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PHOTOVOLTAIC MECHANISMS IN POLYCRYSTALLINE THIN-FILM SOLAR CELLS

Quarterly Technical Progress Report No. 3, April 27—July 27, 1979

By
K. Zanio

October 1979

Work Performed Under Contract No. ET-78-C-01-3412

Hughes Research Laboratories
Malibu, California

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3011 Malibu Canyon Road
Malibu, CA 90265

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For period 27 April 1979 through 27 July 1979

Prepared for

DEPARTMENT OF ENERGY
Division of Distributed Solar Technology
Washington, D.C. 20545

Monitored by

SOLAR ENERGY RESEARCH INSTITUTE
Photovoltaic Program Office
Golden, CO 80401

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FOREWORD

This report was prepared by Dr. Kenneth Zanio of the Hughes Research Laboratories (Malibu, California), a division of Hughes Aircraft Company, for the Photovoltaic Branch of the Division of Solar Energy of DOE under Contract ET-78-C-01-3412. The technical monitor is Dr. Kim Mitchell at SERI in Golden, Colorado.

The program is being undertaken by personnel in the Chemical Physics Department under the supervision of Dr. R. Knechtli, Dr. G.S. Picus, Mr. M. Braunstein, and Dr. E. Rudisill. The program manager and principal investigator is Dr. Zanio. Important contributions to the program are being made by Messrs. F. Krajenbrink, L. Hershenson, K. Miller, P. Hoberg, and H. Montano.

TABLE OF CONTENTS

ABSTRACT

Indium phosphide films were prepared on (100) InP substrates by the planar reactive deposition technique in the temperature range 220 to 260°C. At 260°C and growth rates of about 1 μm/hr, complete single-crystal epitaxy was achieved. The onset of the single-crystal to polycrystalline transition at 245°C is characterized by a mosaic structure. Parallel studies to eventually passivate the grain boundaries in polycrystalline films were undertaken. A $5HCl:3HNO_3:4HF$ etch was found to preferentially attack 90% of the grain boundaries in bulk polycrystalline InP wafers. Canyons with depths greater than 10 μm and widths less than 1 μm were the most common form of attack. Although the etch had no effect on simple twin boundaries, preferential attack was observed at interfaces formed by multiple twinning events.

SECTION 1

INTRODUCTION

This report summarizes efforts at Hughes Research Laboratories (HRL) during the third quarter under Department of Energy (DOE) contract ET-78-C-01-3412 to investigate the effects of grain boundaries on InP-based solar cells and to develop approaches for alleviating the adverse effects of these grain boundaries. We expect the leakage currents to be higher and the open-circuit voltages to be lower for polycrystalline p-n junctions than for single-crystal p-n junctions. Our program therefore includes preparing thin-film InP p-n junctions with and without grain boundaries under growth conditions as nearly identical as possible in order to isolate the effect of grain boundaries on the p-n junction. Single-crystal films were grown in the second quarter. Films grown as low as 260°C were single crystalline. Modifications to our deposition equipment during the third quarter allowed substrate temperatures to be reduced to 200°C, allowing the preparation of polycrystalline films.

The second part of our program is directed towards reducing grain boundary leakage currents. During the second quarter, we demonstrated that single-crystal InP can be epitaxially prepared at 260°C. This is important because the passivation required to counteract the diffusion of unwanted impurities along the grain boundaries to the p-n junction from the substrate, windows, or contacts may not need to be as extensive if structures can be prepared at reduced temperatures. However, if the intrinsic nature of the grain boundary is detrimental to cell performance, extensive passivation may still be required. In the third quarter, the initial step of our passivation scheme, to etch away the grain boundary, was completed.

The growth of single-crystal and polycrystalline InP is discussed in Section 2. Sections 3 and 4 discuss, respectively, our etching studies and future plans.

SECTION 2

InP THIN-FILM GROWTH

A. HEAT SHIELD MODIFICATION

During the second quarter, single-crystal InP films were grown at 260°C. This was the lowest substrate temperature achievable in our apparatus. This temperature limit was undesirable in that part of our program is to prepare p-n junctions containing grain boundaries. Although the new substrate heating/cooling assembly, shown in Figure 1, did reduce the substrate temperature, heat from the source prevented cooling below 260°C. Normally the heat from the source irradiates about 40 cm^2 of the rotatable Mo plate on which the Mo substrate blocks are positioned. During this quarter, a heat shield was inserted below the rotatable plate. An extension of the shield from position A to position B allows only the InP and an immediate area of about 10 cm^2 to be exposed to and therefore heated by the source. Such a modification allows the substrate temperature to be reduced to about 150°C. This approach reduces the potential substrate area on which InP can be deposited. However, if larger area depositions are required at low temperatures, the heat shield could be removed and a larger area cooling assembly installed.

This equipment modification required a temperature recalibration of the Mo substrate blocks. The use of a rotating plate prevents the temperature of the Mo blocks from being measured directly during a run. Consequently, the temperature of the Mo block, T_{Mo}, is calibrated against the temperature of the nonrotating heating/cooling assembly. Figure 2 shows the temperature of the Mo block plotted versus the temperature of the substrate heating/cooling assembly, T_A, for different source temperatures, T_K. The source temperature is not the actual temperature within the Knudsen cell but refers to a lesser temperature measured below the cell by a chromel alumel thermocouple enclosed in a stainless-steel sheath and a Mo cap. The source temperature strongly influences the Mo substrate temperature. For source temperatures above 700°C, the Mo

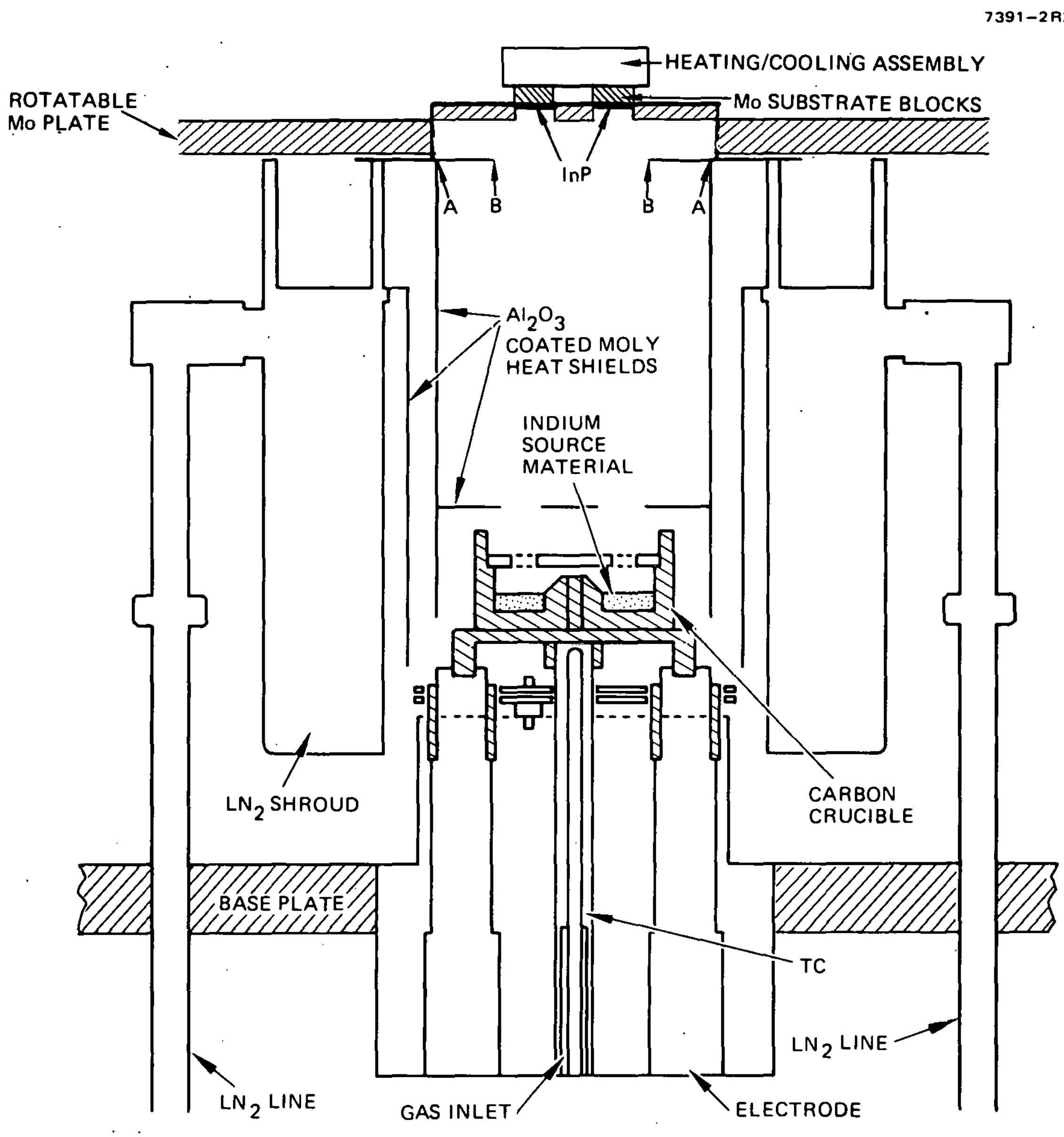

Figure 1. Cross section of PRD chamber.

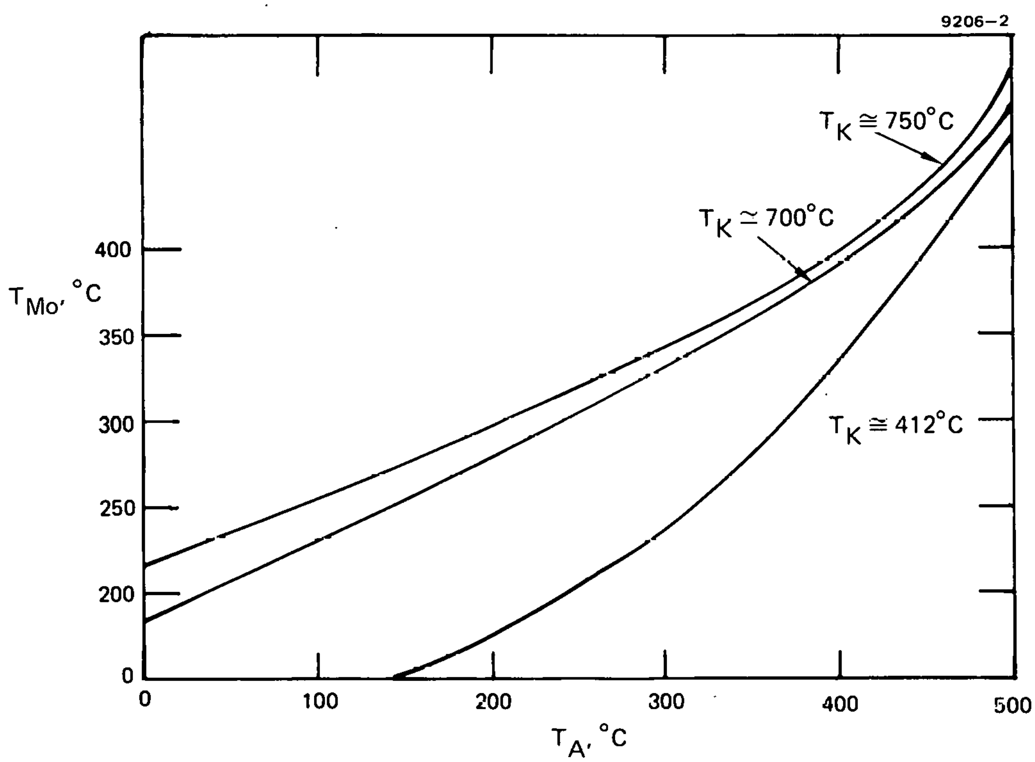

Figure 2. Temperature of the Mo substrate blocks, T_{Mo}, versus the temperature of the heating/cooling assembly, T_A, for different source temperature, T_K.

substrate temperature is higher than the assembly temperature, indicating that the heat flow occurs from the Mo substrate to the assembly and that the temperature of the InP might be higher than indicated by the Mo substrate temperature. For the source temperature of 415°C, the Mo substrate temperature is lower than the assembly temperature, indicating that the heat flow occurs from the assembly to the Mo substrate and that the temperature of the InP might be lower than indicated by the Mo substrate temperature. We are concerned about determining the temperature of the InP during growth because our transition temperature from single-crystal to polycrystalline InP is reported to be about 50°C lower than for films prepared by MBE. To increase our confidence in determining the temperature at the bottom of the Mo block, we prepared substrate blocks of different heights and with different thermal conductivities. From an analysis of the resulting gradients, we assumed that, within our range of deposition conditions, the temperature difference between the bottom of the Mo blocks and T_{Mo} is within 20°C.

B. InP MORPHOLOGY

In the second quarter, we found that films prepared above 260°C were single crystalline. For depositions done in the third quarter at 245°C, complete single-crystal epitaxy was not evident. Further runs done at 220°C were polycrystalline. An SEM analysis of the deposition at 220°C showed a faceted surface with characteristic dimensions of ∿0.5 μm. The X-ray Read analysis showed both rings characteristic of crystallites having a preferred (100) orientation. Quantifying the degree of crystallinity in the polycrystalline films is difficult. Evaluating the degree of crystallinity at the onset of the single-crystal to polycrystalline transition at 245°C is even more difficult. The spots on the Read picture are diffuse as compared with the single-crystal spots and there is only a slight indication of bands between the spots. Probably the most quantitative method of examining the quality of transitional films is by X-ray rocking curves. X-ray rocking curves were taken of epitaxial layers and single-crystal substrate material adjacent to the epitaxial layer. For epitaxial layers prepared above

260°C, there was no difference between the rocking curves. However, for layers prepared at 245°C, significant differences existed. Figure 3 contains (422) rocking curves of epitaxial layers deposited on (100) substrates at 245°C and of the (100) substrate material itself. The two peaks for each curve are characteristic of $Cu_{K_{\alpha 1}}$ and $Cu_{K_{\alpha 2}}$ radiation. The baseline of the curve representing the epitaxial layer is higher than the curve representing the substrate. The raised baseline indicates that a mosaic structure exists. A mosaic structure was confirmed by X-ray topographs. In addition, the resolution of the curve representing the epitaxial layer is poorer than the resolution of the curve representing the substrate. Broadening is associated with dislocations, native defects, and other crystal defects.

These studies show that the transition from single-crystal to polycrystalline material is not abrupt and probably spans a temperature range of 50°C. Therefore, in preparing p-n junctions with grain boundaries, it will be necessary to grow polycrystalline film at about 200°C on single-crystal substrates. After polycrystalline grain growth is well established, the substrate temperature will be increased to about 260°C and the p-n junction incorporated.

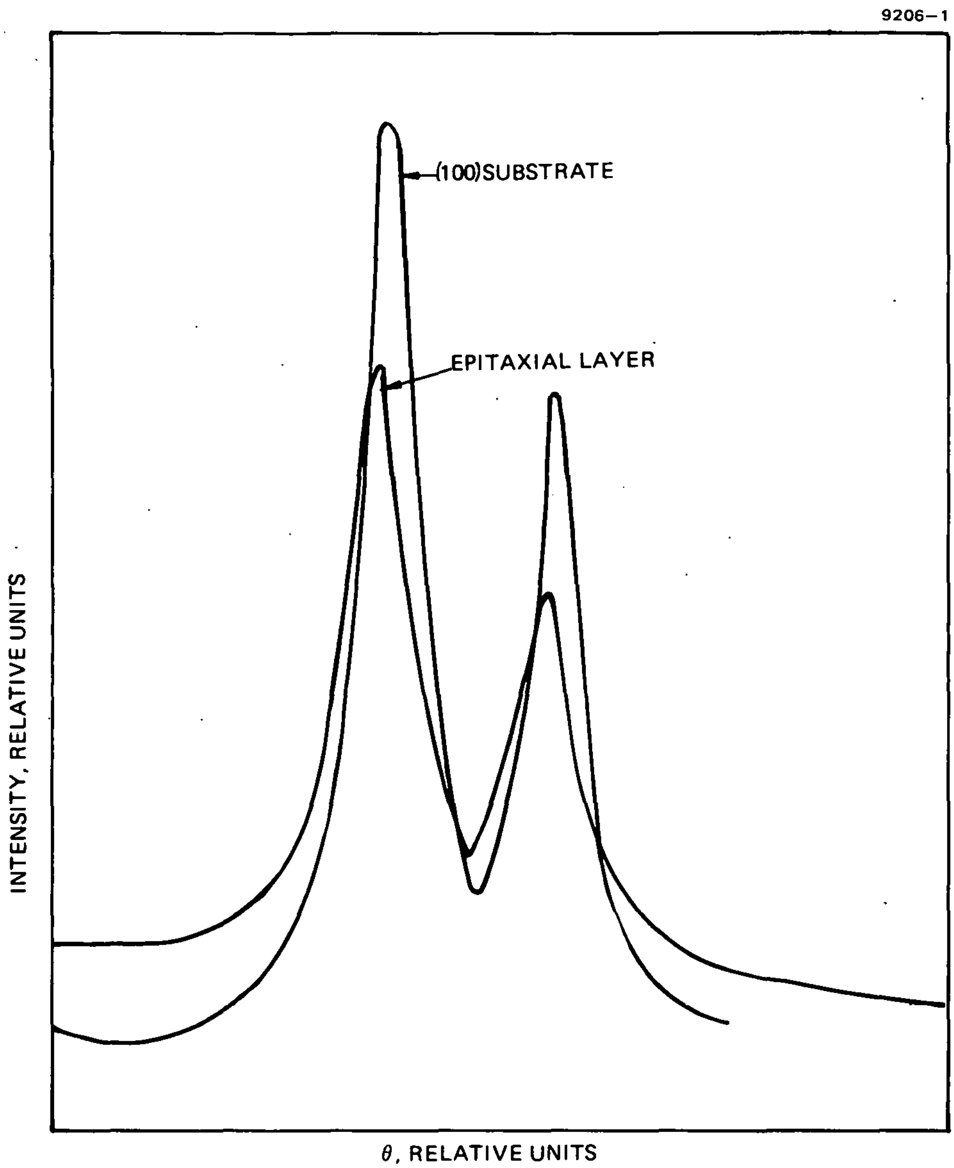

Figure 3. X-ray rocking curves of (100) InP substrates and epitaxial InP layers prepared at 245°C for the (422) reflections of $Cu_{K_{\alpha 1}}$ and $Cu_{K_{\alpha 2}}$.

SECTION 3

ETCHING STUDIES

One approach to reducing leakage current due to grain boundaries is to remove the InP grain boundary by chemical etching and to passivate the surfaces of the resulting free-standing single-crystal mesas containing the p-n junction. Figure 4 (top) depicts such an approach for a heteroface-homojunction structure. The literature suggests methods for passivating the fresh surface. This report is addressed to the initial problem of preferentially etching the semiconductor at the grain boundary. In the second quarter, we found that a $3HNO_3$:HCl etch preferentially etched the grain boundaries in bulk polycrystalline InP. This report summarizes work in the third quarter improving this etch.

Studies were undertaken on polycrystalline wafers purchased from Metals Research and received as complimentary samples from Bell Laboratories. In our initial studies, the surfaces were saw cut. No chemical processing was undertaken so as to not interfere with the effect of the subsequent etch. When HF was added to the HNO_3:HCl etch, the degree of preferred etching increased. Wafers were etched in a mixture of 5 parts (by volume) of semiconductor grade 37% aqueous hydrochloric acid, 3 parts of electronic grade 70% aqueous nitric acid, and 4 parts of semiconductor grade 48% aqueous hydrofluoric acid. The 5HCl:$3HNO_3$:4HF etch preferentially attacked about 80% of the grain boundaries. This is to be compared with the 10% yield found earlier with the HCl:HNO_3 etch. The arrows in Figure 4 (bottom, left) show positions along the grain boundaries that were examined after etching with the HCl:HNO_3:HF etch. The symbol P refers to grain boundaries that were preferentially etched resulting in grooves. The symbol N refers to grain boundaries that were not preferentially etched. In one case, noted by the question mark, the manner of attack was not clear. The lower right photograph shows an enlarged region of one of the preferentially attacked grain boundaries. Besides the higher yield of preferred grain boundary etching as compared with the HCl:HNO_3 etch, the HCl:HNO_3:HF etch appears to etch surfaces of different orientations much more slowly and at a more uniform rate.

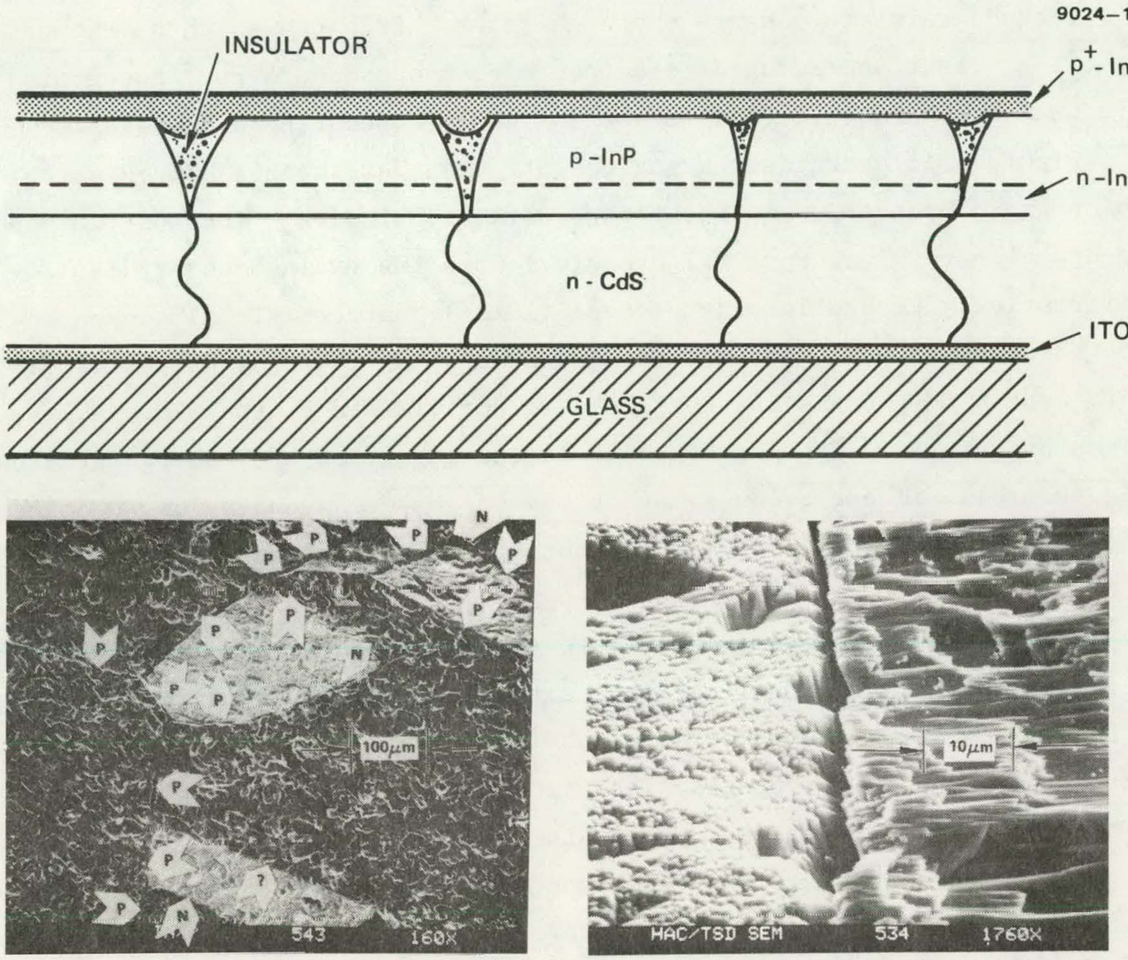

Figure 4. (Top) Suggested approach for passivating grain boundaries in InP/CdS all-thin-film system. (Bottom) SEM photographs showing (left) preferential (P) and nonpreferential (N) etching of grain boundaries in bulk polycrystalline InP by $HCl:HNO_3:HF$ and (right) preferred etching of grain boundaries at higher magnification.

When we found that the $5HCl:3HNO_3:4HF$ etch produced vastly improved results, more detailed experiments were undertaken. Wafers with numerous millimeter-size grains were polished to a mirror finish and etched for 5 min to delineate the grain boundaries. Wax dots were then applied to selected grains to measure the etch rates. Etching was then resumed for 1 hr. Light and scanning electron microscopes and X-ray Laue-grams were used to characterize the resulting grain boundaries and grains.

Figure 5 illustrates the various effects that the $HCl:HNO_3:HF$ etch has on grain boundaries in these more detailed studies. The most common and dramatic result occurs (Figure 5(a)) when the grain boundary is preferentially etched leaving a deep (>10 μm), narrow (<1 μm) canyon with parallel sides. Measurement of the depth of the canyons was difficult, and in most cases the bottoms were not visible by the SEM. A less common preferential etching behavior is the formation of V-shaped grooves (Figure 5(b)). These grooves may or may not have canyons below the grooves. Figure 5(c) shows a preferentially etched grain boundary where a transition occurs from the "canyon-type" etching to the "V-type groove" etching. The transition may be due to the change in orientation of the grain boundary plane with respect to either the two crystallites or the surface. However, in only a few cases (Figure 5(d)) did preferred etching of the boundary not occur. Table 1 summarizes the effects of the etch on the grain boundaries. Forty three of the 47 (or 90%) grain boundaries observed underwent some degree of preferential etching. Confirmed twin boundaries were not preferentially attacked. In general, submicrometer steps were found across grain boundaries due to different etch rates on crystallites of different orientations. As expected, these step heights were less than the thickness of the InP removed from the crystallites. From less than 1/4 μm to 2-3/4 μm was removed from the grains over the 1-hr etch. In general, the depth of the grain boundary attack was much greater than the surface of the adjacent grains.

In the all-thin-film InP/CdS system, where InP is deposited onto recrystallized CdS, the normals of the heterostructure grains have a preferred orientation. However, the degree of preferred orientation is so slight that grain boundaries enclosing grains of all orientations must

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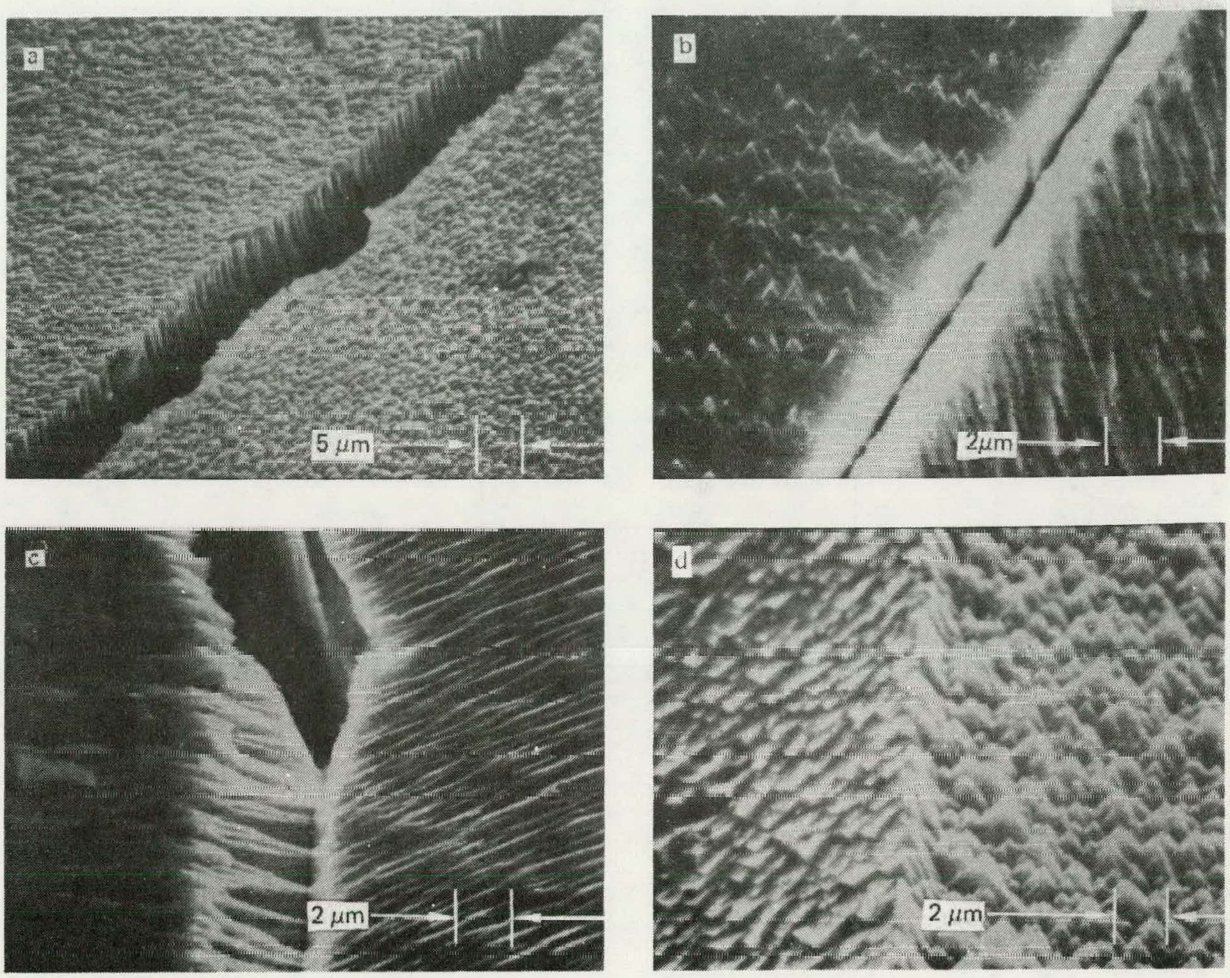

Figure 5. Scanning electron microscope pictures of the effects of the $HCl:HNO_3:HF$ etch on the grain boundaries in bulk InP: (a) Canyon attack, (b) V-groove attack, (c) transition from canyon to V-groove attack, and (d) step attack but no preferential etching down grain boundary.

Table 1. Summary of Effect of $HCl:HNO_3:HF$ Etch on Grain Boundaries in Bulk InP

Boundary Type	Type of Attack						
	Canyons	V-Groove	Canyon and V-Groove	Fraction of Boundary Attacked	Ambiguous Result	No Preferential Attack	Total
Grain boundaries	34	6	2	1	2	2	47
Twin boundaries (confirmed)	0	0	0	0	0	10	10
Twin boundaries (suspected)	0	0	0	0	0	3	3
Twin boundaries (lacking identical twins)	0	2	0	0	0	3	5

6843

be considered in any passivation scheme. In our study, about 10% of the grain boundaries were not preferentially etched. An attempt was made to establish conditions under which preferred etching did not occur. There was no obvious correlation between preferred etching and either the normals of adjacent grains as determined by Laue-grams or the relationship between the grains. Two additional factors that might affect grain boundary etching are the presence of accumulated impurities at the grain boundaries and the orientation of the grain boundary plane with the surface. Investigation of these factors was beyond the scope of these studies.

During ideal homoepitaxial growth of nuclei, the periodicity of the lattice in the direction normal to the substrate is replicated. During subsequent lateral growth in the remaining two dimensions, periodicity is also maintained where nuclei coalesce. During heteroepitaxial growth of InP on CdS, periodicity is not preserved. For example, in the c direction, the ABAB structure of the CdS transforms to either an ABAB/ABCDBC or ABAB/CABCAB structure. (Here the CdS-to-InP transition is indicated by "/".) The lateral coalescence of nuclei having different stacking sequences could result in a boundary with some form of symmetry but with a degree of disorder that might result in a high density of deep electronic levels at the boundary. Extreme cases of low symmetry comparable to a grain boundary may be evidenced by preferential etching. In our studies, preferred etching was not generally observed across the twin boundaries. However, since preferred etching did occur across two of these boundaries, we investigated the nature of these boundaries in more detail. The insert in the upper left corner of Figure 6 shows a heavily twinned section of the polycrystalline wafer. The region of interest is outlined in the insert and magnified in the remainder of Figure 6. Grain 10 is used as a reference for the twinning events. Proceeding counterclockwise in the magnified region, region 10T is a twin of region 10, region 10TT is a twin of region 10T, and region 10TTT is a twin of region 10TT. Preferential etching does not occur across any of these twin boundaries. Where this loop closes (i.e., where 10 meets 10TTT), the neighboring crystallites have been displaced by three twinning

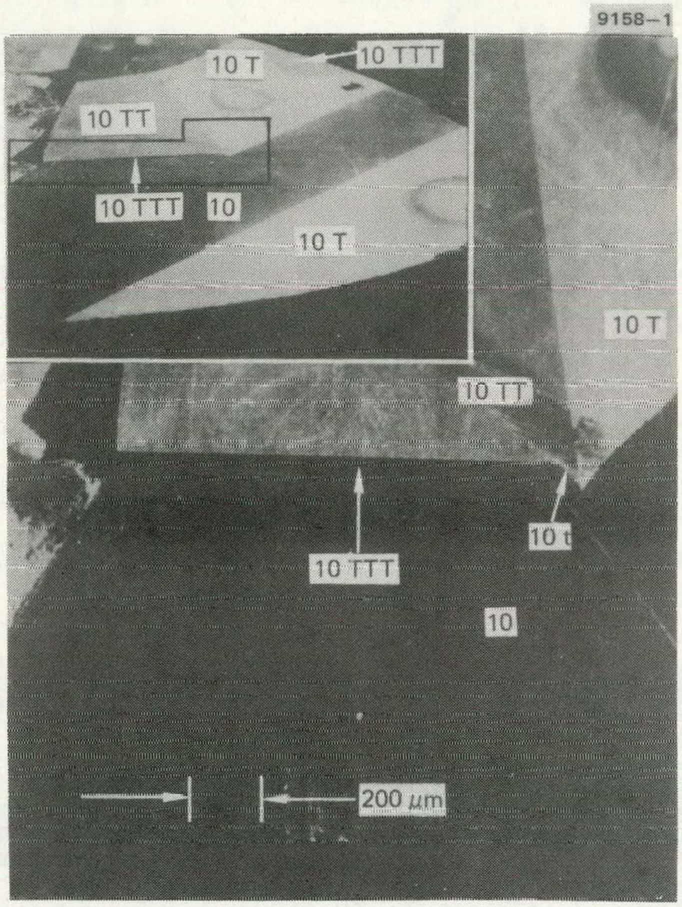

Figure 6. Scanning electron microscope picture of (upper left corner) heavily twinned bulk polycrystalline InP wafer and (remainder of picture) expanded view of insert showing a boundary between grains 10TTT and 10T which was formed by multiple twinning events and was also preferentially etched by a $5HCl:3HNO_3:4HF$ etch.

events in different directions in three dimensions. The second such sequence, not discussed here, occurs at 10t. The cumulative lattice mismatch, or stress tending to cause mismatch, may reasonably be expected to have reached values comparable to those of actual grain boundaries. These are the only two actual or suspected twin boundaries in the specimen that are not substantially rectilinear and also the only ones that exhibit preferential attack by the etchant. The attack took the form of V grooves similar to that shown in Figure 5(b), rather than deep canyons as in Figure 5(a). A lattice mismatch resulting from the coalescence of nuclei with different stacking sequences could conceivably lead to high leakage currents in the InP/CdS thin-film system. We anticipate that a preferential etch would also attack such a mismatched region.

This work was a preliminary effort to identify an etchant for preferentially removing grain boundaries on InP prepared by vapor deposition techniques. The $HCl:HNO_3:HF$ etch meets the criterion of slow attack on grains regardless of orientation. Although these results were obtained on bulk polycrystalline material, there is no reason to expect this behavior to change for material prepared by other techniques. The preferential attack at the grain boundaries could be enhanced by the segregation of impurities at grain boundaries. However, such an extreme degree of preferred etching could hardly be associated with impurities alone. No explanation was found as to why the $HCl:HNO_3:HF$ etch attacked only 90% of the grain boundaries. However, the degree of success justifies either modifying the etchant or developing an alternative reagent. These studies also brought to our attention that under special conditions interfaces formed from twins and stacking faults might contain such a high degree of disorder that if they were not passivated they also might contribute to leakage currents at the p-n junction.

SECTION 4

FUTURE PLANS

Having established control over the preparation of single-crystal and polycrystalline films, we intend during the next quarter to prepare p-n junctions with and without grain boundaries. The structure containing grain boundaries will consist of (poly p^+InP/poly p-InP/poly n-InP/single n^+ InP substrate). These studies will complement work on the all-thin-film InP/CdS system, which uses CdS as the substrate. The structure of the InP/CdS system is (poly p^+-InP/poly p-InP/poly n-CdS/ poly n^+ITO).

The experimental part of the etching studies in the InP grain boundaries are completed. However, it is not apparent why only 90% of the grain boundaries are preferentially attacked. Consequently, during the next quarter we will analyze our experimental data, in particular the orientation of the crystallites with respect to the grain boundaries, to uncover reasons why all the grain boundaries are not preferentially attacked.

APPENDIX

GRAIN BOUNDARY ETCHING IN InP

Larry Hershenson and Ken Zanio

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Abstract

Grain boundaries in bulk polycrystalline InP wafers were found to be preferentially attacked by a $5HCl:3HNO_3:4HF$ etch. Canyons with depths greater than 10 μm and widths less than 1 μm were the most common form of attack. Although the etch had no effect on simple twin boundaries, preferential attack was observed at interfaces formed by multiple twinning events.

Supported by the Department of Energy under Contract ET-78-C-01-3412.

The efficiencies of solar cells prepared from polycrystalline semiconductors are less than the efficiencies of cells prepared from corresponding materials in their single-crystal form. In direct bandgap materials such as GaAs,[1] InP,[2] and some chalcopyrites,[3] the efficiency loss is associated largely with lower open-circuit voltage. This, in turn, is attributed to increased leakage currents at grain boundaries.[5] Because of the need to develop higher efficiency thin-film solar cells, there is increasing effort[4,5] to passivate grain boundaries in various semiconductors. In our studies of the InP/CdS system, we have adopted a different approach towards reducing grain boundary leakage currents. The proposed procedure is to remove the grain boundary by chemical etching and to passivate the surfaces of the resulting free-standing single-crystal mesa containing the p-n junction. Although some methods of passivation have been discussed in the literature,[6] the problem has not yet been completely resolved and the topic is not further discussed in this paper. This letter addresses the problem of preferentially etching the semiconductor at the grain boundary. To our knowledge, this is the first report of the intentional selective removal of grain boundaries in a semiconductor by chemical etching.

To reduce leakage currents, the grain boundary must be etched through the junction. Therefore, we are considering the case of an InP p-n homojunction structure deposited on a CdS window. Two criteria of the required etchant are that it preferentially remove at least a few micrometers of grain boundary material and that the thickness of the layers removed from the surface of the single-crystal grain be small compared to the depth of the preferentially etched grain boundary region. Studies were undertaken on polycrystalline wafers of InP (purchased from Metals Research and received as complimentary samples from Bell Laboratories). So as not to interfere with the effects of subsequent etching, no chemical processing was performed. Initial studies with $FeCl_3$, HNO_3, HCl, aqua regia/acetic, AB, and bromine/methanol etches on flat, saw-cut surfaces showed no preferential etching at the grain boundaries. Evidence of preferential etching was found with aqua regia. When we found that a $5HCl:3HNO_3:4HF$ etch produced the desired results, a wafer with numerous millimeter-sized grains was mechanically polished to a mirror finish. The specimen was etched for 5 min in a mixture of 5 parts (by volume) of semiconductor grade 37% aqueous hydrochloric acid, 3 parts of electronic grade 70% aqueous nitric acid, and 4 parts of semiconductor grade 48% aqueous hydrofluoric acid. After wax dots were applied to selected grains to provide unetched areas for measurement of step heights, etching was resumed for 1 hr. Light and scanning electron microscopes and X-ray Laue-grams were used to characterize the resulting grain boundaries and grains.

Figure 1 illustrates the various effects that the $HCl:HNO_3:HF$ etch has on grain boundaries in InP. The most common and dramatic result occurs (Figure 1(a)) when the grain boundary is preferentially etched leaving a deep (>10 μm), narrow (<1 μm) canyon with parallel sides. Measurement of the depth of the canyons was difficult, and in most cases the bottoms were not visible by the SEM. A less common preferential etching behavior is the formation of V-shaped grooves (Figure 1(b)). These grooves may or may not have canyons below the grooves. Figure 1(c) shows a preferentially etched grain boundary where a transition occurs from the "canyon-type" etching to the "V-type groove" etching. The transition may be due to the change in orientation of the grain boundary plane with respect to either the two crystallites or the surface. However, in only a few cases (Figure 1(d)) did preferred etching of the boundary not occur. Table I summarizes the effects of the etch on the grain boundaries. Forty three of the 47 (or 90%) grain boundaries observed underwent some degree of preferential etching. Confirmed twin boundaries were not preferentially attacked. In general, submicrometer steps were found across grain boundaries due to different etch rates on crystallites of different orientations. As expected, these step heights were less than the thickness of the InP removed from the crystallites. From less than 1/4 μm to 2-3/4 μm was removed from the grains during the 1-hr etch. In general, the depth of the grain boundary attack was much greater than the surface of the adjacent grains.

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In the all-thin-film InP/CdS system, where InP is deposited onto recrystallized CdS, the normals of the heterostructure grains have a preferred orientation. However, the degree of preferred orientation is so slight that grain boundaries enclosing grains of all orientations must be considered in any passivation scheme. In our study, about 10% of the grain boundaries were not preferentially etched. An attempt was made to establish conditions under which preferred etching did not occur. There was no obvious correlation between preferred etching and either the normals of adjacent grains as determined by Laue-grams or the relationship between the grains. Two additional factors that might affect grain boundary etching are the presence of accumulated impurities at the grain boundaries and the orientation of the grain boundary plane with the surface. Investigation of these factors was beyond the scope of these studies.

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The authors acknowledge valuable discussions with Roger Turk and Frans Krajenbrink and technical assistance by Art Timper and Henry Montano. Metallographic preparation was done in the laboratory directed by Arun Kumar. Special thanks are due to Ken Miller for his interpretation of the Laue-grams and to Gerry Meldrum for interpreting the SEM results.

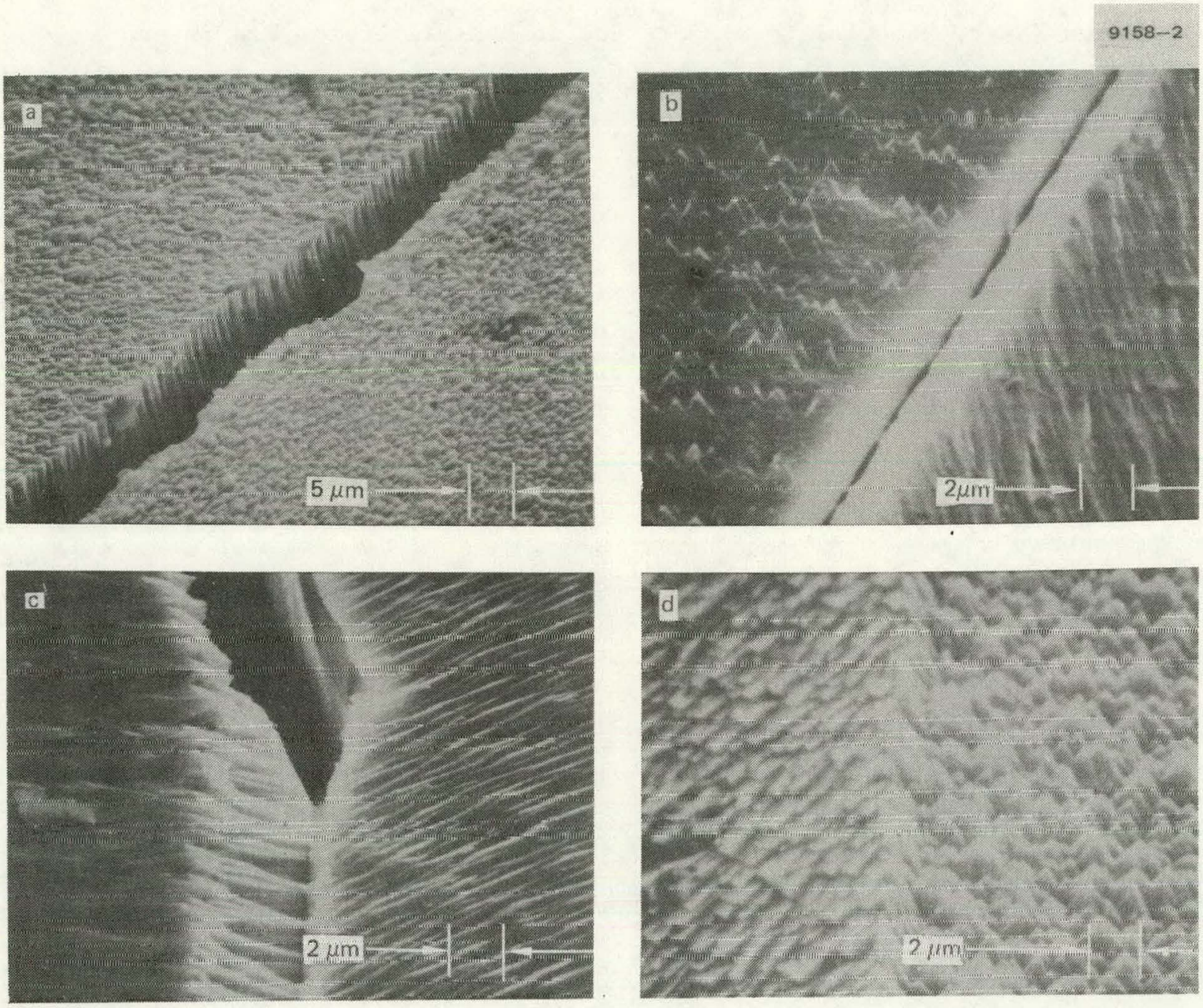

Figure 1. Scanning electron microscope pictures of the effects of the $HCl:HNO_3:HF$ etch on the grain boundaries in bulk InP: (a) Canyon attack, (b) V-groove attack, (c) transition from canyon to V-groove attack, and (d) step attack but no preferential etching down grain boundary.

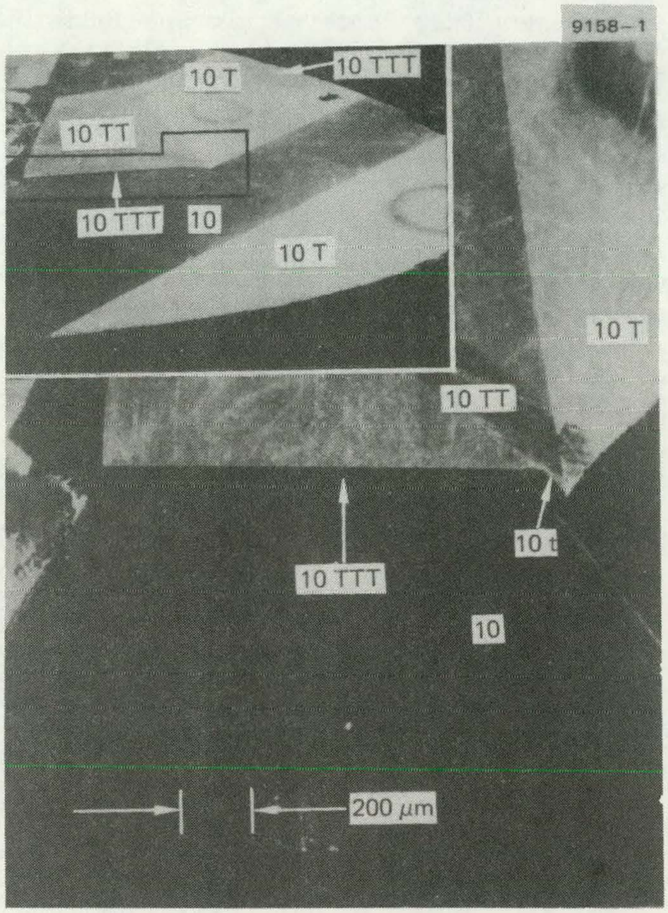

Figure 2. Scanning electron microscope picture of (upper left corner) heavily twinned bulk polycrystalline wafer and (remainder of picture) expanded view of insert showing a boundary between grains 10TTT and 10T which was formed by multiple twinning events and was also preferentially etched by a $5HCl:3HNO_3:4HF$ etch.

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