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## HIGH QUALITY InP-on-Si FOR SOLAR CELL APPLICATIONS

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### SUMMARY

InP on Si solar cells combine the low-cost and high-strength of Si with the high efficiency and radiation tolerance of InP. The main obstacle in the growth of single crystal InP-on-Si is the high residual strain and high dislocation density of the heteroepitaxial InP films. The dislocations result from the large differences in lattice constant and thermal expansion mismatch of InP and Si. Adjusting the size and geometry of the growth area is one possible method of addressing this problem. In this work, we conducted a material quality study of liquid phase epitaxy overgrowth layers on selective area InP grown by a proprietary vapor phase epitaxy technique on Si. The relationship between growth area and dislocation density was quantified using etch pit density measurements. Material quality of the InP on Si improved with both reduced growth area and increased aspect ratio (length/width) of the selective area. Areas with etch pit density as low as  $1.6 \times 10^4 \text{ cm}^{-2}$  were obtained. Assuming dislocation density is an order of magnitude greater than etch pit density, solar cells made with this material could achieve the maximum theoretical efficiency of 23% at AM0. Etch pit density dependence on the orientation of the selective areas on the substrate was also studied.

### INTRODUCTION

The material quality of InP films on silicon has not yet achieved acceptable levels. The critical issue is the reduction of dislocation density and residual strain. Yamaguchi (ref. 1) has estimated the material quality characteristics required for obtaining high performance devices using III-V films on silicon. A dislocation density of  $10^6 \text{ cm}^{-2}$  and a residual strain of  $10^9 \text{ dyne/cm}^2$  are the estimated requirements for a solar cell. The lowest reported dislocation density of  $3 \times 10^7 \text{ cm}^{-2}$  (ref. 2) for InP-on-silicon has not yet reached this level. Hence, state-of-the-art accomplishments are not within the high performance solar cell realm.

Both dislocation density and residual strain can be decreased by using a reduced growth area. It may be possible to improve the quality of InP on Si solar cells by exploiting this property. Instead of planar growth, a mosaic structure of closely spaced selective area growths can be grown. These mosaic units can then be monolithically interconnected to form a large area InP on Si solar cell structure.

Reductions in dislocation density resulting from reduced growth area have been reported by many groups for many different heterostructures. Noble (ref. 3) best described the reduction in dislocation density by the illustrations shown in Figure 1. Limiting the film area limits the effective dislocation length, which in turn reduces the probability of dislocation interaction and multiplication, and reduces the dislocation density of the material. Figure 1 illustrates the reduction in dislocation density as a function of effective dislocation length alone (dislocation interaction and multiplication are not illustrated).

Reductions in residual strain through limiting growth area have been reported by several groups for GaAs-on-silicon (refs. 4,5,6). Strain-relief in selectively grown films can be expressed by the bi-metal model as:

$$\epsilon = \epsilon_0 (1 - \exp [-k(w-x)])$$

where  $\epsilon$  and  $\epsilon_0$  are residual strain for selective area growth and planar growth, respectively,  $w$  is half the patterned width,  $x$  is the distance from the center of the patterned film and  $k$  is the interfacial compliance parameter (ref. 4). This equation shows that a reduction in film area (i.e., a reduction in  $w$ ) causes a reduction in residual strain ( $\epsilon < \epsilon_0$ ). For selective GaAs films on silicon, residual strain has been reduced to zero by limiting film area to a  $10 \mu\text{m}$  by  $10 \mu\text{m}$  square (ref. 5).

The goal of this research was to quantify the benefits of reduced area InP films on silicon using a combined vapor phase epitaxy (VPE) and liquid phase epitaxy (LPE) growth process. Etch pit density measurements quantified the relationship between the growth area dimensions and dislocation density as well as the relationship between dislocation density and the orientation of the selective areas. On the basis of the demonstrated reduced area and combined technology benefits of GaAs films on silicon, we expected a significant reduction in etch pit density that would bring the quality of InP films on silicon within the device realm.

## APPROACH

Single crystal n-type InP was grown on selectively masked on-axis (111) n-type Si substrates by a proprietary VPE technique. The average thickness of the VPE buffer layer was  $.5 \mu\text{m}$ . The growth areas were defined by chemically etching selective areas in a thermally grown  $\text{SiO}_2$  masking layer. The growth geometry was evaluated using two different selective area patterns. Figure 2 displays the mask used to evaluate growth area size and aspect ratio. This pattern had selective areas ranging in size from  $60 \mu\text{m}$  by  $60 \mu\text{m}$  up to  $4000 \mu\text{m}$  by  $4000 \mu\text{m}$ . Figure 3 displays the mask used to test the orientation. This pattern had  $400 \mu\text{m}$  wide selective areas oriented every  $30^\circ$ . On a (111) wafer the  $\langle 110 \rangle$  and  $\langle 112 \rangle$  equivalent directions are aligned in alternating  $30^\circ$  intervals. The masks were aligned with one edge parallel to the  $\langle 110 \rangle$  edge. Therefore, on the mask in Figure 2 the selective areas were aligned with one dimension in the  $\langle 110 \rangle$  direction and the perpendicular dimension in the  $\langle 112 \rangle$  direction. On the mask in Figure 3 the selective areas were aligned in alternating  $\langle 110 \rangle$  and  $\langle 112 \rangle$  directions. The initial vapor phase growth produced stray InP crystals on the  $\text{SiO}_2$  surface that created melt carryover problems during the LPE overgrowth. To prevent this, the selectively grown areas were masked with photoresist and any excess InP crystals were chemically etched from the substrate surface prior to LPE. In preparation for the LPE overgrowth, the substrates were cleaned in organic solvents and etched in  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$  (2:16:1000) for 30 sec.

The LPE growth system used for these experiments consisted of a quartz reactor tube, a 3-zone moveable furnace, a mechanical vacuum pump, and gas sources of nitrogen and palladium-diffused hydrogen. A graphite multi-well horizontal slider boat transported the substrate to the various growth melts. In order to protect the VPE InP layer from thermal degradation, a Sn-In-P overpressure melt as well as an InP polycrystalline cover wafer were used over the substrate prior to LPE growth. To enhance wetting of the growth area, the first growth melt contained In:Sn (3:1) solvent. Successive melts contained pure In solvent. The method of growth used was a two-phase ramp cool. Best results were obtained with a growth temperature of  $694^\circ\text{C}$ , a supercool of  $6^\circ\text{C}$ , and a cooling rate of  $0.7^\circ\text{C}/\text{min}$  for the first layer and  $0.25^\circ\text{C}/\text{min}$  for each subsequent layer. It is necessary to grow multiple layers to distribute the strain associated with the lattice mismatch of InP and Si. Growths with 3 and 5 layers exhibited good crystal quality, free of cracks. The average total thickness of the LPE growth layers was  $5 \mu\text{m}$ . Figure 4 is an illustration of the growth structure. Figure 5 shows the surface of a typical growth.

The dislocation density of the growth surface was quantified with etch pit density (EPD) measurements. To reveal the etch pits, the growth surface was etched in HBr:H<sub>2</sub>O<sub>2</sub>:HCl:H<sub>2</sub>O (10:1:10:40) for 10 sec. The etch pits are visible as triangular wells or depressions as in Figure 6. The EPD was then determined by counting the etch pits in a known area on a photomicrograph. By analyzing several areas across the growth region, an average EPD was accurately determined.

## RESULTS AND DISCUSSION

The first area of focus of this research was to determine the relationship between the selective area dimensions and film quality of the LPE overgrowth layers using the pattern shown in Figure 2. Etch pit densities of the selective area growths were determined using the method previously outlined. Most growths had EPD between  $4 \times 10^5$  and  $2 \times 10^6$  cm<sup>-2</sup> for the different selective areas. The lowest etch pit density of  $1.6 \times 10^4$  cm<sup>-2</sup> was obtained for a selective area with dimensions of 80 μm by 2000 μm. Figure 7 shows a graph of EPD versus selective area for a typical growth. As expected, the EPD decreased with decreasing area. The sets of two data points connected by vertical lines represent selective areas with the same dimensions but aligned perpendicular to each other. There was no substantial difference between selective areas oriented in the two different directions. The numbers next to the data points are the aspect ratios (length/width) of the selective areas. As seen in the graph, the data fall into two distinct groups. The group having lower etch pit densities consists of those selective areas with large aspect ratios (length/width). All of these selective areas have a short dimension of 500 μm or less. Figure 8 is a plot of the etch pit densities versus the short dimension of the selective area for three different long dimensions. Above a width of 500 μm there is little dependence on the short dimension. Below 500 μm there is a strong linear dependence on the short dimension. The etch pit density reduces at a rate of about 2000 cm<sup>-2</sup> for every 1 μm reduction in the short dimension. Reducing the short dimension from 500 μm to 100 μm causes an order of magnitude reduction in etch pit density. Holding the short dimension constant and varying the long dimension shows almost no change. These results indicate that a long thin selective area will have substantially better material quality than a square selective area with the same total area. We believe the explanation for this lies in the fact the material quality improves near the edge of the selective area due to lateral overgrowth onto the masking layer. As the selective area becomes thin, this effect starts to become significant.

The second area of interest was dependence of material quality on substrate orientation. Si substrates were masked with the pattern shown in Figure 3. InP was then grown in these selective areas using our vapor phase InP overgrown with LPE InP. After growth, etch pit density measurements were performed on two of these samples. One had an average EPD of  $4.05 \times 10^5$  cm<sup>-2</sup> in the <110> directions and  $7.64 \times 10^5$  cm<sup>-2</sup> in the <112> directions. The other sample had an average EPD of  $1.39 \times 10^6$  cm<sup>-2</sup> in the <110> directions and  $9.74 \times 10^5$  cm<sup>-2</sup> in the <112> directions. This result, along with the lack of orientation dependence of the quality of growth in the first experiment, indicates that the material quality is independent of the orientation.

While the etch pit density was not dependent on the orientation, the growth morphology was. The selective area edges oriented in the <110> directions had jagged overgrowth while the selective area edges oriented in the <112> directions had very smooth growth. The photograph in Figure 9 shows this effect. We believe this is due to the fact that the InP growth nucleates in a triangular pattern that has its flat side in the <112> direction. Figure 10 shows a photograph of an InP growth with only partial nucleation. The triangular nucleation areas have a flat side parallel to the edge of the selective area oriented in the <112> direction. For most applications, having the long edge of the selective area in the <112> direction would be more desirable.

## CONCLUSIONS

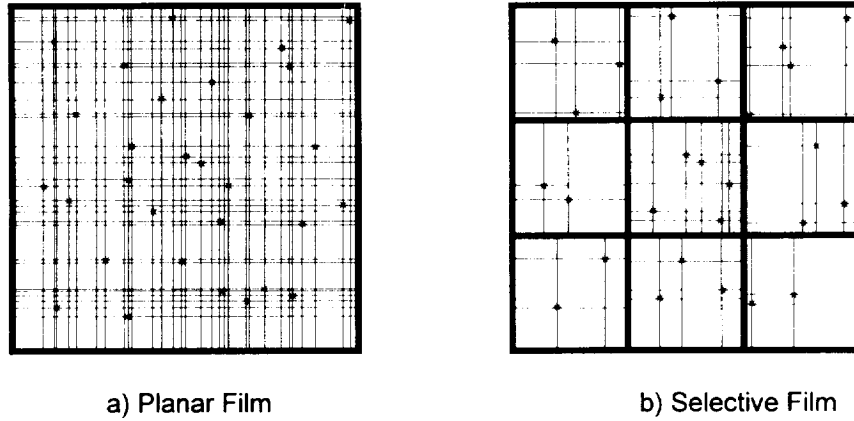
Using selective area growth is one method for improving the quality of heteroepitaxial InP on Si. Using a vapor phase buffer layer overgrown with LPE, etch pit densities as low as  $1.6 \times 10^4$  were obtained. The following conclusions about the effects of selective area growth were reached.

1. The etch pit density of the InP/Si heteroepitaxial growth can be significantly reduced by reducing one dimension of the selective area below 500  $\mu\text{m}$ .
2. The etch pit density is not strongly dependent on the orientation of the selective area on the Si substrate.
3. Jagged overgrowth occurs on the selective area edges that are aligned in the  $\langle 110 \rangle$  directions.

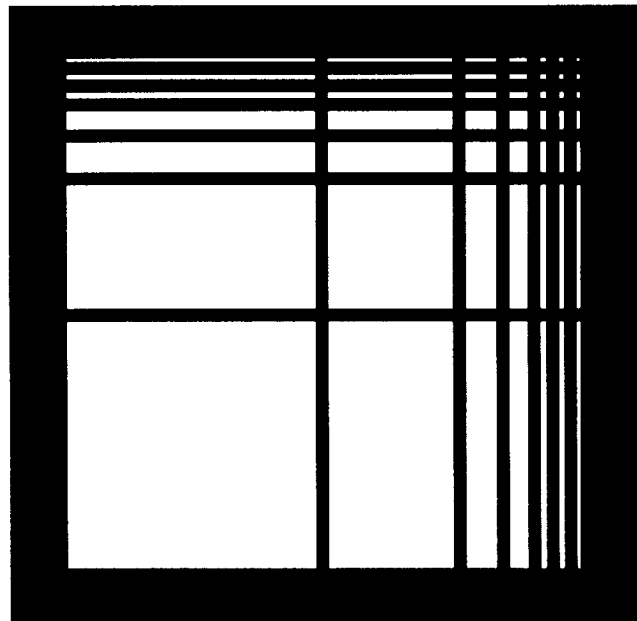
These results show it is possible to grow InP on Si by LPE with sufficient quality to support high performance solar cells. In order to make use of the benefits of selective area growth for high performance solar cells, methods to interconnect the individual areas must be developed.

## REFERENCES

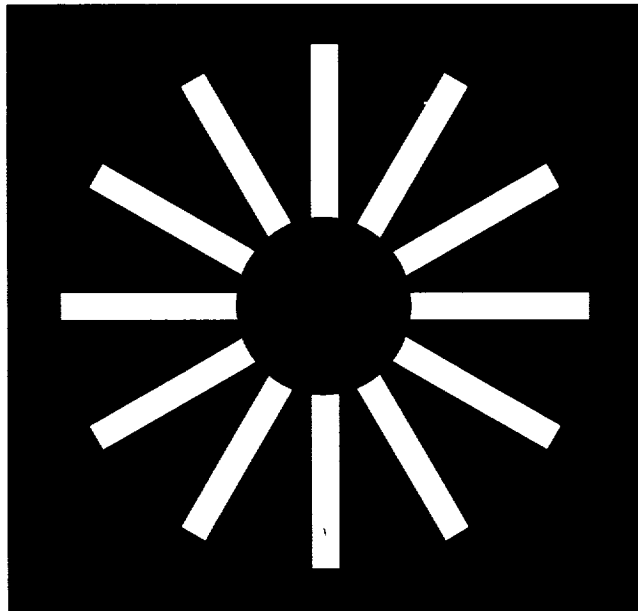
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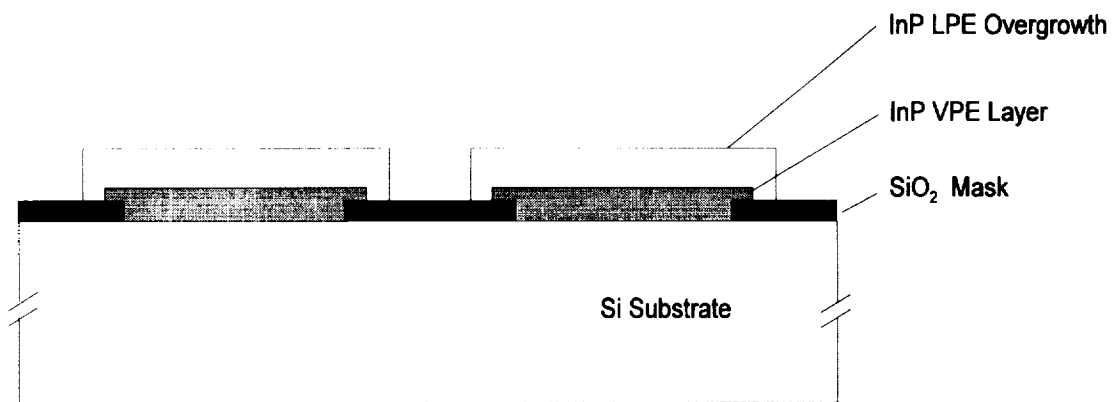
**Figure 1:** The effect of growth area on dislocation density (ref. 4). Heavy lines represent oxide stripes, narrow lines represent dislocation segments, and stars represent dislocation nucleation sources.



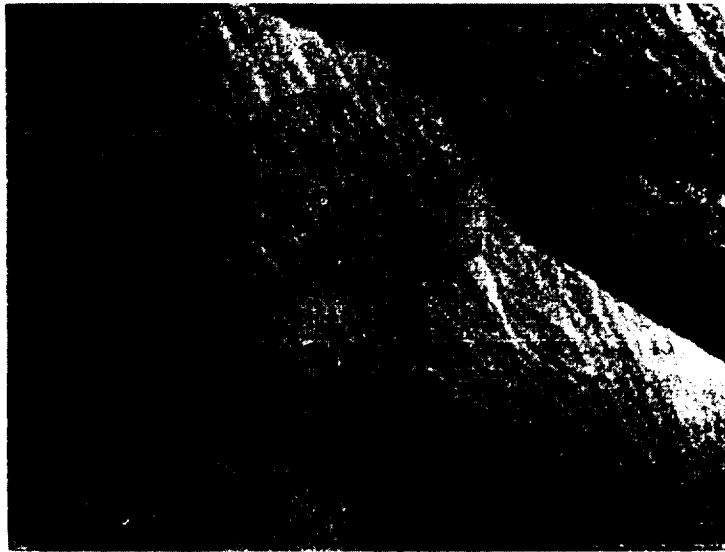
**Figure 2:** Mask design for film area vs. film quality study (scale = 10X).



**Figure 3:** Mask design to determine optimum selective area orientation (scale = 10X).



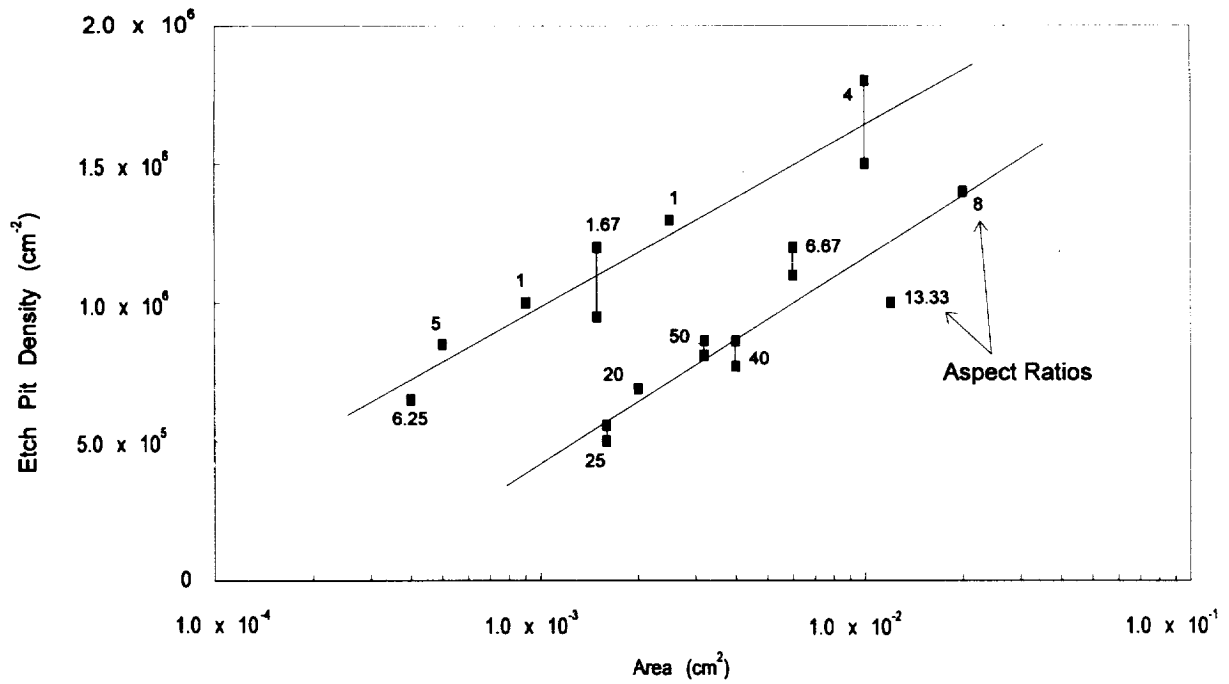
**Figure 4:** Growth structure.



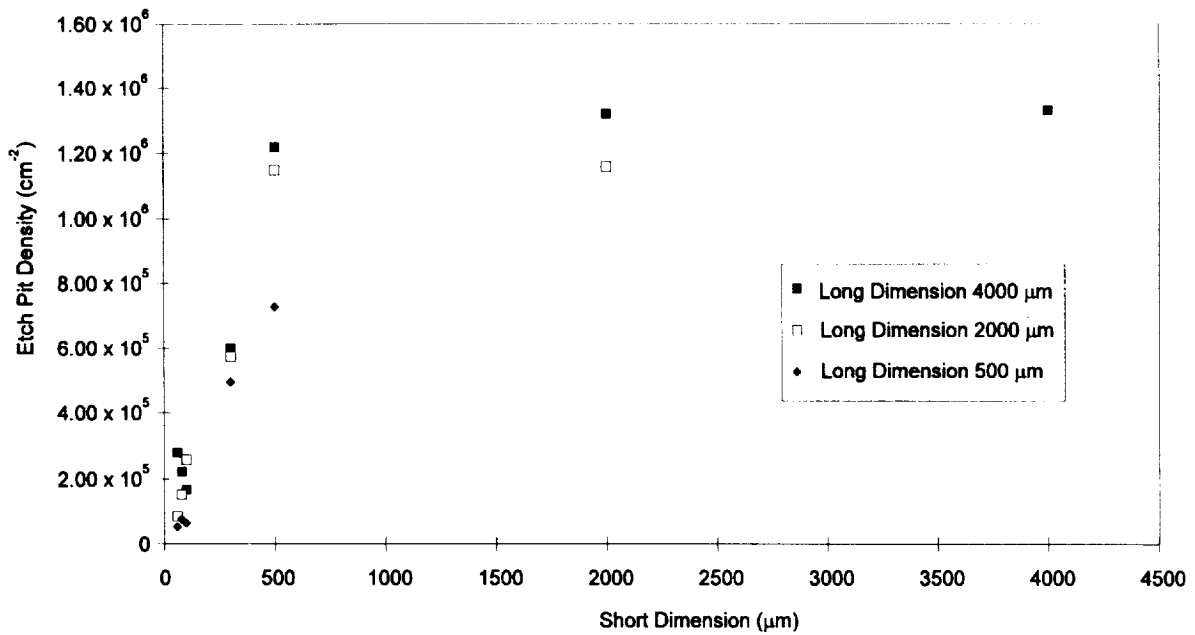
**Figure 5:** Typical LPE overgrowth surface (scale = 200X).



**Figure 6:** Typical LPE overgrowth surface showing etch pits (scale = 1000X).



**Figure 7:** Graph of etch pit density vs. film area for growth J11605.

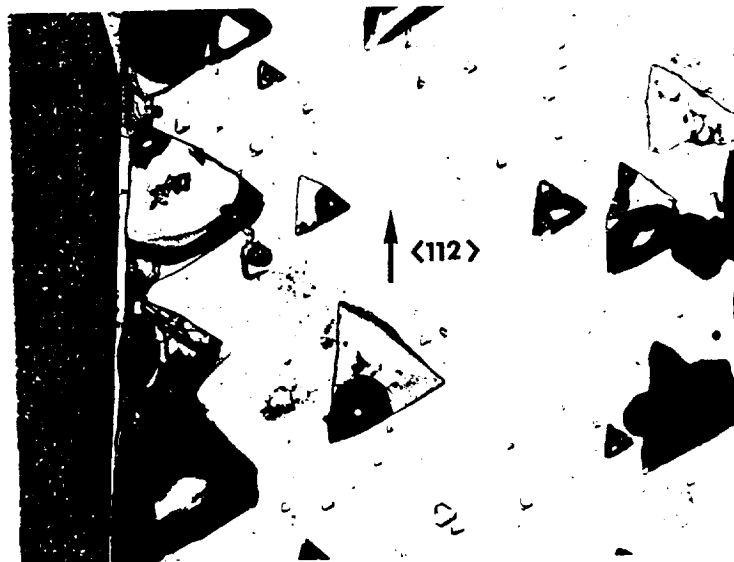


**Figure 8:** Graph of etch pit density vs. short dimension for growth J11707.





**Figure 9:** Edges of growth areas in  $\langle 110 \rangle$  and  $\langle 112 \rangle$  directions (scale = 100X).



**Figure 10:** Nucleation areas near  $\langle 112 \rangle$  oriented edge (scale = 100X).

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