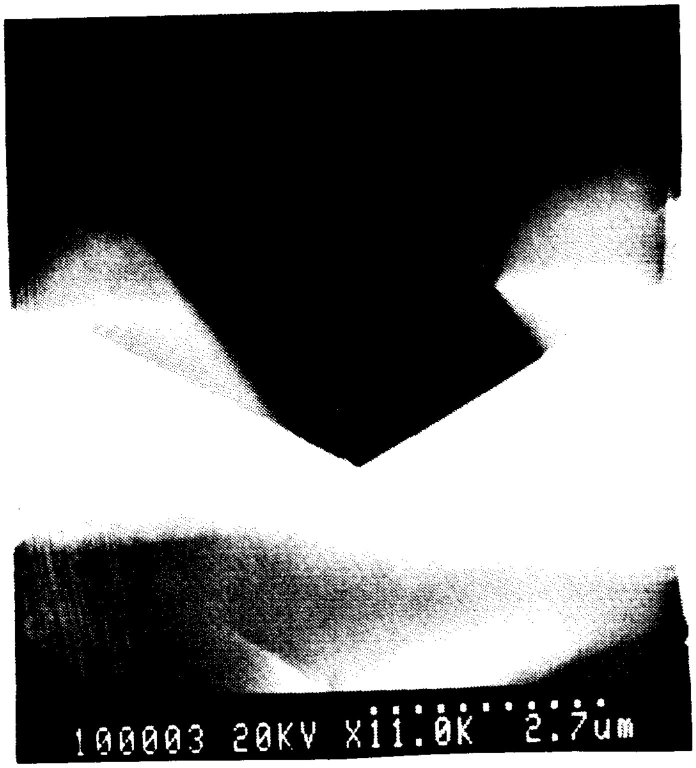

Figure 3. InP (Zn: 2E16 cm^{-3}) etched in HCl

Figure 4. InP (Zn: 2E16 cm^{-3}) etched in 10HBr:1H_2O_2:1HCl

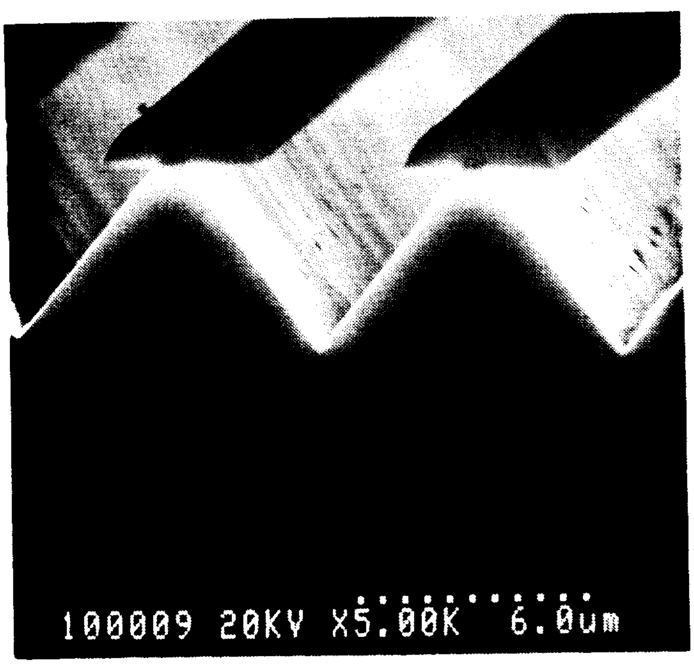

Figure 5. InP (Zn: 2E16 cm^{-3}) with native oxide; etched 6 minutes

Figure 6. InP (Zn: 2E16 cm^{-3}) without oxide; etched 10 minutes

EFFECT OF CARRIER CONCENTRATION

The etching results are also influenced by the carrier concentration, as is shown in Figures 7 and 8. Anisotropic etching can be achieved for all substrates with carrier concentrations lower than 1E18 cm^{-3}. Substrates with carrier densities greater than 1E18 cm^{-3} etch anisotropically at the initial stage of etching, but rapidly become isotropic. The mask lines in this case parallel the primary flat illustrated in Figure 2.

The orientation of the photoresist stripes is also important. When the mask lines are perpendicular to the primary flat, the resulting geometries are shown in Figures 9 and 10. Again, the etching changes from isotropic to anisotropic when the carrier concentration increases, however, as expected, in neither case is a V-grooved profile obtained.

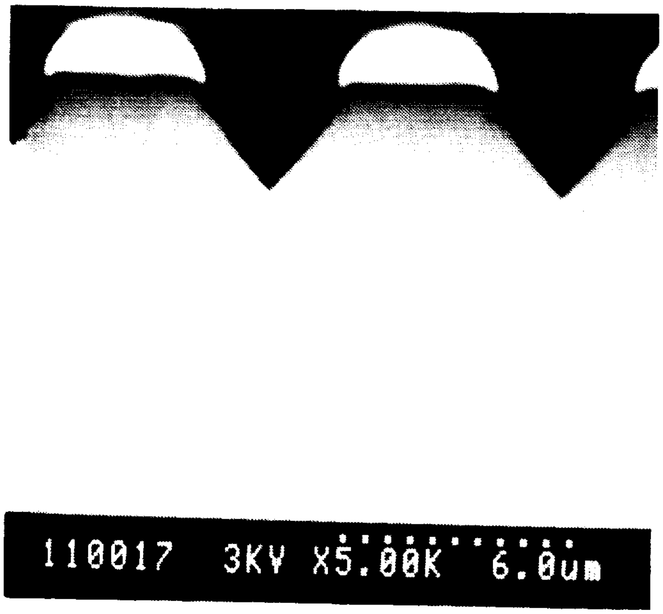

Figure 7. $[01\bar{1}]$ direction; Zn: 4E17 cm^{-3} etched 1 minute

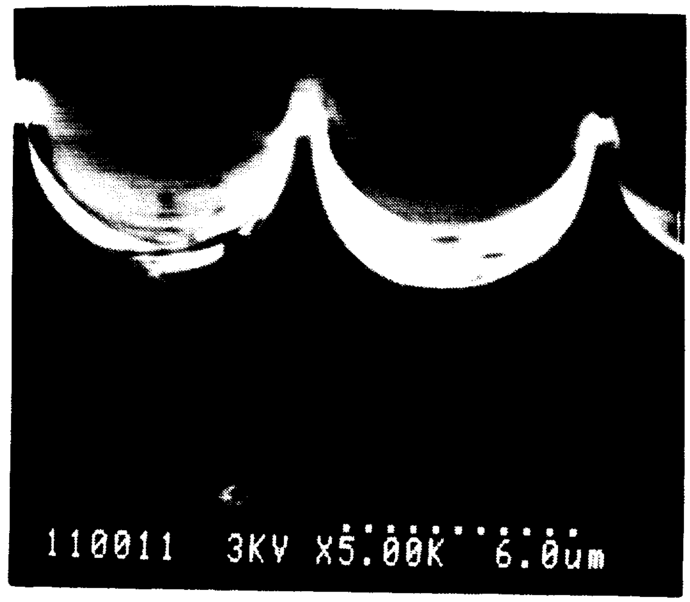

Figure 8. $[0\bar{1}\bar{1}]$ direction; Zn:1.5E18cm^{-3} etched 1 minute

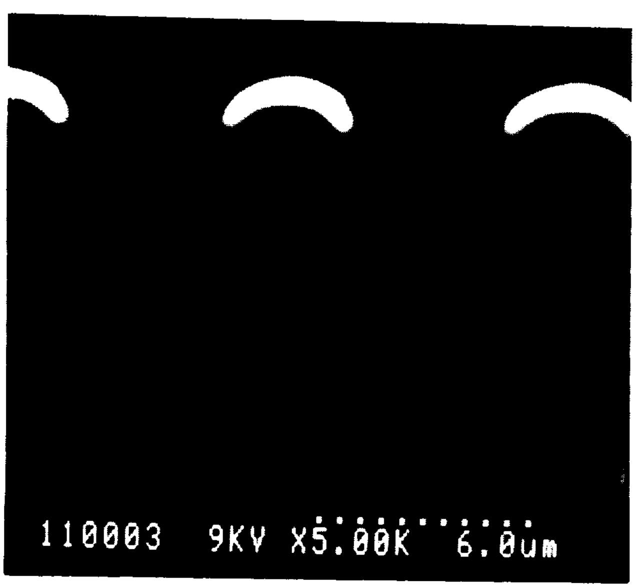

Figure 9. $[01\bar{1}]$ direction; Zn: 4E17cm^{-3}; etched 1.5 minutes

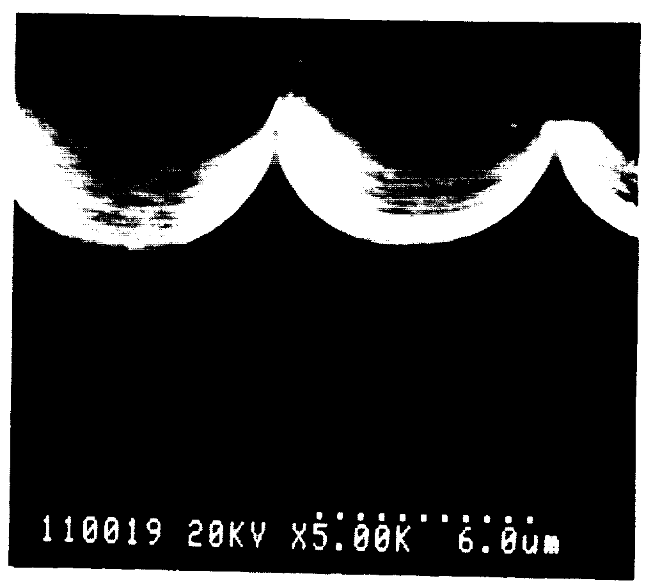

Figure 10. $[0\bar{1}\bar{1}]$ direction; Zn: 1.5E18cm^{-3}; etched 1.5 minutes

The etching time has a dramatic effect on the surface geometry of samples with carrier concentrations greater than 1E18 cm^{-3}. The rate of lateral versus vertical etching can be controlled on samples with lower concentrations to produce a complete saw tooth, with the vertical depth of etching controlled by the mask line widths and spacing. However, in the case of samples with higher concentrations, the effect of etching time is marked by a change from anisotropic to isotropic etching. This is shown in Figures 11 and 12.

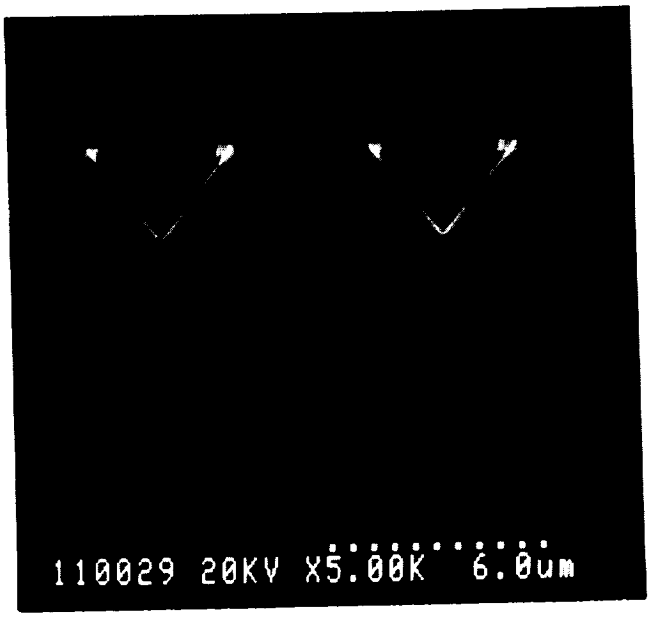

Figure 11. [$01\bar{1}$]direction; Zn: 1.5E18cm^{-3}; etched 30 seconds

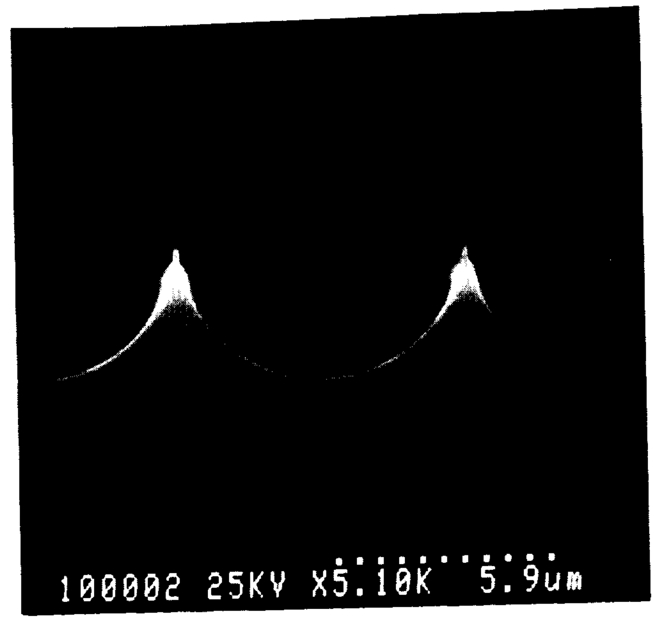

Figure 12. [$0\bar{1}\bar{1}$] direction; Zn: 1.5E18cm^{-3}; etched 60 seconds

UNMASKED V-GROOVES

It is also possible to produce low-angle V-grooves on InP without a photoresist mask [Ref. 6]. The low-angle groove process uses concentrated HCl (assay 37%) as an etchant at 17°C in room light. The grooved surface produced by this process is shown in Figure 13. Approximately 100 microns of InP are removed before grooves of approximately 2.4 µm cover the entire surface. This effect is not dependent on the carrier concentration or type. These grooves are approximately 23.2° with respect to the (100) plane which is typical of the (311) plane which is preferentially exposed by an HCl etchant.

These low-angle V-grooves can also be used to decrease the surface reflectivity in solar cells which include a glass cover. This effect is achieved by the use of total internal reflection at the air/coverglass interface [Ref. 6].

ORIGINAL PAGE
BLACK AND WHITE PHOTOGRAPH

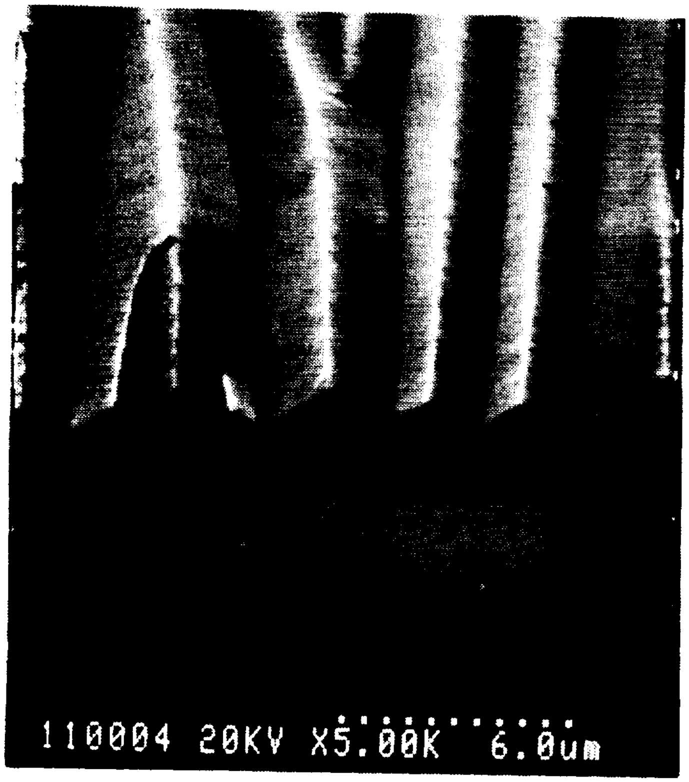

Figure 12. SEM image of low-angle V-grooves formed after etching InP in concentrated HCl

CONCLUSIONS

Geometric etching can be controlled in InP by an appropriate choice of etchant and mask orientation. The conditions required for a given geometry are dependent on the dopant concentration and oxide thickness between photoresist and substrate. There is a transition from anisotropic to isotropic etching when substrate carrier concentrations exceed $10^{18}/cm^3$. Recent work has indicated that isotopic profiles are possible in InP when a diffusion-controlled reaction dominates [Ref. 5]. The lateral etch rate was found to be strongly dependent on the surface conditions. The desired sharp-topped (111) V-grooves are most readily achieved with an etchant of 10HBr:1 H_2O_2:1 HCl at -20°C. An alternative maskless process in HCl can be used to produce low-angle (311) grooves.

REFERENCES

1. S. G. Bailey, G. A. Landis, and D. M. Wilt, *J. Electrochem. Soc.*, Vol 136, No. 11, Nov. 1989, pp. 3444-3449.
2. S. G. Bailey, N. S. Fatemi, G. A. Landis, D. J. Brinker, *Proceedings of the Second International Conference on Indium Phosphide and Related Materials*, 1990, pp. 73-79.
3. T. D. Lowes and D. T. Cassidy, *J. Appl. Phys.* **68** (2), July, 1990, pp. 814-819.
4. J. van de Ven, J. J. M. Binsma, and N. M. A. de Wild, *J. Appl. Phys.* **67** (12), June, 1990, pp. 7568-7571.
5. P. H. L. Notten, *J. Electrochem. Soc.*, Vol. 138, No. 1, January, 1991, pp. 243-249.
6. P. Jenkins and G.A. Landis, *3rd Int. Conf. on InP and Related Compounds*, Cardiff, Wales, Apr. 1991.