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Chemical Etching and Organometallic Chemical Vapor Deposition on Varied Geometries of GaAs

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Summary

Results of micron-spaced geometries produced by wet chemical etching and subsequent OMCVD growth on various GaAs surfaces are presented. The polar lattice increases the complexity of the process. The slow-etch planes defined by anisotropic etching are not always the same as the growth facets produced during MOCVD deposition, especially for deposition on higher-order planes produced by the hex groove etching.

Introduction

The technology of anisotropic etching to produce a geometrically structured surface [ref. 1] has become increasingly important in raising the efficiency of silicon solar cells [ref. 2]. Benefits of surface structure produced by anisotropic etching include reduced reflectance, oblique passage of light through the cell, and light trapping. These lead to the possibilities of increased efficiencies and reduced radiation damage. To date, however, little work has been done on the use of anisotropic etching for III-V solar cells. Implementation of these geometrical improvements in GaAs solar cells will require an understanding of etch characteristics and the growth process of metal-organic chemical vapor deposition (MOCVD) on multiple crystallographic planes with micron-scale periodicity. Wet chemical etching has been shown [ref. 3] to be capable of providing a simple, inexpensive method for fabricating structures with less than two micron spacings. In previous work [3,4] we have demonstrated MOCVD growth on V-grooved surfaces.

Anisotropic etching in GaAs is more complicated than on silicon due to the polar nature of the lattice [ref. 5]. The (111) plane is chemically different from the $(\bar{1}\bar{1}\bar{1})$ plane, and both etching and deposition will behave differently on the different surfaces.

Figure 1 shows a representative solar cell structure using a structured surface. The surface structure we chose here utilizes V-grooves, rather than the pyramidally etched surfaces typically used in silicon cells, because of the difference in etch characteristics of (111) Gallium and the (111) Arsenic faces.

We refer to a plane as (111)Ga because the atomic nature of the surface consists of gallium atoms bonded to arsenic atoms slightly below the surface by three bonds; likewise, (111)As surface consists of surface As atoms bonded to Ga atoms slightly below the surface.

Figure 2 shows the orientation of (111)Ga and (111)As faces on a (100) wafer. Since the (111) plane is a Ga plane, [111] planes with an even number of barred indices, such as (111) or $(1\bar{1}\bar{1})$, will be gallium planes, while planes with an odd number of barred indices, such as $(1\bar{1}1)$ or $(\bar{1}\bar{1}\bar{1})$, are Arsenic planes. The (111)Ga planes are the least reactive (slowest etching) planes, and are the

planes preferentially revealed in the anisotropic etch. Note that V-grooves running perpendicular to one another on the same side are *not* equivalent; if the V-groove running in the $(01\bar{1})$ direction shows a (111)Ga planes, one perpendicular to it (*i.e.*, in the (011) direction) would show a (111)As plane. In general (111)As grooves cannot be formed by anisotropic etching. The (111)Ga V-groove on the back side is perpendicular to one on the front side.

Anisotropic Etching

The process of etching V-grooves consists of

(1) masking the surface with photoresist stripes, alligned in the $(01\bar{1})$ direction;

(2) etching in an anisotropic etch.

Figure 3 shows a Scanning Electron Microscope (SEM) photograph of a surface after the photoresist step. The photoresist used was AZ 4110. The photomask we used produces fine groove spacings, either 4.2μ photoresist stripes separated by 1.3μ openings ("5.5 micron pattern"), or separated by 2.8μ openings ("7 micron pattern").

Several anisotropic etches for GaAs exist [ref. 5]. In this work, the etch used was the Caros etch, consisting of 5:1:1 proportions of H_2SO_4, H_2O_2, and H_2O respectively. Etch temperature was 24° C. This etch does not attack photoresist, so that the photoresist was sufficient to serve as a mask. We also looked at etches with different proportions [ref. 6], such as "vertical" etch (1:8:1 H_2SO_4:H_2O_2:H_2O) and "horizontal" etch (1:1:50), which produced faster and slower etch rates respectively.

Figure 4 shows the etch process when the photomask is aligned in the "correct" direction, *i.e.*, stripes running in the $(01\bar{1})$ direction. The Caros etch proceeds much faster in the (100) direction than in the (111) direction; the (111)Ga is a slow-etch face. The V-grooves are nearly flat-bottomed during the etch process; the width of the flat decreases as the etch proceeds. As the etch nears completion, the photoresist is slowly undercut. To make sharp-topped grooves, we terminate the etch just before the photoresist is undercut at the groove tops, typically about two minutes into the etch for the groove spacings (7μ periodicity) used here. For flat-topped grooves the etch is terminated earlier. The photoresist is then removed with acetone and the surface given a solvent clean before growth.

Quite different results are shown when the photoresist stripes are oriented in the opposite (011) direction, as shown in figure 5. In this case the V-groove walls would be (111)As planes, however, the (111)As face is not a slow-etch plane, and V-grooves are not formed. Instead a "hex" groove is formed. The photoresist is undercut much more rapidly than in the V-groove etch. In this case, however, the GaAs is cut through even more rapidly, and the photoresist peels from the surface when the GaAs cuts through, leaving a narrow wedge of GaAs attached to the photoresist as shown in figure 5C.

The bottoms of the hex-groove is slightly rounded, rather than nearly flat as in the case of the V-groove etch, a result of the divergent etch front, rather than convergent.

The upward facing walls are (111)As and the downward facing walls are (441) Ga faces.

Note that in this orientation the striations on the etched surface are much more pronounced than in the case of V-groove formation. This is due to the fact that the (111)As plane revealed here is more easily attacked than the (111)Ga plane revealed by the V-groove etching.

Some researchers [ref. 7] have seen "dovetail" grooves, as in figure 6, for stripes oriented in this direction, where the downward-facing walls are the slow-etch (111)Ga faces. We have not observed this groove shape in etches done on GaAs.

Identification of Crystal Planes

When specific crystal planes are identified here, identification is based on comparing angles measured on SEM photographs of a cleaved surface with theoretical angles of the crystal planes. Causes for error in the measured angle include residual distortions in the SEM photograph, misalignment of the grooves, cleavage at a slight angle from the theoretical cleavage plane, observations taken with the sample not perpendicular to the beam, and inaccuracies in the angle measurement.

In samples with a MO-CVD overgrowth, the epitaxial layer can be seen in the SEM photograph as a brightness difference between the p and n type material. This voltage contrast results from the Fermi level changing from p to n which changes the probability of secondary electron emission, and thus the apparent brightness.

Epitaxial Growth on V-Grooves

Table 1 shows the conditions used for the epitaxial deposition. The growth rate is a strong function of crystal orientation [ref. 8,9], which can result in preferential formation of certain crystal planes, or "faceting".

Table One: MOCVD Growth Conditions

Reactor: Horizontal geometry cold-wall reactor; RF Induction heated substrate
Sample clean: Solvent degrease followed by DI H_2O rinse and N_2 blow dry
Source: TMGa and AsH_2 (10% in H_2)
Dopant: Diethyl Zinc
Growth Temperature: 620°C
Growth Pressure: 190 Torr
Ga Mole Fraction: $1.5 \cdot 10^{-4}$
V/III Ratio: 20
Growth Rate: About 0.1μ/min.

In general, a crystal plane which is slow to etch will also be a plane which is slow to grow, since an etch process can be viewed conceptually as the reverse of a deposition process. However, since the kinetics of epitaxial growth are not identical to those of etching, it is not always true that the growth facets will necessarily be the same as those revealed by etching.

Figure 7 shows a typical epitaxial growth on a fully etched normal V-groove. The interface between the n-type buffer layer and the n substrate shows as a narrow white line; the p surface layer

as a lighter color. The gas flow for this growth was parallel to the grooves. The growth is slightly thicker toward the groove bottom.

In this growth we found the (100) surface at the groove tops to grow at a rate about equal to that on the (111)Ga surface of the groove walls. In other work (using slightly different growth conditions, [ref. 4]) we have found growth on the (100) surface to be up to 2.2 times faster than that on the (111)Ga face.

Figure 8 shows a slightly more complex growth, on partially etched V-groove (1-minute Caros etch) with flat tops to the grooves. In this case, two crystal planes are revealed. The angle between planes on the groove walls is about 10 degrees. (Note also that the tops of the grooves are slightly tilted. The epitaxial growth follows the true (100) face, and the wafer is cut 4 degrees off (100)).

Angle measurements show that neither of these planes is the true (111); the planes are tilted 5 degrees off (111) respectively toward and away from (110). This is reasonable if the (100) faces on the tops and bottoms of the grooves grow slightly faster than the (111)Ga face on the sides of the grooves. The (divergent) faster growth at the (100) groove tops tends to stabilize planes tilted slightly more than (111), while the (convergent) faster growth at the (100) groove bottoms tends to stabilize planes tilted slightly less than (111).

Expitaxial Growth on "Hex" Grooves

Figure 9 shows MOCVD growth on the hex orientation groove. In this sample the grooves were etched about 30 seconds. The deposition forms facets of high-order planes. The original (100) surface has been faceted with (111)As faces. The bottoms of the grooves are beginning to develop (411) facets.

Figure 10 shows the results when growth is done on a hex-groove which has been etched to completion (*i.e.*, until the groove walls cut through and the photoresist spontaneously peels, as seen in figure 5C). In this case, quite clear (411) facets form on the bottoms of the grooves.

The (411) plane is, like the (111), a polar plane. As seen in figure 11, the (411) plane can be cleaved in such a way that the exposed surface atoms are predominantly Ga atoms bonded to the surface with two bonds, with some As atoms bonded to the surface with three bonds.

Figure 12 shows the groove walls and the edges of the (411) planes in more detail. The groove walls, nominally (111)As faces, are seen to be ridged. The actual surface consists of (211) facets.

Conclusions

The polar nature of the lattice makes etching and chemical vapor deposition on GaAs a considerably more complex process than on non-polar material such as silicon. The slow-etch planes defined by anisotropic etching are not always the same as the growth facets produced during MOCVD deposition, especially for deposition on higher-order planes produced by the hex groove etching.

References

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[2.] M.A. Green, S.R. Wenham and A.W. Blakers, *Nineteenth IEEE Photovoltaic Specialists Conference*, 6-12 (1987).

[3.] R.P. Leon, S.G. Bailey, G.A. Mazeris and W.D. Williams, Appl. Phys. Lett, **49**, 945-947 (1986).

[4.] S.G. Bailey, R.P. Leon and A. Arrison, *Nineteenth IEEE Photovoltaic Specialists Conference*, 421-426 (1987).

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[19.] R.P. Gale, R.W. McClelland, J.C. Fan and C.O. Bozler, *Inst. Phys. Conf. Ser. No. 65*, 101-108 (1982).

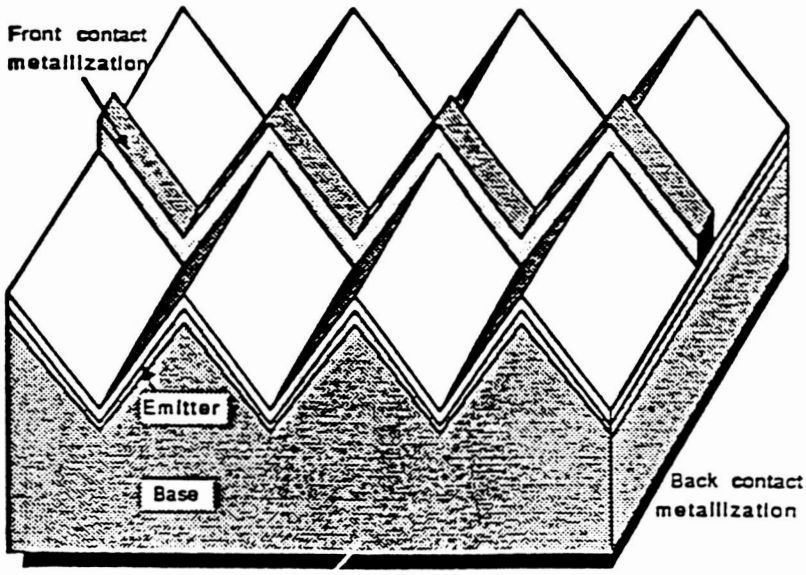


Figure One: Schematic of V-groove Gallium Arsenide Solar Cell (not to scale).

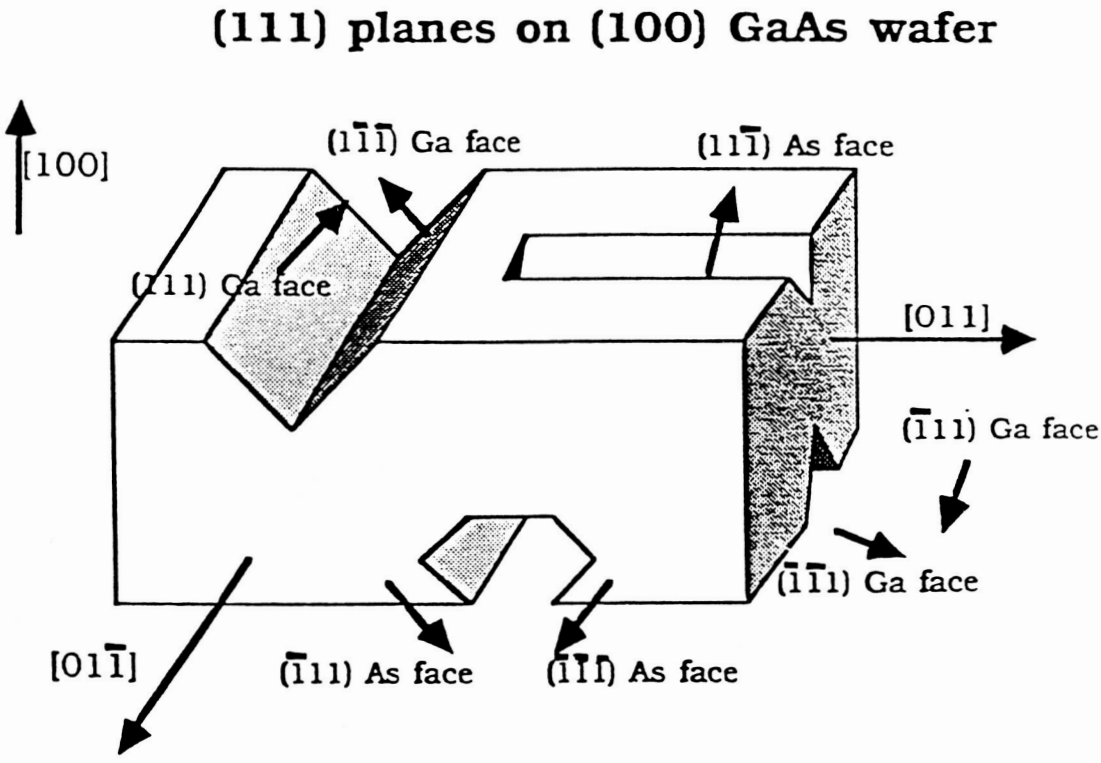
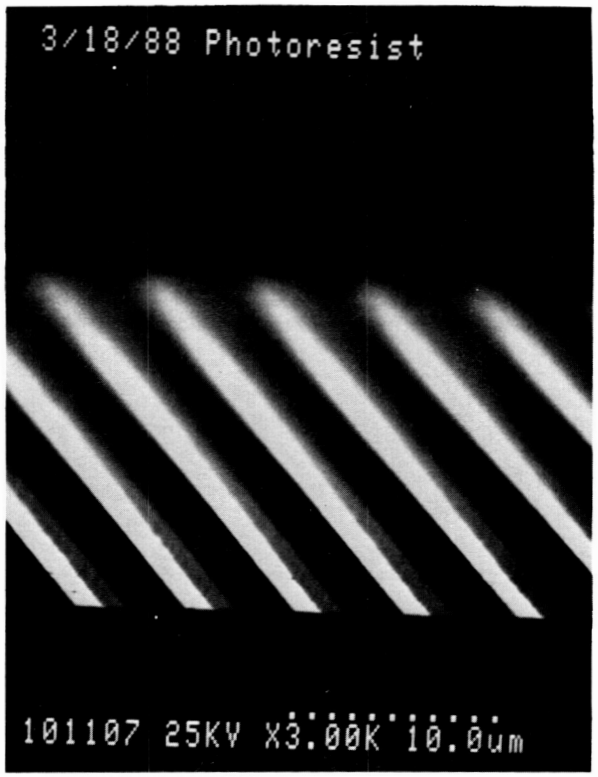


Figure Two: (111) Planes on (100) GaAs Wafer. There are two non-equivalent types of (111) plane; the (111)Ga and the (111)As planes. Anisotropic etching preferentially defines the (111)Ga face.



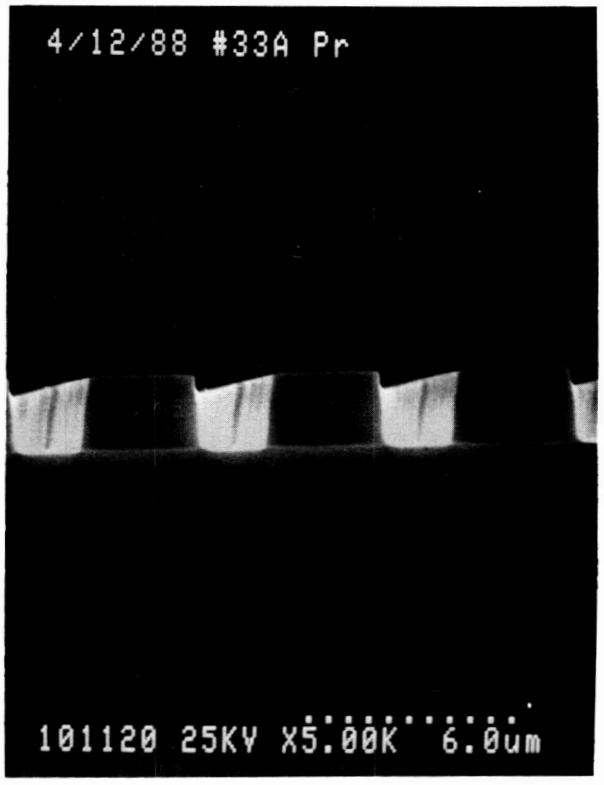


Figure Three: SEM Photograph of Photoresist Stripes on GaAs Wafer.

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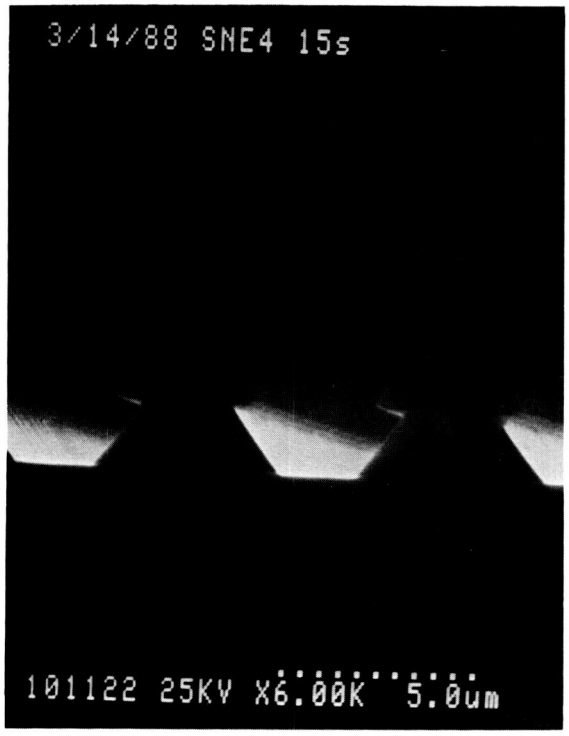
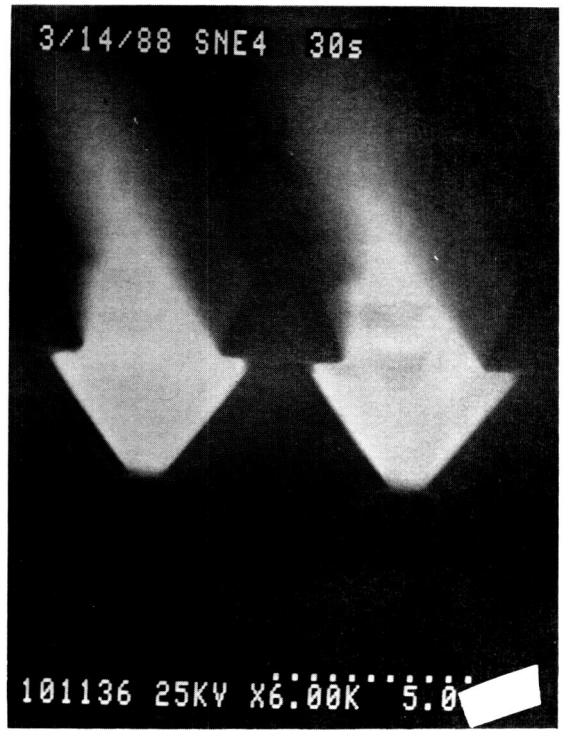
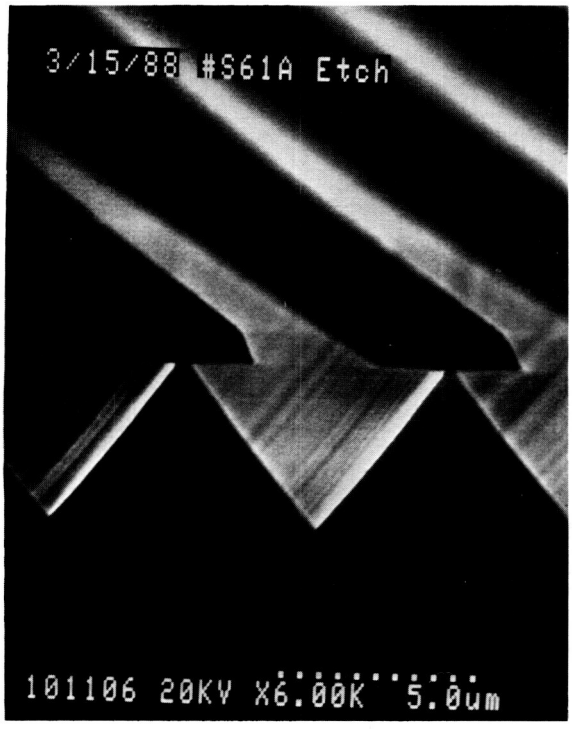


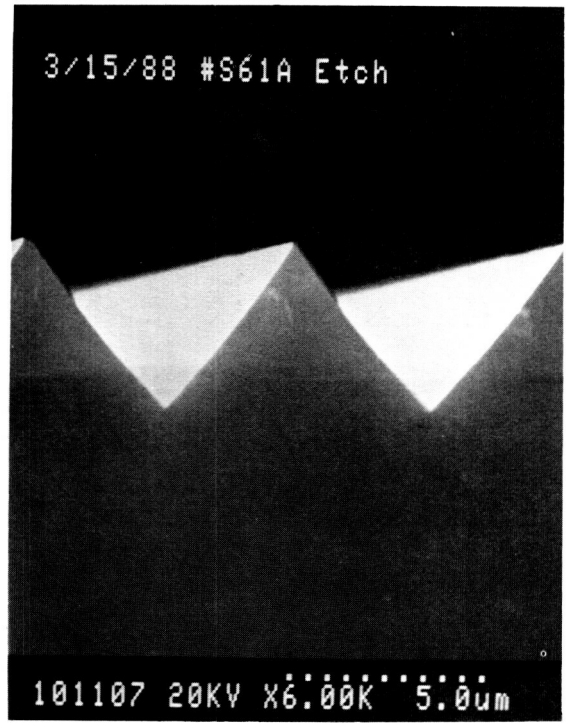
4A: after 15 seconds of etch



4B: after 30 seconds

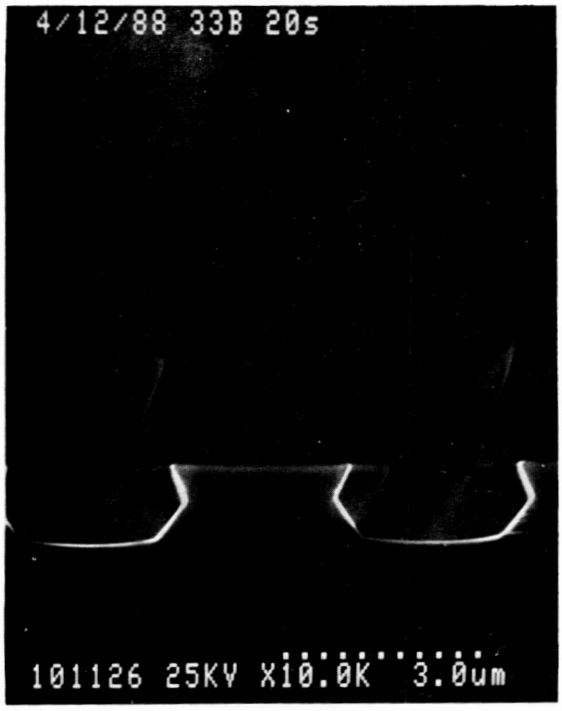


4C: after two minutes

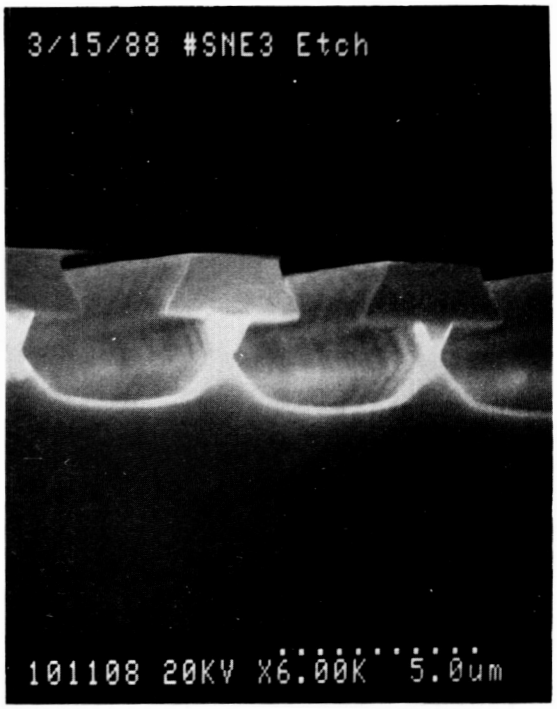


4D: after removal of photoresist.

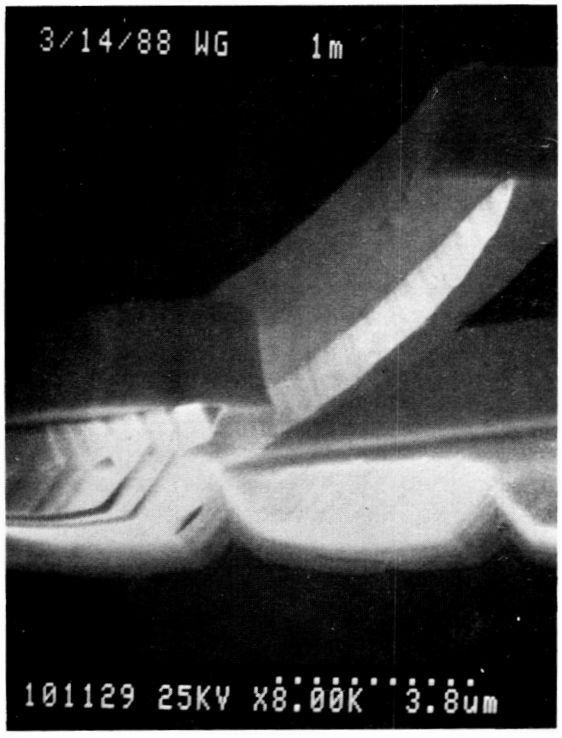
Figure Four: SEM **Photog**raphs of V-Groove Etch Process:

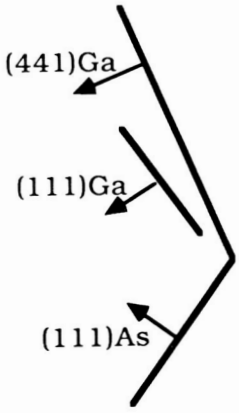


5A: after 20 seconds of etch



5B: after one minute of etch





5C: after one minute, showing etch-through and resist stripping

Figure Five: SEM Photographs of "Hex" Groove Etch Process:

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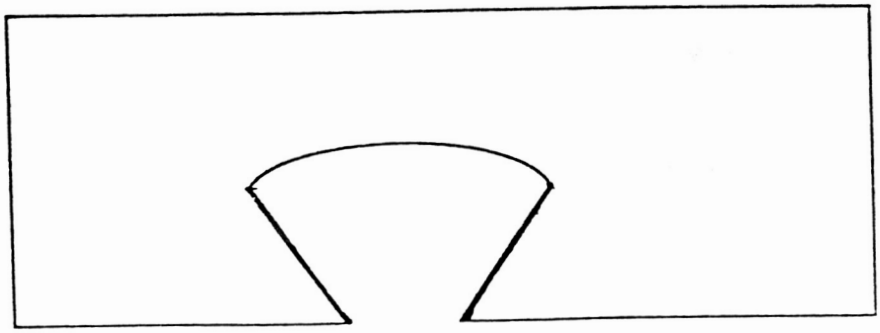


Figure Six: Some experimenters have seen "Dovetail" cross-section grooves as shown above. None of our experiments produced this pattern.

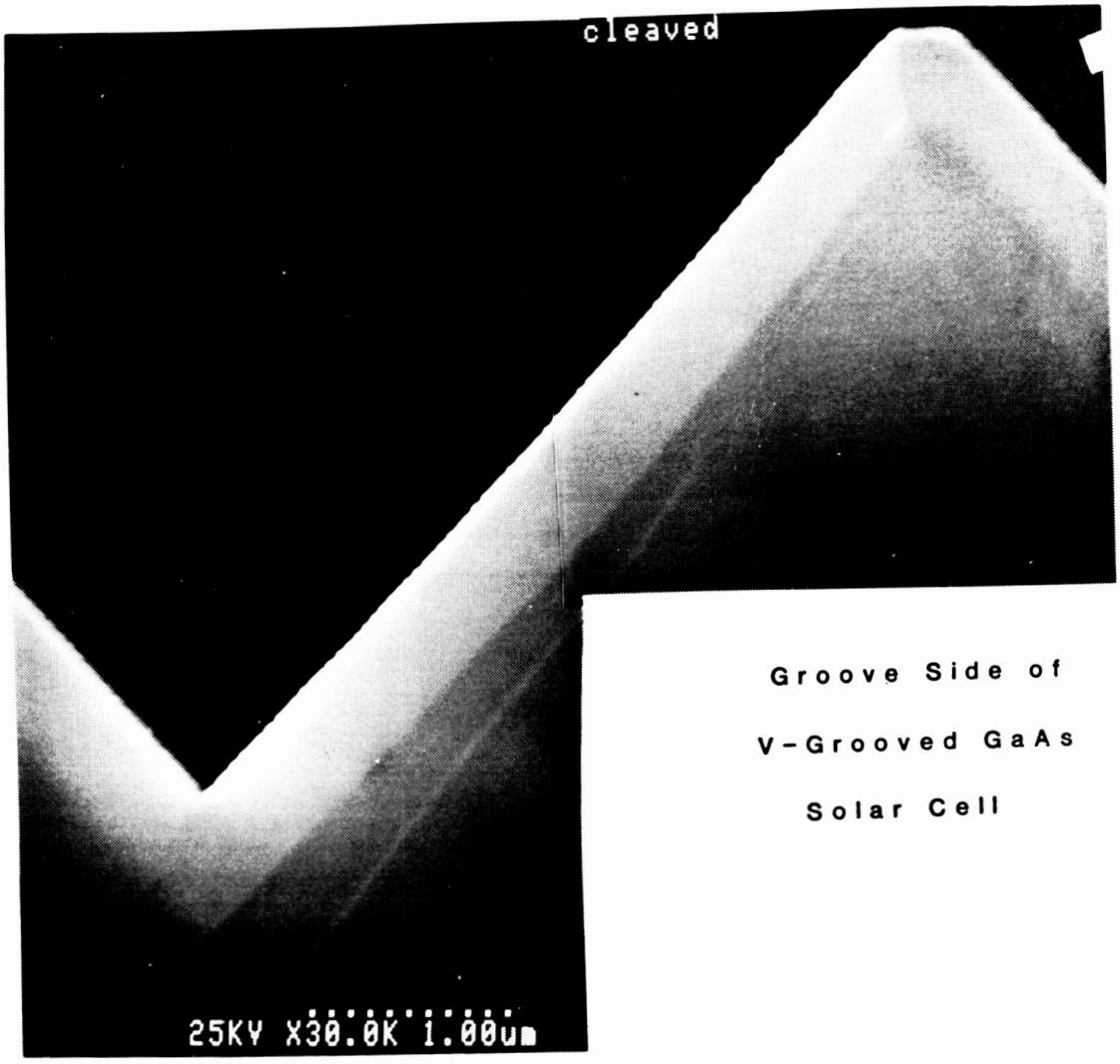


Figure Seven: SEM Photograph of Cleaved Cross-section of Epitaxial p-n junction on Fully V-Grooved Etched GaAs surface.

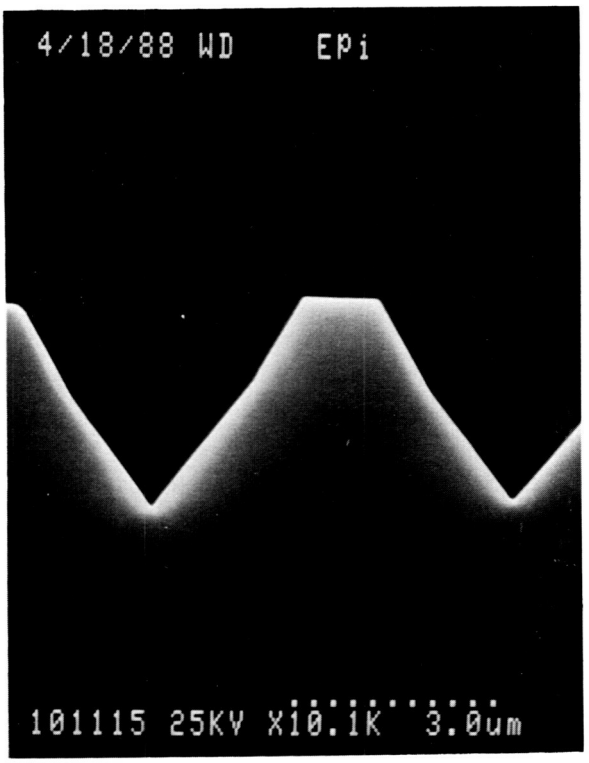
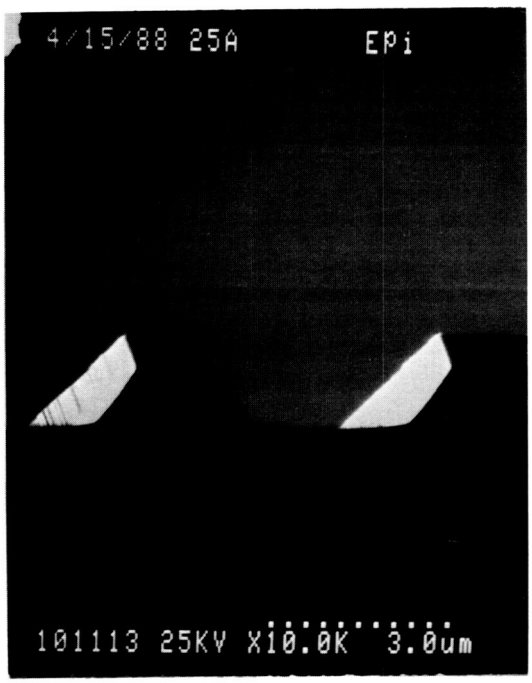
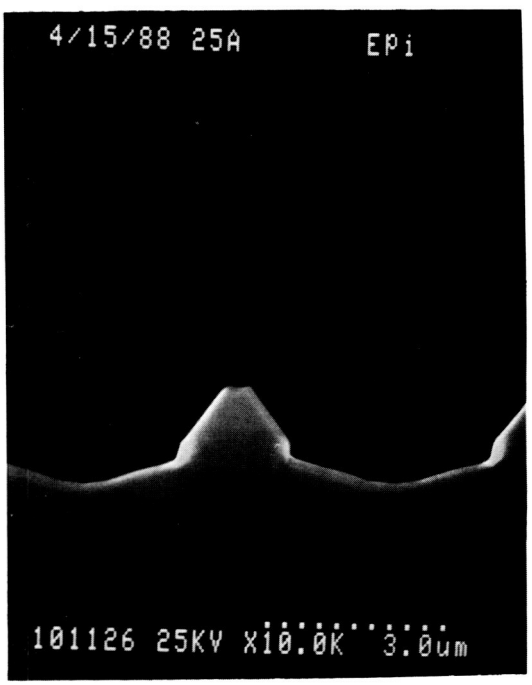


Figure Eight: SEM Photograph of Epitaxial Growth on Partially V-Groove Etched Surface.



8A: Before growth.



8B: After growth.

Figure Nine: Epitaxial Growth on "Hex" Groove:

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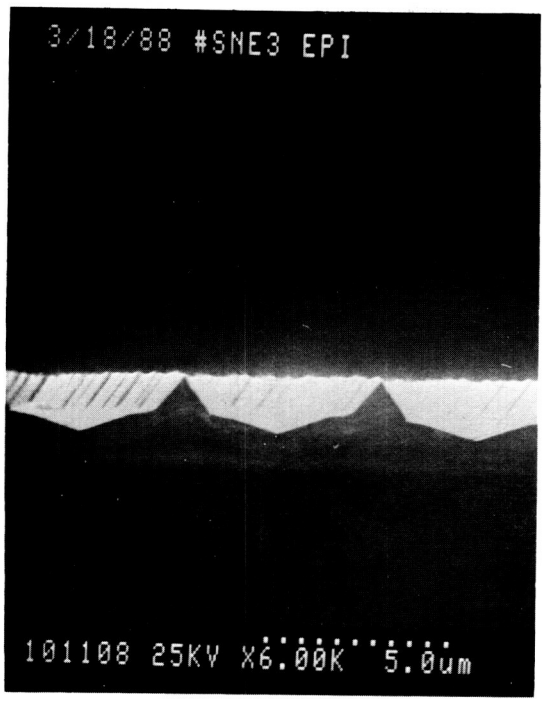
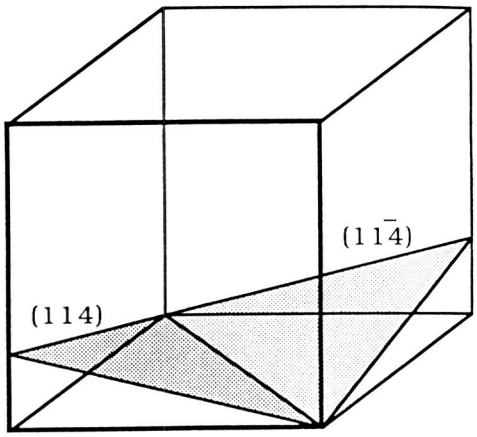




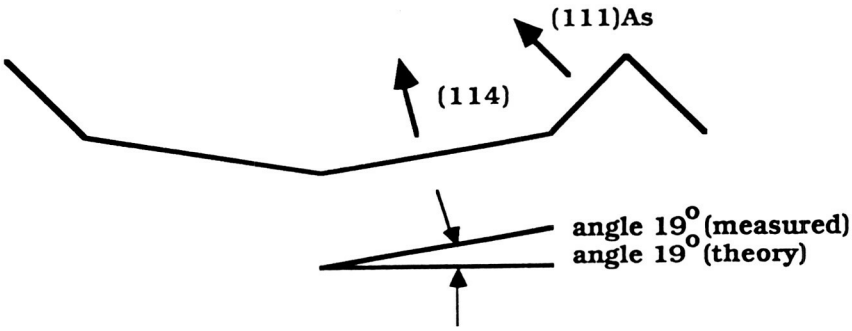


Figure Ten: Epitaxial Growth on "Hex" Groove etched to Completion, showing orientation of major planes.

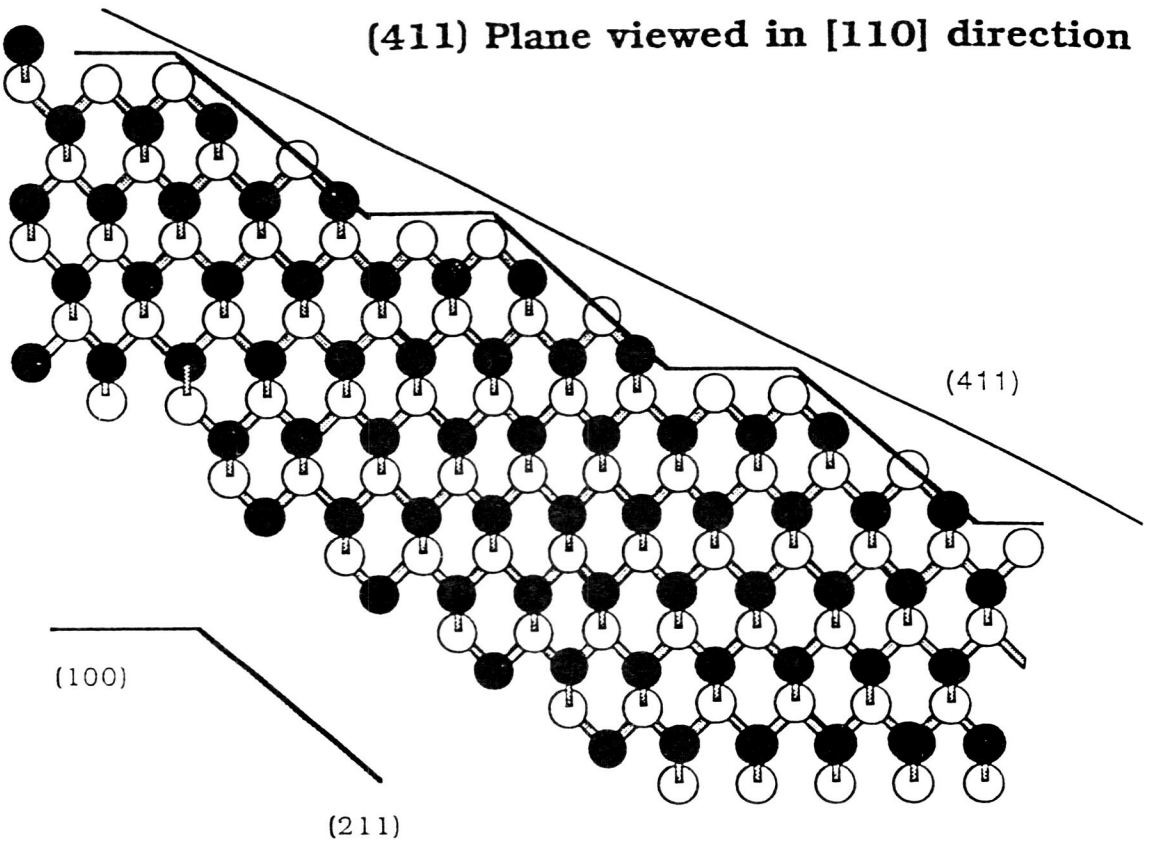
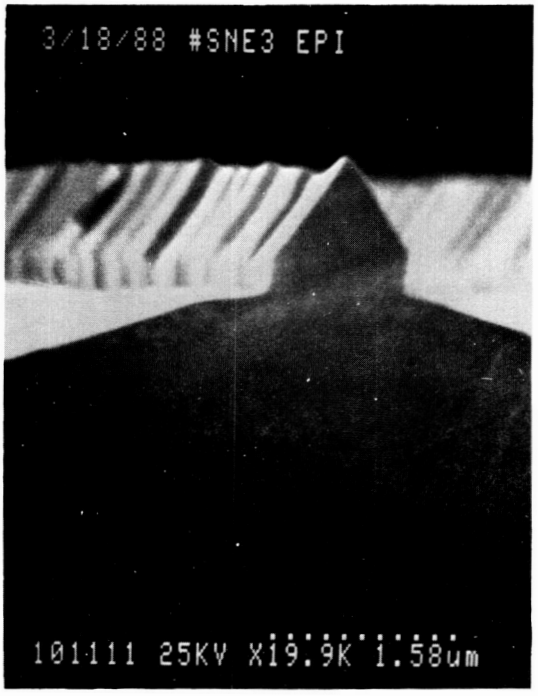
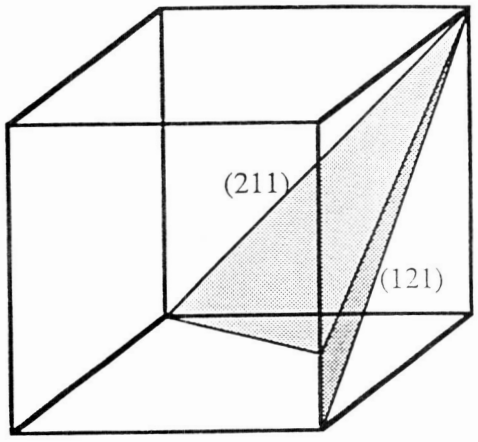


Figure Eleven: GaAs Lattice, showing (411) Plane. Ga atoms (white) are held to the surface with two bonds, while As atoms (black) are held to the surface with three bonds. For the ($\bar{4}11$) surface, the situation is reversed.





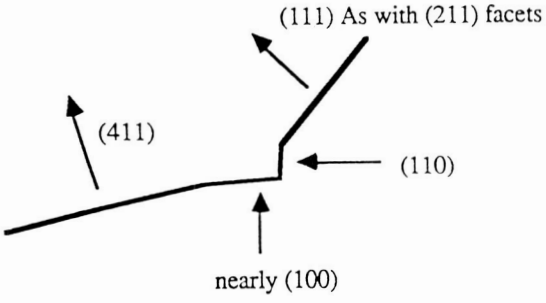


Figure Twelve: Detail of Epitaxial Growth on "Hex" Groove Etched to Completion, showing (211) facets on the (111)As face.