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Thermal Oxidation of Indium Phosphide

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ABSTRACT

Transmission electron microscopy has been used to study the thermal oxidation of indium phosphide. When the oxidation was carried out at temperatures lower than 450°C and pressures of approximately 10 torr of oxygen the product was amorphous. At higher temperatures polycrystalline In_2O_3 was the final product after decomposition of epitaxially grown $InPO_4$. The sequence of events taking place during the reaction seems to indicate that a dielectric layer might be grown on InP with $InPO_4$.

INTRODUCTION

Indium phosphide has received increasing attention in recent years. Its high electron mobility and suitable bandgap makes it attractive for applications in a wide range of microelectronic devices (6). A recent publication (5) highlights the main problems which InP MISFET technology is currently facing in terms of obtaining an appropriate insulator. Thermally grown oxide appears as one possible alternative, which however has not been thoroughly investigated yet. When compared to GaAs, InP is expected to provide better interface properties of insulating layers due to its higher resistance to oxidation (6).

Wagner and Wilsen (2) studied the growth rate and the chemical composition of thermally grown oxides in dry oxygen. The oxide was found to grow very slowly below 350°C and rapidly above that temperature. All the oxides produced between 350°C and 450°C consisted of approximately 70-75% In_2O_3 and 25-30% P_2O_5. Wagner

at high temperatures and low pressures. During the course of the experiments no direct evidence was found of the presence of P_2O_5 or any phosphorus containing phases other than InP and $InPO_4$. Nevertheless our observations led us to postulate a likely reaction sequence for the oxidation at temperatures between 450°C and 600°C:

$$2\ InP + 4\ O_2 \rightarrow 2\ InPO_4 \rightarrow In_2O_3 + P_2O_5 \quad [1]$$

Due to the lack of experimental description provided by Petford-Long and Smith (8) it is difficult to compare their results to ours. However one should note that the thinner the observed area, the less representative it is of the bulk material. Hence, fast $InPO_4$ decomposition according to [1] and P_2O_5 loss might account for the failure to detect phosphate in reference (8).

Figure 4 shows a set of diffraction patterns of a thin foil of InP submitted to oxidation at 600°C. Pattern 4A was obtained prior to oxidation; pattern 4C from an area near the edge of the foil which had been fully oxidized (similar to the one shown in Figure 3 at 20 min); pattern 4B was taken from an area which had been partially oxidized. The latter is magnified in Figure 5, where the reflections of the $InPO_4$ formed according to reaction [1] are indicated. One can see that $InPO_4$ did not grow randomly oriented but has very specific crystallographic relations to the parent phase (InP). Three orientation relationships could be identified and those are indicated by their subscript in Figure 5 and listed below with the corresponding letter:

RESULTS AND DISCUSSION

At temperatures below 450°C oxidation of InP produced predominantly an amorphous layer. Below 350°C the oxide growth is extremely slow and any film is barely noticeable, even after long oxidation periods (Figure 1). This agrees with the kinetic information provided by Wagner and Wilsen (2), according to which more than three hours are required to produce an oxide film of 50 Å. The amorphous oxide growth rate becomes increasingly faster as the temperature is raised, but surface degradation becomes more evident, as shown in figure 2 and pointed out by Simonne (6).

Electron diffraction has indicated that the ultimate product of oxidation at temperatures above 450° is polycrystalline In_2O_3, in agreement with previously reported results (1-8). Figure 3 shows a thin foil of InP before and after being oxidized for 20 minutes at 500°C. Formation of In_2O_3 is associated with either phosphorus volatilization from the oxide layer or to its accumulation at the InP/oxide interface with subsequent diffusion of P into the substrate. The latter alternative is severely limited by the low solubility of P in InP. Thus most of the P which is rejected from the oxide layer into InP should precipitate out. Some previous investigations (9) have in fact reported accumulation of P at the interface.

The oxidation reaction, as found here however, appears to proceed by initial formation of $InPO_4$ which then transforms into In_2O_3 while P either volatilizes or is rejected into the InP. The former effect is likely to occur to a greater extent than the latter because P_2O_5 is extremely volatile and the e-cell is kept

As one can conclude from the previous paragraphs, it does not appear that a complete understanding of the oxidation reaction has been achieved yet. Some disagreement on the nature of the product phases as well as on the temperatures at which they are formed still remains. The present work attempts to examine the structural changes which take place during thermal oxidation of InP at temperatures between 300°C and 600°C. In-situ transmission electron microscopy was performed in order to observe this reaction and the several phases which form during its development. The results were partially explained in terms of the O-lattice concept proposed by Bollmann (10).

EXPERIMENTAL PROCEDURE

Undoped indium phosphide (100) wafers provided by CrystaCom Inc. were used throughout this work. Transmission electron microscope samples were prepared by thinning the original wafers from the back unpolished surface to approximately 200 μm. At this stage 3mm disks were cut, dimpled and chemically polished by immersion in a 2% Br-in methanol solution until a hole was produced.

Electron microscopy was carried out in two high voltage microscopes: a KRATOS EM1500 and a HITACHI HU650. Both microscopes were equipped with an environmental cell of the side entry type as described elsewhere (11). The experiments consisted of loading the specimen into the cell, heating it in an inert atmosphere to the oxidation temperature and starting the flow of oxygen. The tested temperatures ranged from 300°C to 600°C and all the oxidations were carried out at an oxygen partial pressure of 10 torr.

(2) also found some evidence of low concentration of another bonding state of P. Yamaguchi and Ando (3) studied the thermal oxidation of InP and the properties of the oxide films. They concluded that the process is controlled by diffusion through a polycrystalline film made of In_2O_3 and P_2O_5. Resistivities of the oxide film, measured at room temperature, range from 10^{+8} to 10^{+9} ohm.cm and decreased with increasing oxidation temperature and time. Such a decrease was proposed to be due to loss of P_2O_5 (3). Another study (4) detected elemental phosphorus at temperatures between 350°C and 550°C, and concluded that the dominant reaction product is $InPO_4$ at the higher temperatures.

Simonne (6) has recently indicated that for MOS applications, oxidation temperatures should be kept below 350°C to minimize degradation of the substrate. In this temperature interval Simonne (6) found $InPO_4$ and In_2O_3 as the resulting phases with excess phosphorus appearing at the interface between oxidation products and semiconductor. The same products were obtained by Fathipour et al. (7) after photoenhanced thermal oxidation of InP at temperatures between 200°C and 400°C.

Recently Petford-Long and Smith (8) used high resolution electron microscopy to study the evolution of the oxidation reaction of In III-V compound semiconductors, among them InP, but have not found any phosphate forming. They identified the majority of the product crystallites as In_2O_3 and also reported the formation of some metallic In. Unfortunately the description of their experimental conditions is quite poor and no details are provided regarding temperature or pressure of the oxidizing agent.

a) $[001]_{InP}$ // $[001]_{InPO_4}$

$(110)_{InP}$ // $(110)_{InPO_4}$

b) $[001]_{InP}$ // $[001]_{InPO_4}$

$(110)_{InP}$ // $(1\bar{1}0)_{InPO_4}$

c) $[001]_{InP}$ // $[001]_{InPO_4}$

$(110)_{InP}$ ^ $(110)_{InPO_4}$ = 25^{o}*

*This notation means that the angle between the two planes is 25^{o}.

Orientation relationships presented in (a) and (b) are twin related as one can see in the schematic representation shown in Figure 6a. This figure also contains a (001) view of the InP lattice. Figure 6b contains the representation of the two lattices, InP and $InPO_4$, oriented according to (c). Figure 7 shows a bright field image of an indium phosphide thin foil oxidized at $500^{o}C$ to a point where indium phosphide and phosphate are present, as detected by electron diffraction. The epitaxial $InPO_4$ stands out in the micrograph for the staightness of its twin boundaries.

In order to explain the crystallographic relations between the InP and $InPO_4$, the O-lattice concept (12) was invoked. The O-lattice theory is an extension of the coincidence site lattice theory. It provides a means to calculate crystallographic relations between two known lattices, which are most favorable regarding the criterion of minimum misfit between equivalent classes in both lattices. The usefulness of geometric description of crystalline metal-oxide interfaces in the study of mechanisms governing growth of scales has been demonstrated elsewhere (13).

Here calculations were made, according to Bollmann's formalism (12), of the determinant of (I-A') as a function of the rotation angle around [001] of one lattice with respect to the other. I is the identity matrix and A'is given by

$$A' = U \cdot A^{-1}$$

where U is the transformation matrix which accounts for near neighbor correspondence and A is the matrix which transforms one lattice into the other. Only rotation around the z-axis, i.e. [001], was considered here for the sake of simplification. The determinant of (I - A') is plotted versus the rotation angle in Figure 8. According to the O-lattice theory, the best fit between InP and $InPO_4$ occurs at angles which minimize the absolute value of det(I-A'). Those are shown below and compared with the ones resulting from the observed crystallographic relations.

PREDICTED BY O-LATTICE	MEASURED FROM ELECTRON DIFFRACTION PATTERNS
10	11 (a)
72	76 (b)

The agreement between the predicted and measured angle of rotation between the two phases is very good if one considers that only a pure rotation between the two lattices was taken into account. The O-lattice theory was not able to predict the orientation relationship (c) which appeared in Figure 5. The main reason for this is an inherent limitation in using linear transformations for describing the relation between two different crystals. In the case where the relation between lattice points can be directly associated to relation between atoms in the crystal, the theory works quite well. However if the two crystals

involve more than one atomic species, as it is the case here with In and P, a linear transformation is not always able to relate the two crystals atom to atom, but only the two lattices point to point. In other words, the O-lattice theory is appropriate to relate lattices, geometric entities, but fails to relate structures, physical entities, if the bases are non-trivial.

For device processing purposes, as described by Yamaguchi and Ando (3), the decrease in phosphorus content in the oxidation products is not a desired event. In order to avoid such a problem, P overpressures might be used during the processing. Some other complications may arise from such a practice since the effect of this new parameter on the structure of the product phases is still unknown.

CONCLUSIONS

Thermal oxidation of indium phosphide was studied by means of dynamic experiments in high voltage electron microscopes. The low temperature results have indicated the formation of an amorphous product which grows at very slow rates. This agrees with previous observations described elsewhere (2).

At temperatures from 450°C to 600°C formation of orthorhombic $InPO_4$ precedes that of In_2O_3. The former evolves to the latter if sufficient time is allowed for loss of phosphorus. The $InPO_4$ grows epitaxially on InP according to three distinct orientation relationships:

a) $[001]_{InP}$ // $[001]_{InPO_4}$

$(110)_{InP}$ // $(110)_{InPO_4}$

b) $[001]_{InP}$ // $[001]_{InPO_4}$

$(110)_{InP}$ // $(1\bar{1}0)_{InPO_4}$

c) $[001]_{InP}$ // $[001]_{InPO_4}$

$(110)_{InP}$ ^ $(110)_{InPO_4}$ = 25^{o}

$InPO_4$ in relation (a) is twinned with $InPO_4$ in relation (b) along a (110) reflection plane. These orientation relationships agreed with the ones predicted by the O-lattice theory. Such a theory is not capable of predicting all three crystallographic relations because it ignores the effects of the different basis in the two crystals.

Based on experimental observations we expect that use of phosphorus overpressures can be beneficial for the purposes of producing a dielectric layer on InP. Such a layer would consist of $InPO_4$ instead of In_2O_3.

ACKNOWLEDGMENT

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FIGURE CAPTIONS

Figure 1. In-situ thermal oxidation of (001) InP at 300°C and total oxygen pressure of 10 torr. Times in minutes are given on the top left hand side of each micrograph. The diffraction pattern was taken at 50 min and shows no sign of reaction.

Figure 2. In-situ thermal oxidation of (001) InP at 400°C and oxygen pressure of 10 torr. Times in minutes are given at the top left hand side of each micrograph. The diffraction pattern indicates the presence of an amorphous phase, which formed faster at the thinner areas (edges) but consists of a thin film covering the entire sample.

Figure 3. In-situ thermal oxidation of (001) InP at 500°C and oxygen pressure 10 torr. Reaction times are indicated at the top left hand side of each micrograph.

Figure 4. Sequences of diffraction patterns taken during an in-situ oxidation at 600°C and 10 torr oxygen. (A) was obtained prior to oxidation, (B) was obtained at an intermediate time and (C) after oxidation was complete.

Figure 5. Same diffraction pattern as in Figure 4B with the $InPO_4$ reflections being indicated. The subscripts refer to the crystallographic relations mentioned in the text with the corresponding letter.

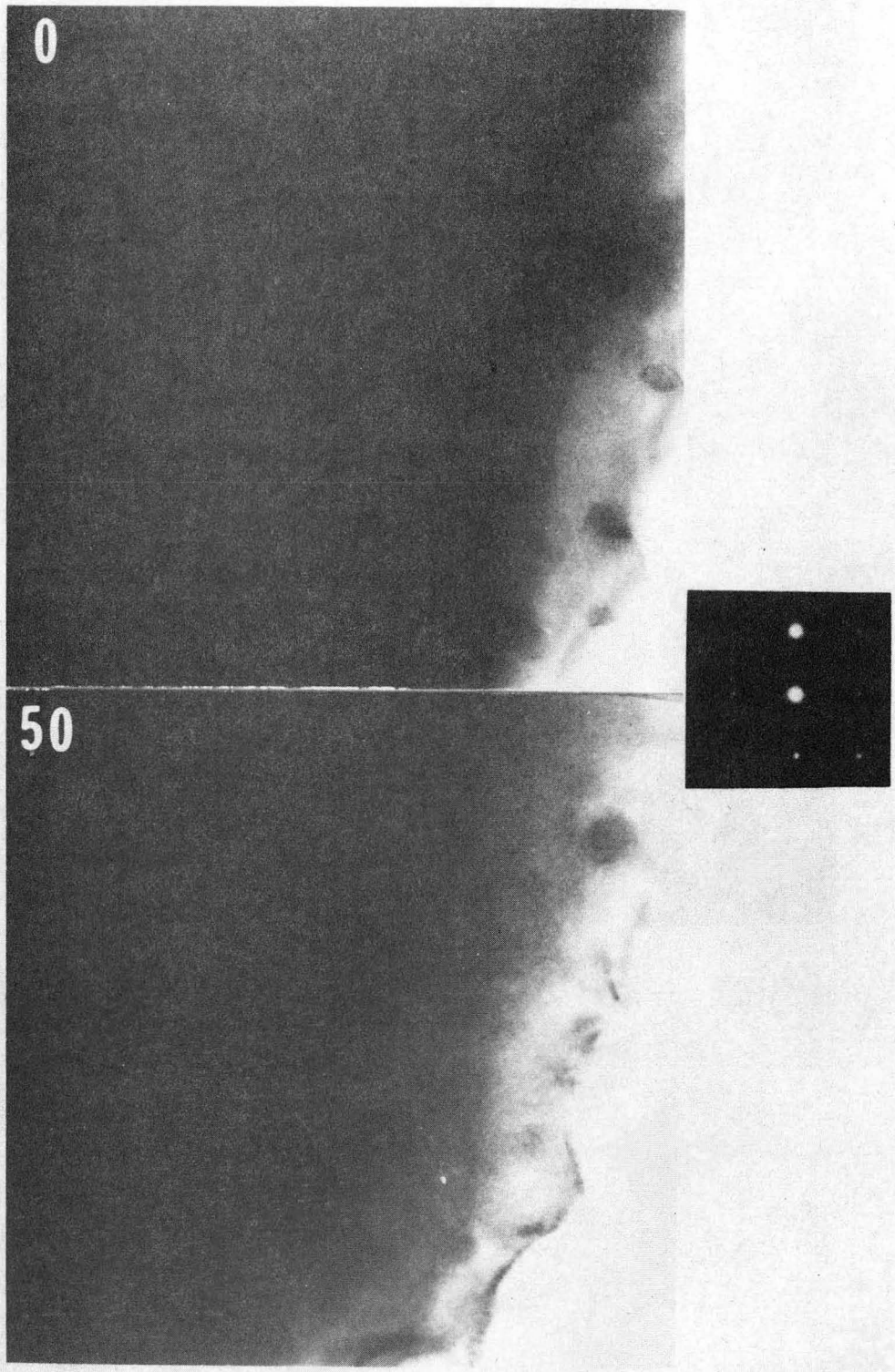
Figure 6a. Schematic representation of (001) InP superimposed on a twinned (001) $InPO_4$. The twin plane is (110). These orientations of $InPO_4$ with respect to InP produced the diffraction patterns (a) and (b) shown in Figure 5.

Figure 6b. Schematic representation of (001) InP superimposed on

(001) $InPO_4$ and rotated with respect to the [001] direction so that $(110)_{InP}$ and $(110)_{InPO_4}$ are about 25^o apart. The orientation corresponds to the diffraction pattern (c) shown in Figure 5.

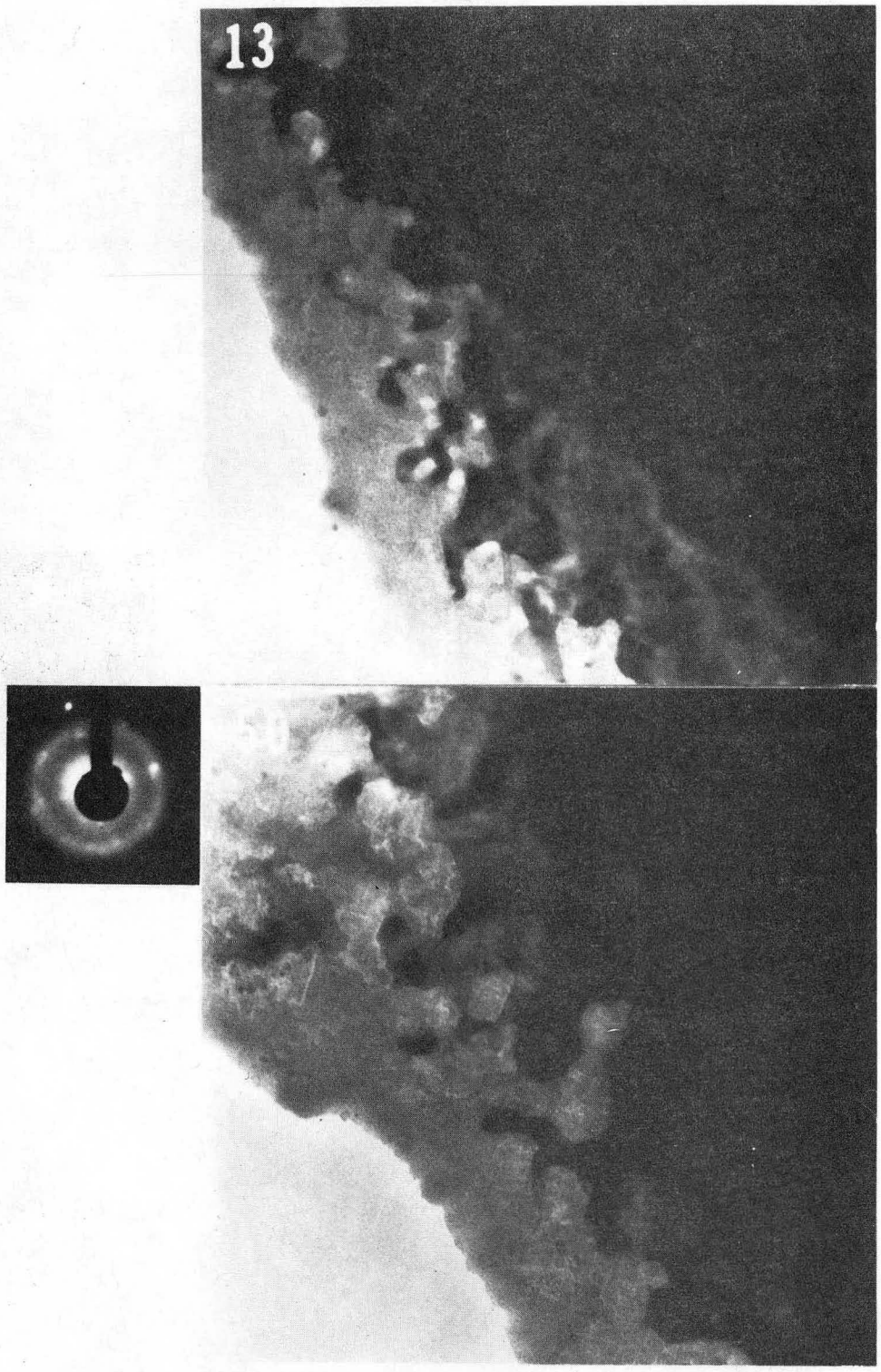
Figure 7. Bright field image of InP oxidized at 500^oC. Phosphate islands are seen to be grown on the InP substrate.

Figure 8. Calculated det(I-A') as a function of the rotation angle around [001] between the InP and the $InPO_4$ lattices.



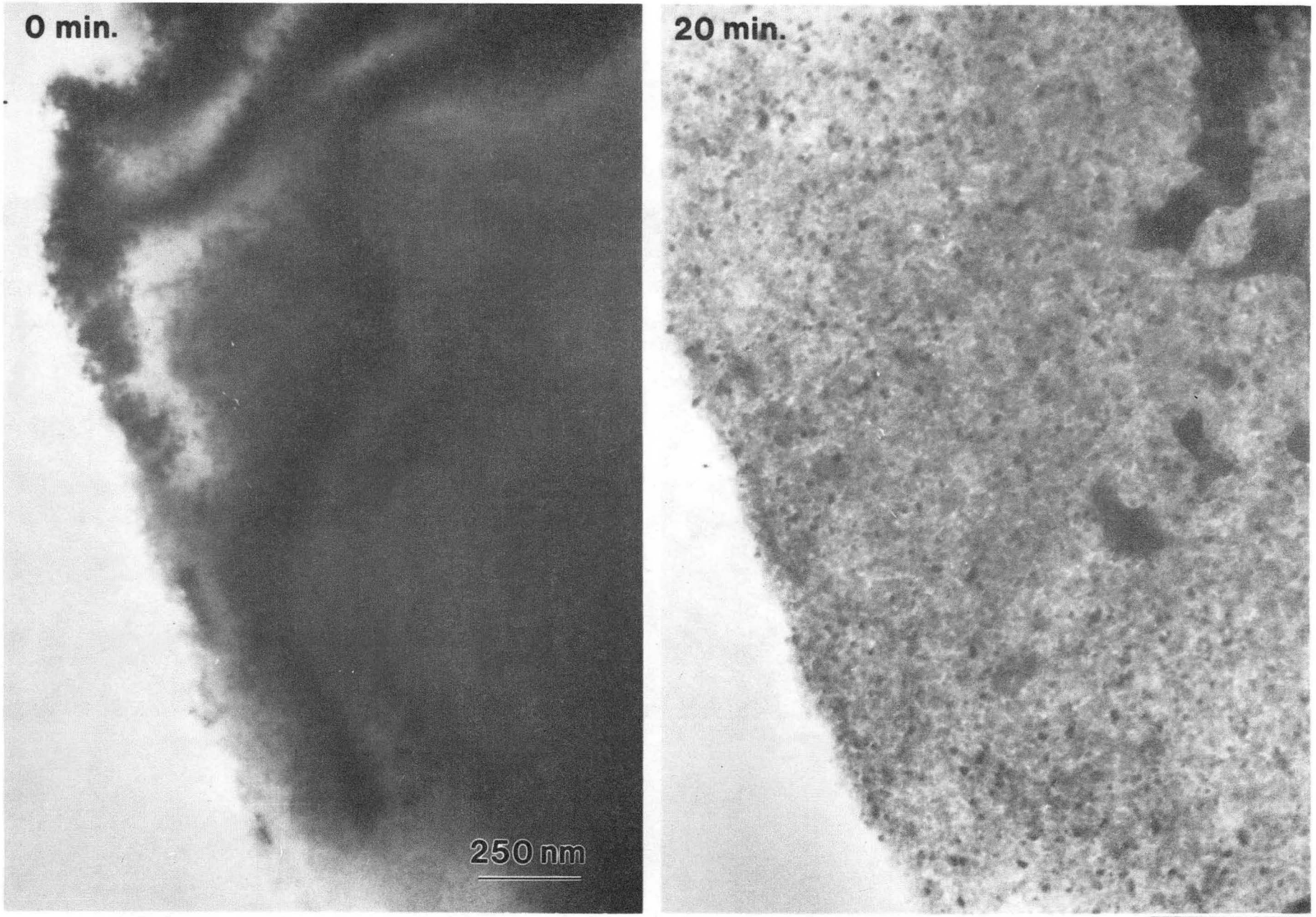
XBB 862-1334

Fig. 1



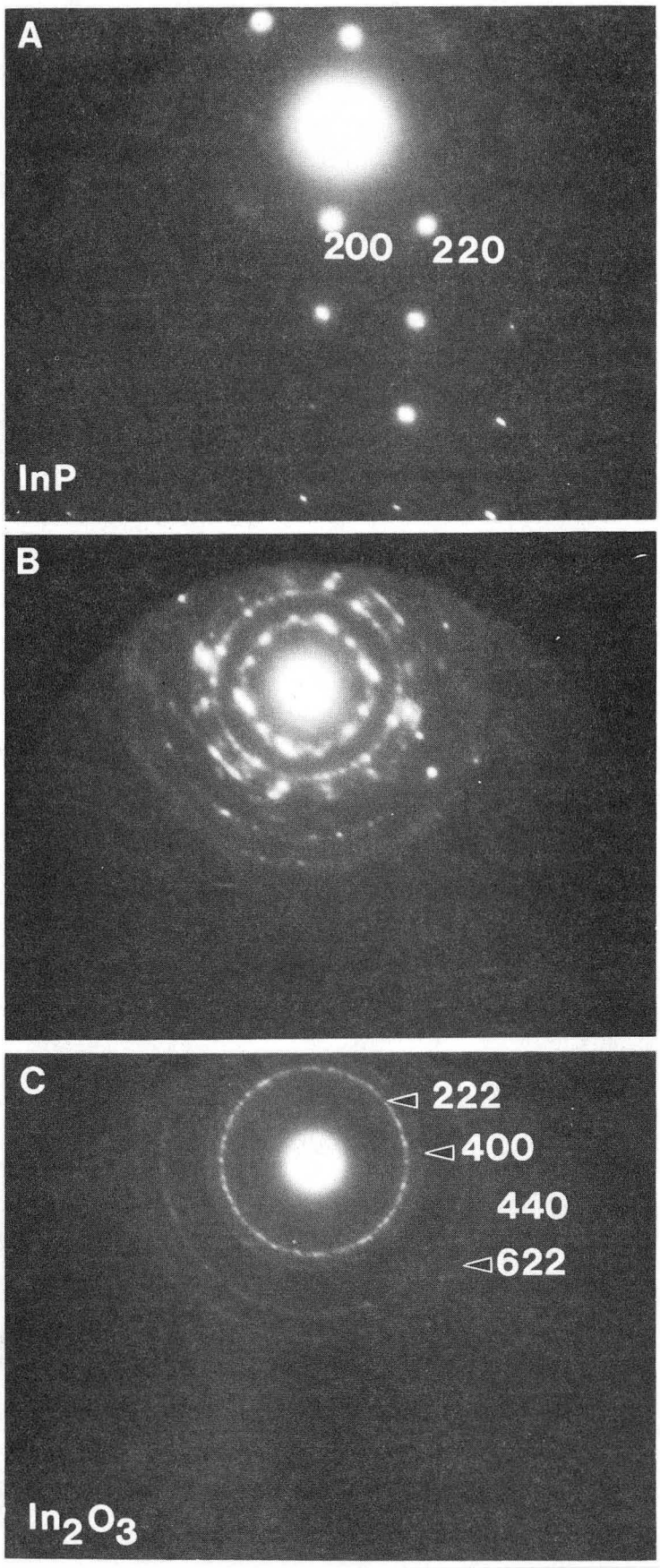
XBB 862-1332

Fig. 2



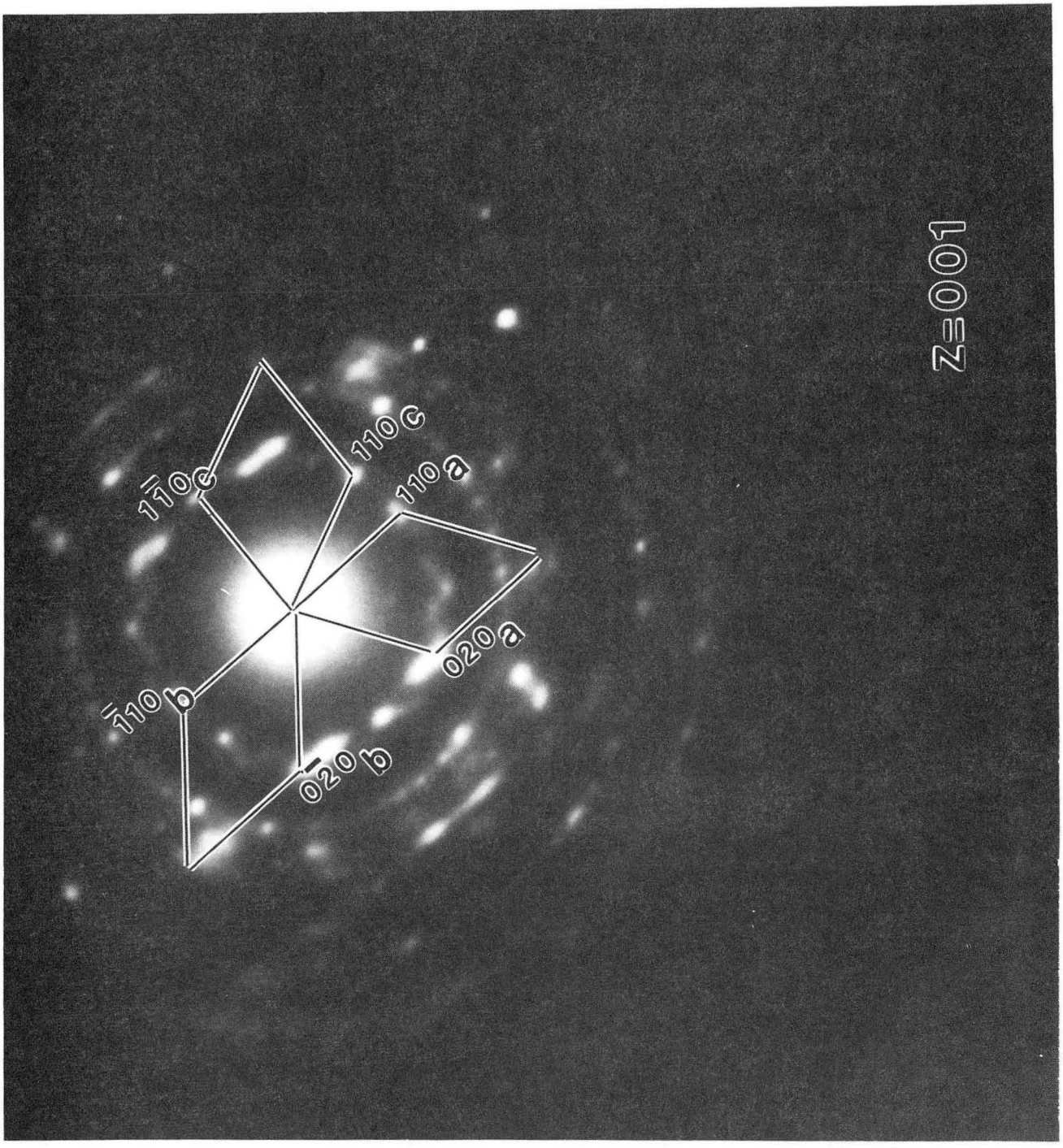
XBB 872-1234

Fig. 3



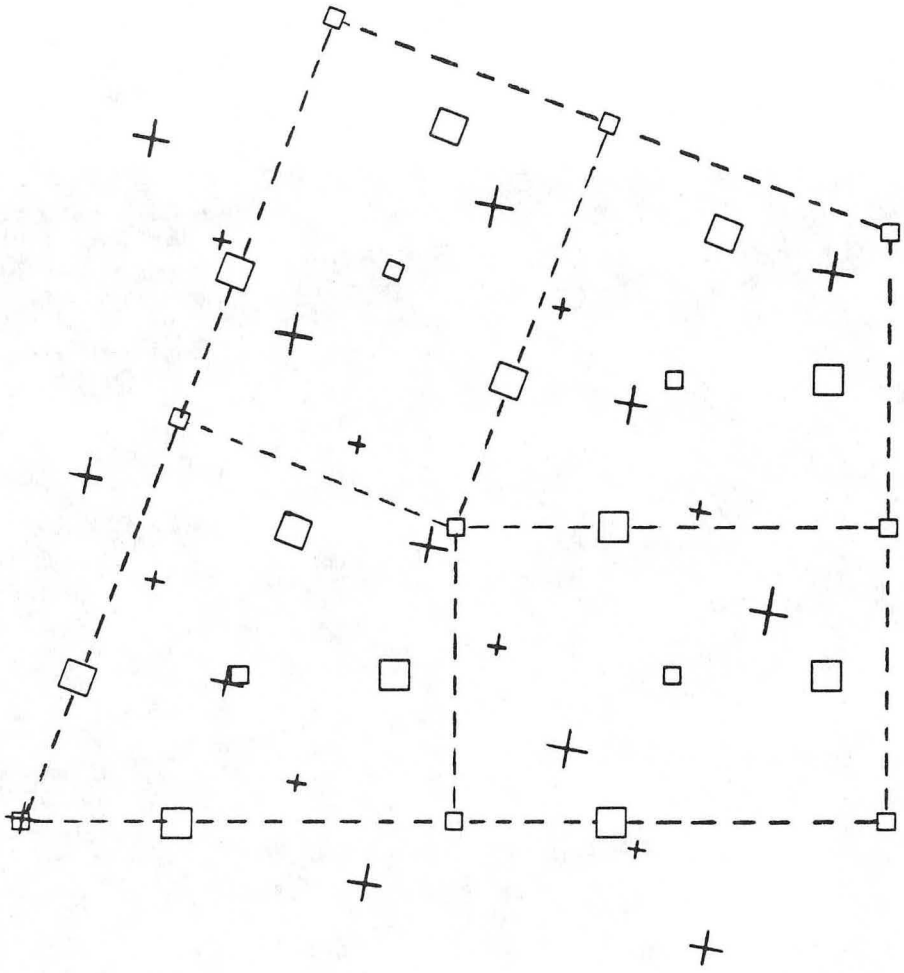
XBB 872-1233

Fig. 4



XBB 874-3013

Fig. 5



$InPO_4$

□ In

□ P

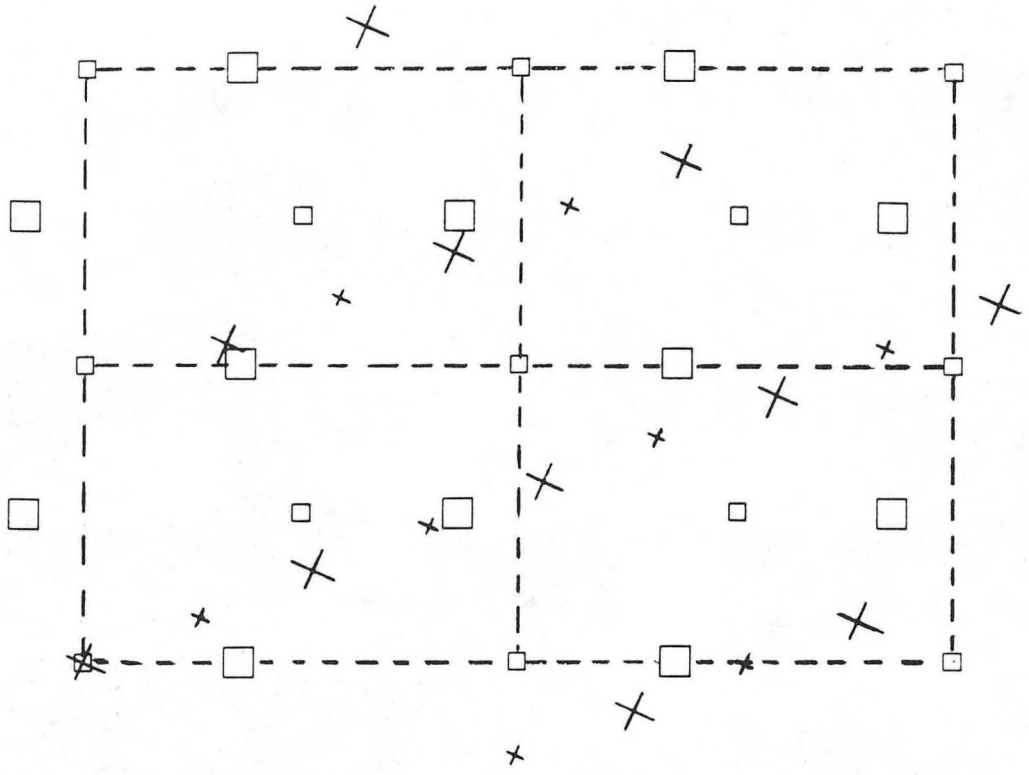
InP

+ P

+ In

XBL 874-1659

Fig. 6a

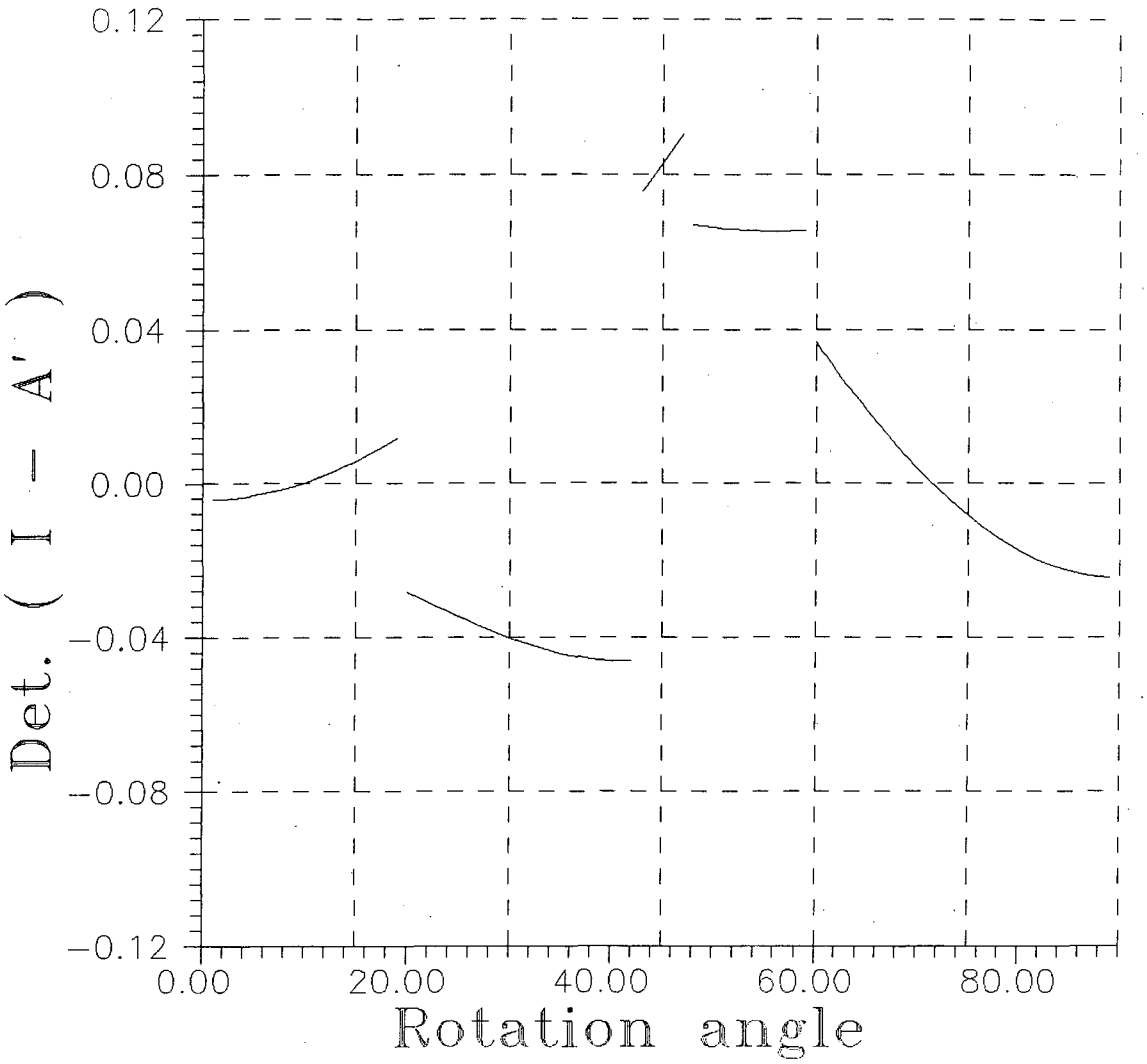


XBL 874-1660

Fig. 6b

Fig. 7

XBB 872-1232



XBL 874-1658

Fig. 8

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