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SOME IN-SITU OBSERVATIONS OF GaAs OXIDATION

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ABSTRACT

The oxidation of doped GaAs was studied using an environmental cell placed in a transmission electron microscope. By means of this device the oxidation was observed at temperatures from 320°C to 600°C under a few tens of torr of oxygen. For temperatures up to 380°C amorphous reaction products were observed, while at temperatures of 450°C and above, polycrystalline β-Ga_2O_3 (formed via intermediate epitaxial γ-Ga_2O_3 and polycrystalline γ-Ga_2O_3) was found. A tentative explanation for this change from one product microstructure to another with temperature is advanced.

INTRODUCTION AND PREVIOUS INVESTIGATIONS

The processing of silicon within the semiconductor industry is facilitated by the ease with which an insulating oxide layer may be grown on single crystal silicon. This is in contrast to the case of gallium arsenide where oxide layers of the desired properties have proven elusive; presently deposited layers of SiN and/or SiO_2 are used in processing GaAs.

The present study has used an environmental cell located within a transmission electron microscope to observe, in-situ, the nucleation, growth and microstructure of oxide films formed on GaAs. While several investigations of the oxidation of GaAs have been described (1-9), none have made use of the in-situ technique. Bull and Sealy (4) performed an ex-situ study of the morphology of the oxide. An unidentified amorphous phase was produced at temperatures below 500°C. At temperatures above 500°C, crystalline β-Ga_2O_3 was produced. Grunthaner, et al. (5) found that oxidation of GaAs produced Ga_2O_3, As_2O_3, $GaAsO_2$, $GaAsO_3$ and $GaAsO_4$. Kazmerski and coworkers (6) reported that dry oxygen at atmospheric pressure and 200°C produced a polycrystalline layer of Ga_2O_3, while wet oxidation at 26°C yielded a layer containing Ga_2O_3 and As_2O_5 with the As_2O_5 concentration varying throughout the oxide layer. Schwartz, et al. (7) studied the oxidation of GaAs by air, As_2O_3/O_2 mixtures and oxygen. They found that As_2O_3/O_2 mixtures produced an amorphous oxide at temperatures below 500°C; above 600°C a crystalline oxide was produced. These investigators also showed that As_2O_3 and As_2O_5 vaporized when dry oxygen was used, leaving a layer of Ga_2O_3 on the substrate. Watanabe and coworkers (8) oxidized GaAs with dry air at temperatures between 500°C and 720°C and reported that gallium was preferentially oxidized over arsenic; an arsenic enriched zone was found in the substrate near the substrate-oxide interface. They found Ga_2O_3 as the only solid oxide produced. Webb and Lichtensteiger (9) have examined the steam oxidation of GaAs.

EXPERIMENTAL APPARATUS AND PROCEDURE

All microscopy was done in the Hitachi 650kV transmission electron microscope at Lawrence Berkeley Laboratory. The microscope was equipped with a Gatan environmental "cell" and a heating stage. The heating stage was equipped with a thermocouple; prior work on the cell has revealed a temperature error of approximately ±10°C in the temperature range of this investigation. Gas was fed to the cell via a delivery system incorporating a pressure regulator, flowmeter, needle valve and pressure gauge. Gas exits the cell via the 100 m apertures of the environmental cell into the "differential" pumping system that prevents a rise in column pressure. Experiments were carried out at pressures below 50 torr; gas flow rates ranged from 25 cm^3/min to 48 cm^3/min (at STP). The side loading environmental cell permits specimen tilting about one axis only, which prevents the ready identification of structural defects.

The GaAs specimens were from wafers supplied by Hewlett-Packard. Two types of n-type wafers were supplied, one Si doped (5×10^{17} atoms/cm^3), the other Te doped (5.3×10^{17} atoms/cm^3); the former had a near (100) orientation, tilted 4° towards (110) while the latter was (100) tilted 2° towards (110). Both were from liquid encapsulated Czochralski ingots.

Specimens were cut from the wafers and first thinned by polishing on emery paper, then using 6 and 1 µm diamond paste. Further thinning and cleaning was done by 15 minute immersion in a 1% Br-methanol bath. Following this the specimens were mounted on standard microscope grids and ion milled.

The oxygen was used directly from a cylinder with no attempt at drying.

RESULTS AND DISCUSSION

Little or no reaction was observed when GaAs (Si doped) was held at 200°C under 50 torr of oxygen for five hours. Slight changes in the appearance of the sample were observable but this may have been due to contamination resulting from this long exposure. Before and after exposure, the electron diffraction pattern was that of single crystal GaAs. A second specimen exposed at 280°C to 40 torr of oxygen for 2-1/4 hours also showed little or no reaction.

Fig. 1 shows a GaAs specimen (Si doped) before (a) and after (b) exposure to 44 torr of oxygen at 320°C for 1 hour. There is little difference between the appearance of the two electron images but the diffraction patterns (inset) are radically different. The specimen has been transformed into an amorphous material, presumably oxide. Fig. 2 shows the appearance of a GaAs specimen (Te doped) as it is oxidized at 380°C under 30 torr of oxygen. 2(a) is the specimen initially, exposure times in minutes are indicated on the other two images. The images are remarkable for their lack of features (in comparison to the images produced by high temperature oxidation, see below). The oxide produced is again amorphous and it appears that oxidation proceeds uniformly across the whole surface of the specimen.

Fig. 3 shows the edge of a GaAs (Si doped) specimen before and after 15 minutes exposure to 46 torr oxygen at 450°C. After 15 minutes of exposure the specimen has an irregular edge and spots corresponding to polycrystalline β-Ga_2O_3 have appeared in the diffraction pattern. Oxidation under these conditions occurs first at the edge of the specimen. This is indicated in the micrographs of Fig. 4 which is of a specimen after 1-1/4 hours. 4(a) is the electron image and diffraction pattern. Two spots indicated by arrows in the diffraction pattern correspond to GaAs (lower spot) and β-Ga_2O_3 (upper spot) and were used to generate the dark field images of 4(b) (GaAs) and 4(c) (β-Ga_2O_3). Clearly the oxide has been formed at the edge of the specimen, indicating that this is a preferred site for the nucleation of the oxide phase.

A careful examination of electron diffraction patterns indicates that γ-Ga_2O_3 is an intermediate in the oxidation to β-Ga_2O_3. Fig. 5 is a sequence of diffraction patterns obtained on exposing a GaAs specimen (Te doped) at 600°C to 30 torr of oxygen. 5(a) is the initial GaAs, 5(b) the diffraction pattern of epitaxial γ-Ga_2O_3 formed after 5 minutes oxidation while at 13 minutes (c) this epitaxy has largely been lost and polycrystalline γ-Ga_2O_3 is observed. Finally, at 18 minutes polycrystalline β-Ga_2O_3 is seen. The lattices in Fig. 5(a) and (b) are epitaxial, $(100)GaAs \| (100)\ Ga_2O_3$.

Fig. 6 shows a sequence taken during the oxidation of GaAs (Te doped) by 30 torr oxygen at 500°C; time in minutes is indicated on each image. The dark bands seen in the initial specimen and in the specimen at 8 minutes are an interference effect due to thickness variations in the wedge shaped specimen and have no physical significance. Again oxide (the lighter phase) is formed at the edge of the specimen and grows across the surface, although some nucleation of oxide is observed a little away from the edge. Changes can be observed in the GaAs ahead of the encroaching oxidation front (e.g. the darker regions that are particularly visible near the oxidation front at 23 and 30 minutes). Reaction at 600°C was morphologically similar but observed to be two to three times as fast (Fig. 7).

The in-situ technique is a particularly appealing technique for the study of microstructural aspects of gas-solid reactions. In contrast to ex-situ studies, the technique reveals the microstructural effects under conditions of reaction without the possibility that the microstructure is altered by heating/cooling or transfer back and forth between a reaction chamber and a microscope. A criticism to which the technique is susceptible is that the electron beam may have an influence on the reaction, for example by local heating of the specimen. In the present study, areas not illuminated by the beam before or during reaction were examined subsequent to reaction and compared to areas that had been illuminated. To the extent that any difference could be discerned it was thought that reaction proceeded more slowly in the illuminated areas.

For the higher temperature oxidations reported above, nucleation of the oxide phase was observed at or near to the edge of the specimen. An attempt was made to determine whether other features such as dislocations provided nucleation sites; no assocation of nucleation and dislocations was observable.

The observations reported above differ from those of Bull and Sealy (4) who, in ex-situ studies, observed single crystal β-Ga_2O_3 on oxidation at temperatures above 500°C. The sole single crystal species observed in the present investigation was the γ-Ga_2O_3 that appears to be an intermediate in the formation of polycrystalline γ-Ga_2O_3, then polystalline β-Ga_2O_3, at temperatures above 500°C. Both investigations are consistent in finding an amorphous reaction product for reaction temperatures below 450°C.

Two hypotheses can readily be formulated for the absence of amorphous reaction product at the higher oxidation temperatures; both invoke the volatility of arsenic (or its oxide) and Fig. 8 gives the relevant vapor pressures as a function of temperature.

The first hypothesis is that the amorphous film incorporates arsenic and that at the higher reaction temperature this film loses arsenic by vaporization, leaving Ga_2O_3 which ultimately forms polycrystalline β-Ga_2O_3. This hypothesis was tested by growing an amorphous layer at 320°C and then heating to 450°C in vacuum. Polycrystalline oxide was not formed; the amorphous layer was unchanged after several hours at 450°C. This result is inconsistent with the first hypothesis.

A second hypothesis is that the oxide layer does not incorporate arsenic but that arsenic is rejected into the GaAs (Si doped) ahead of the advancing reaction front. This enrichment by As was reported by Watanabe et al. (8) and may explain the dark phases appearing ahead of the oxidation front in Figs. 6(c) and (d). If it is postulated that As enrichment lowers the local rate of oxidation then an explanation of the absence of amorphous layers at elevated temperatures becomes possible. Contrast the behaviour of two different regions of the specimen, one covered by amorphous oxide, the other by polycrystalline oxide. It seems likely that diffusion of As would be much more rapid through the polycrystalline layer, resulting in less As enrichment beneath this layer and a more rapid advance of the reaction front, thus polycrystalline oxide is the dominant reaction product. At lower temperatures As vaporization is a less important phenomenon and this, coupled with the lower rates for transformation to a crystalline phase, may favor an amorphous product. The second hypothesis was tested by growing an amorphous layer on GaAs (Si doped) at 320°C and then exposing the specimen to 44 torr of oxygen at 450°C; again no polycrystalline oxide was formed and little or no further oxidation was observed. It appears that this result is more consistent with the second hypothesis than the first.

CONCLUSIONS

In-situ oxidation studies at the TEM have shown that oxidation of doped GaAs becomes significant at temperatures of 320°C when exposed to a few tens of torr of oxygen. Amorphous reaction products were formed at this temperature and at 380°C. Polycrystalline β-Ga_2O_3 was formed at temperatures of 450°C and above, although intermediate reaction products of epitaxial γ-Ga_2O_3 and polycrystalline γ-Ga_2O_3 were observed at the elevated temperatures. No arsenic-containing phases were detected in the reaction product. A hypothesis explaining the experimental results in terms of rejection of As into the GaAs ahead of the advancing reaction front, coupled with its ready vaporization through a polycrystalline layer at the elevated temperatures, was formulated.

ACKNOWLEDGMENT

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FIGURES

<u>1</u> GaAs (Si doped) before (upper image) and after exposure to 44 torr oxygen at 320°C for 1 hour. Electron diffraction patterns are inset; note the amorphous reaction product.

<u>2</u> Appearance of Te doped GaAs undergoing oxidation at 380°C under 30 torr of oxygen. Exposure time in minutes.

<u>3</u> Edge of GaAs specimen (Si doped) after 15 minutes in 46 torr oxygen at 450°C. Polycrystalline β-Ga_2O_3 appears in the diffraction pattern.

<u>4</u> (a) The specimen of Fig. 3 after 1-1/4 hours.

(b) GaAs dark field image

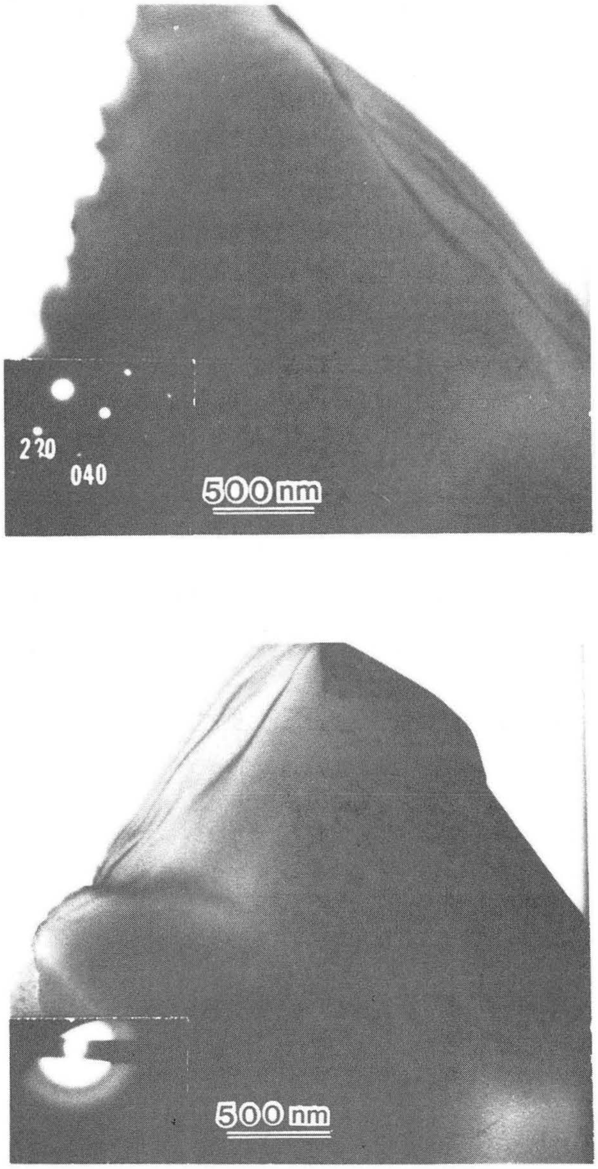
(c) β-Ga_2O_3 dark field image

<u>5</u> Sequence of diffraction patterns obtained on oxidizing GaAs (Te doped) at 600°C under 30 torr of oxygen. (a) Initial GaAs (b) after 5 minutes (c) after 13 minutes (d) after 18 minutes

<u>6</u> Sequence of electron images during the oxidation of GaAs (Te doped) by 30 torr oxygen at 500°C. Time in minutes.

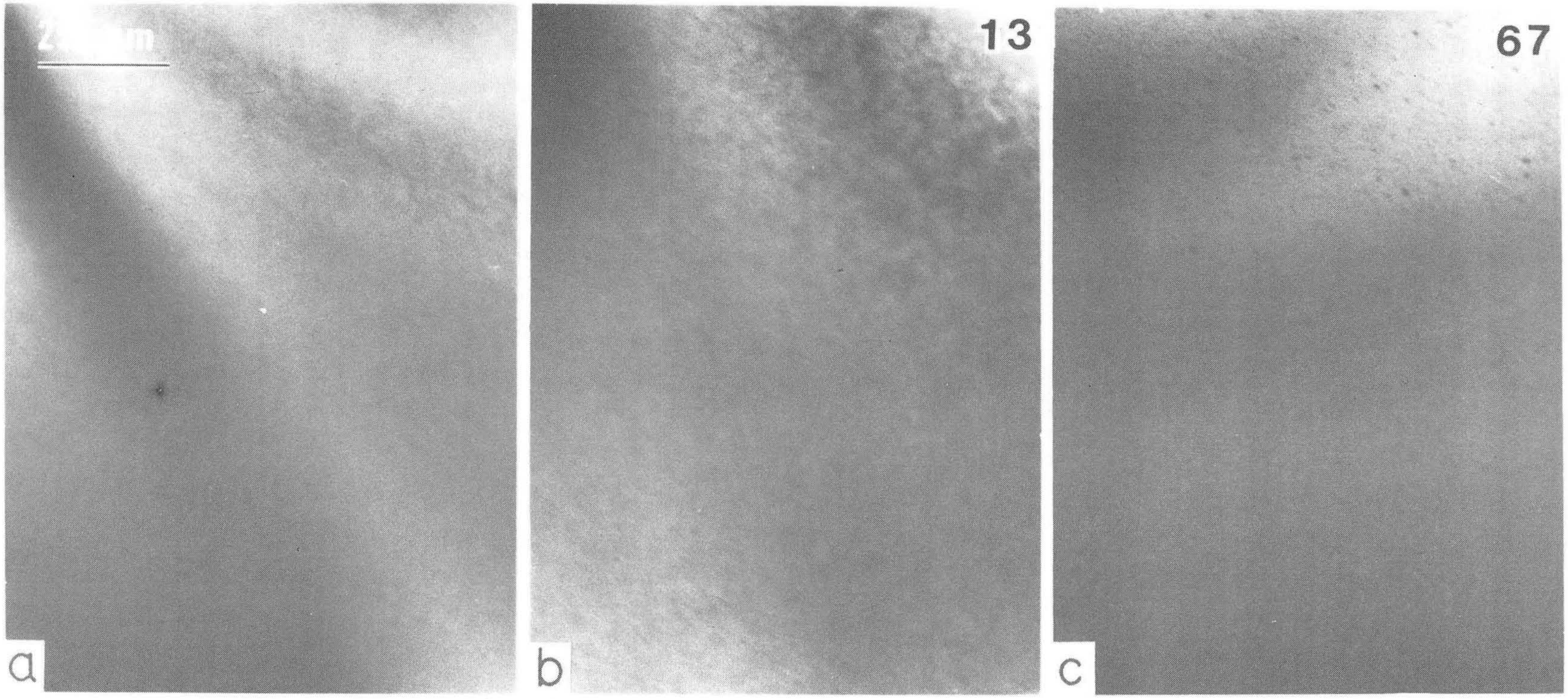
<u>7</u> Similar sequence to Fig. 6 except at 600°C.

<u>8</u> Vapor pressures relevant to this investigation.



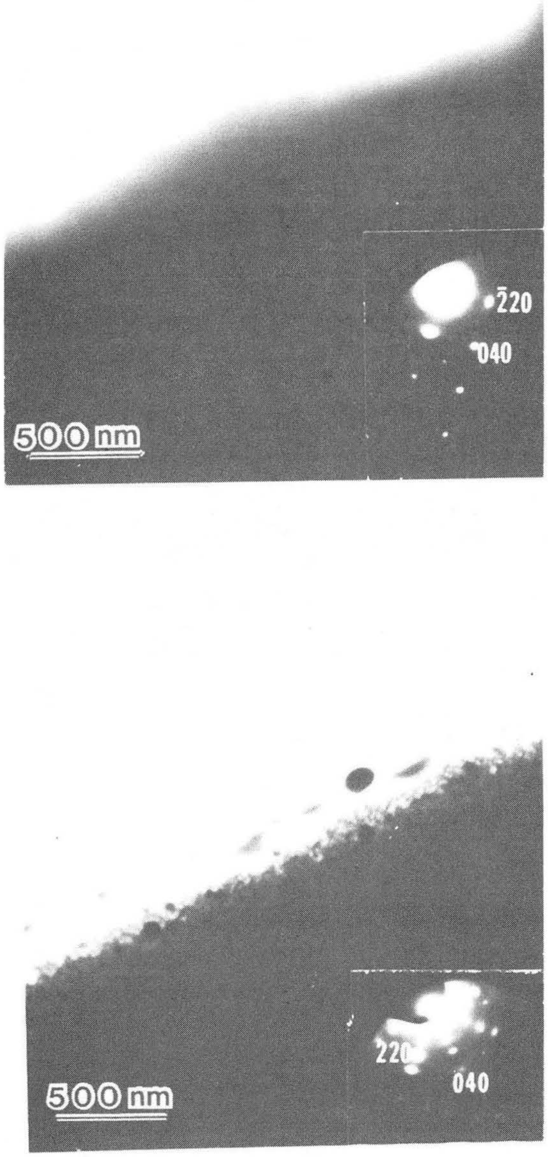
XBB 854-3403

FIGURE 1



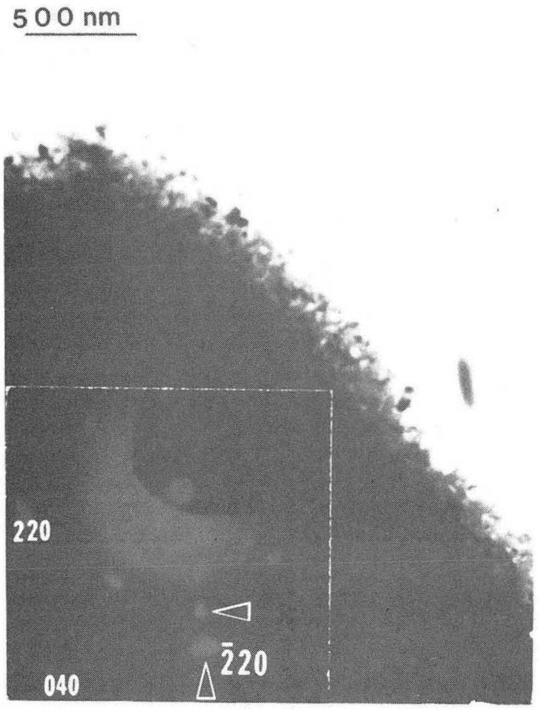
XBB 855-3919

FIGURE 2



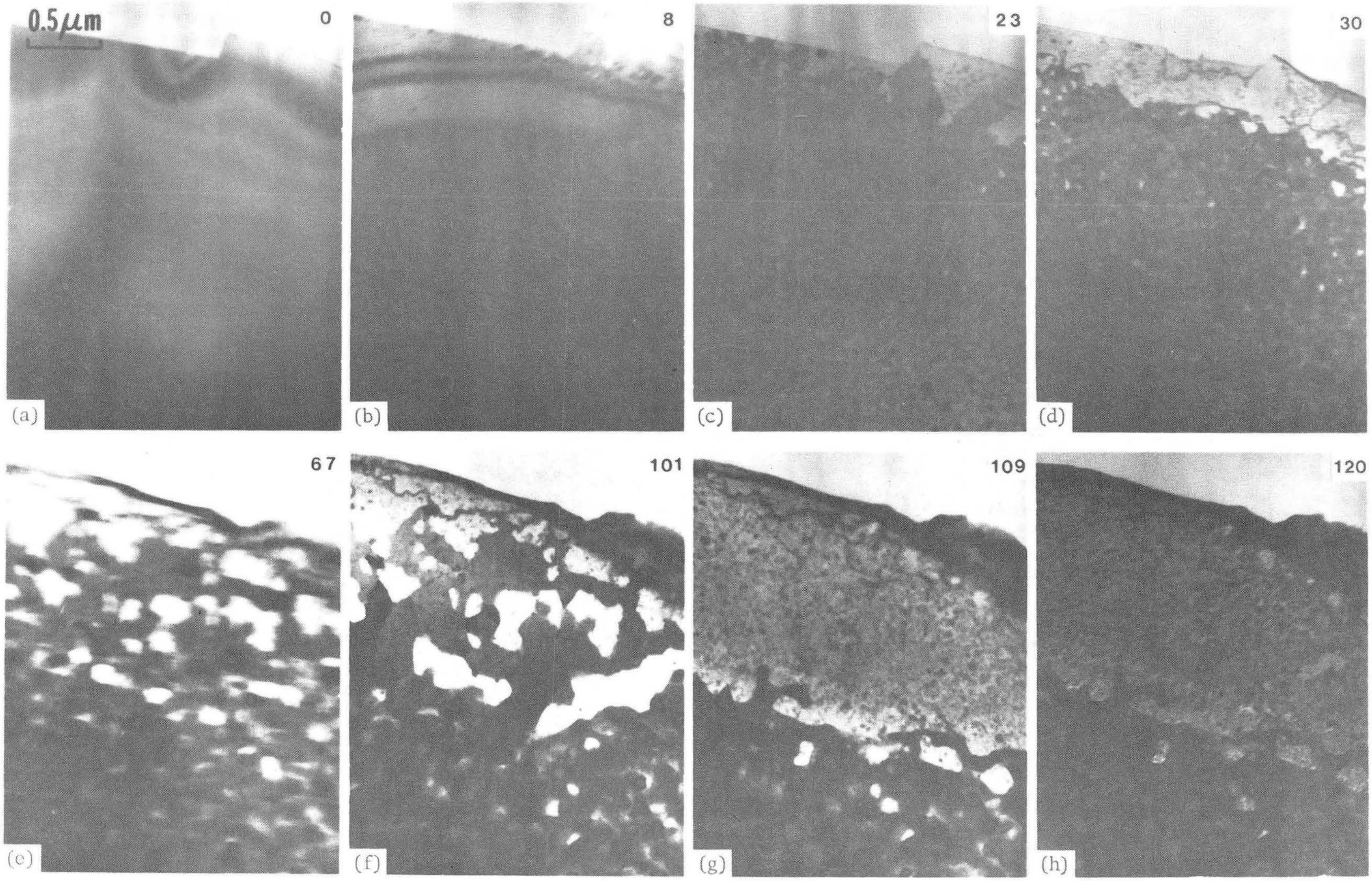
XBB 854-3405

Fig. 3



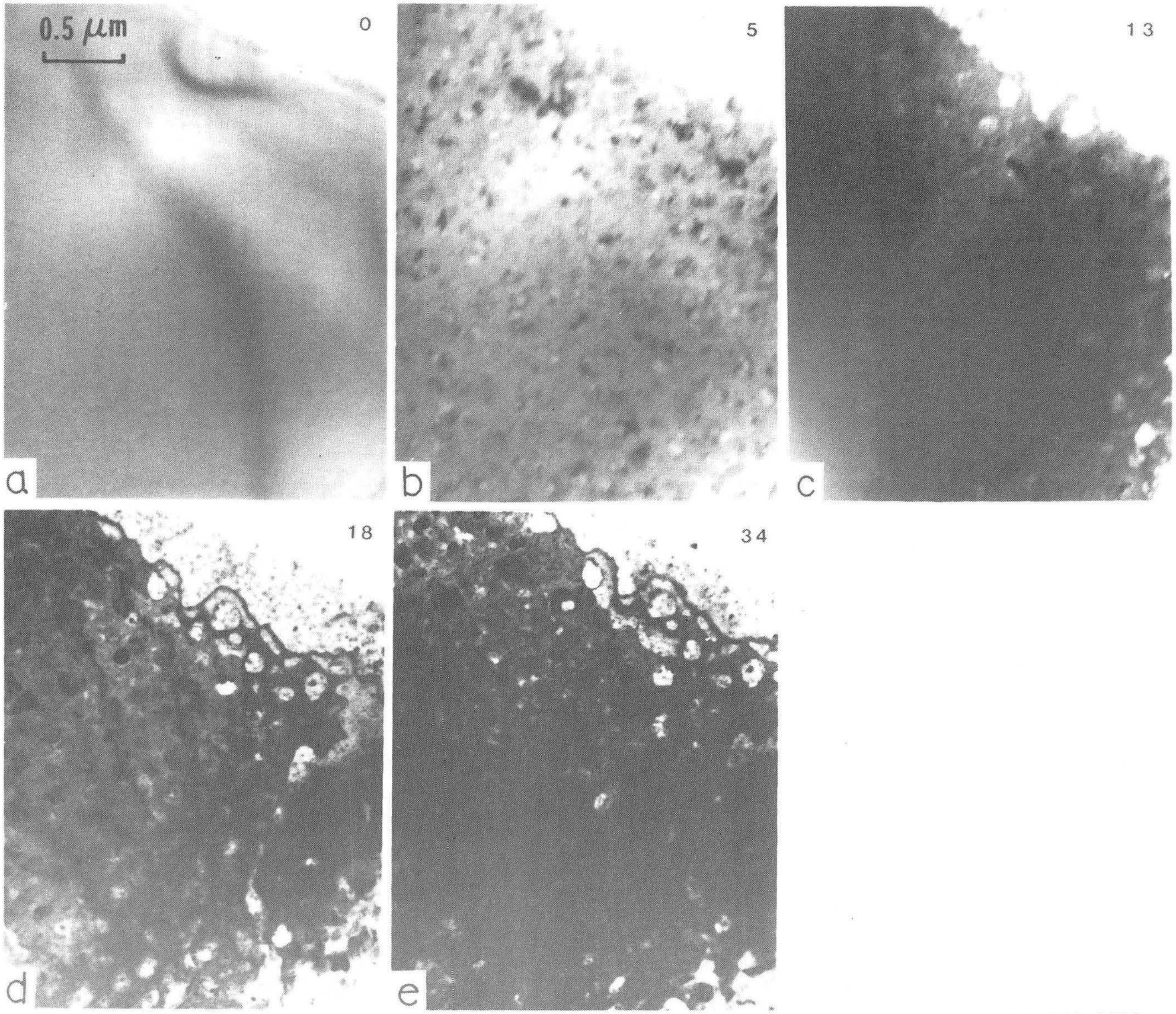
XBB 854-3407

Fig. 4a



XBB 855-3920

Fig. 6



XBB 855-3921

Fig. 7

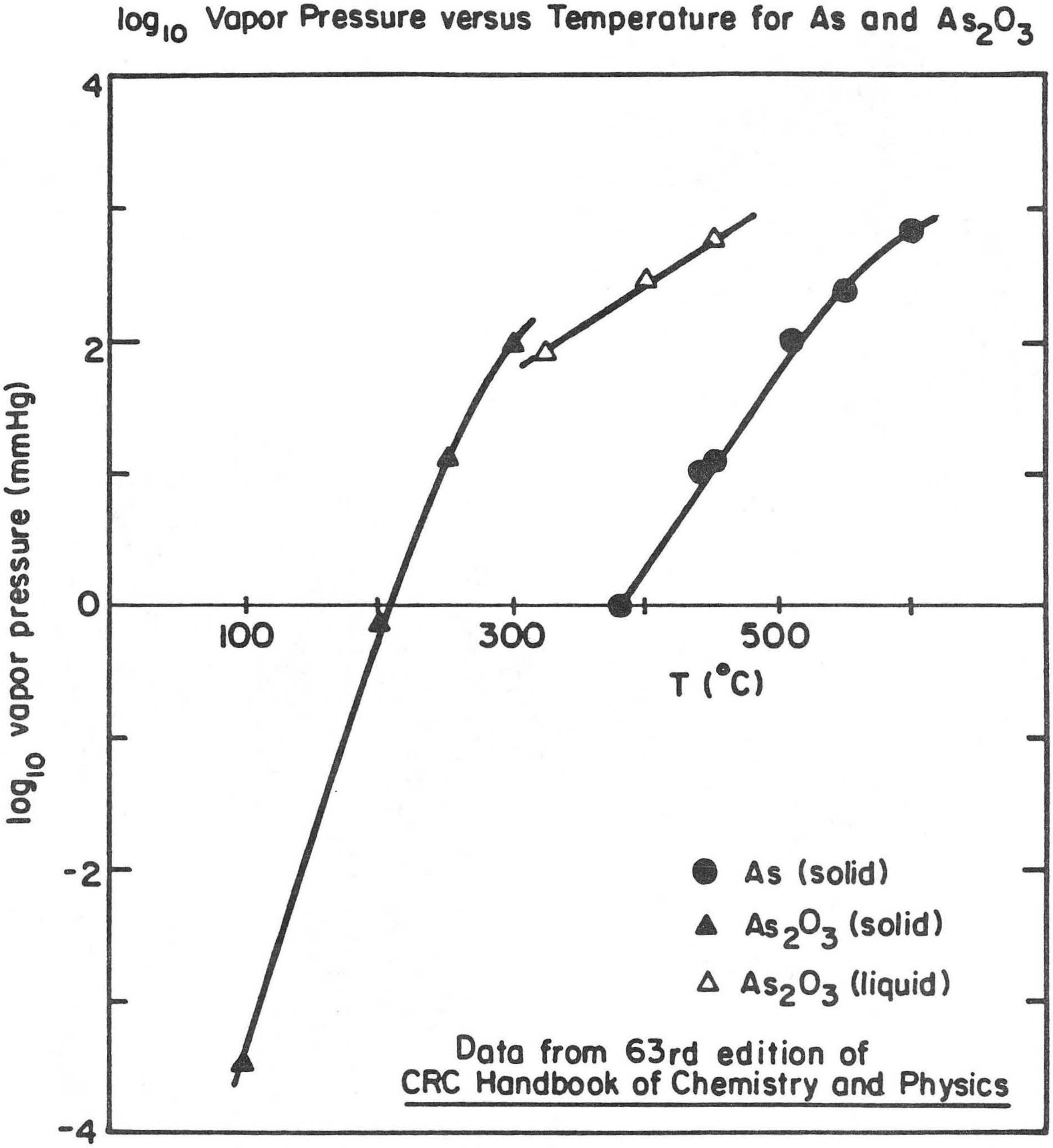

$\log_{10}$ Vapor Pressure versus Temperature for As and As_2O_3
4
2
0
-2
-4
$\log_{10}$ vapor pressure (mmHg)
100
300
500
T (°C)
● As (solid)
▲ As_2O_3 (solid)
△ As_2O_3 (liquid)
Data from 63rd edition of
CRC Handbook of Chemistry and Physics

Fig. 8