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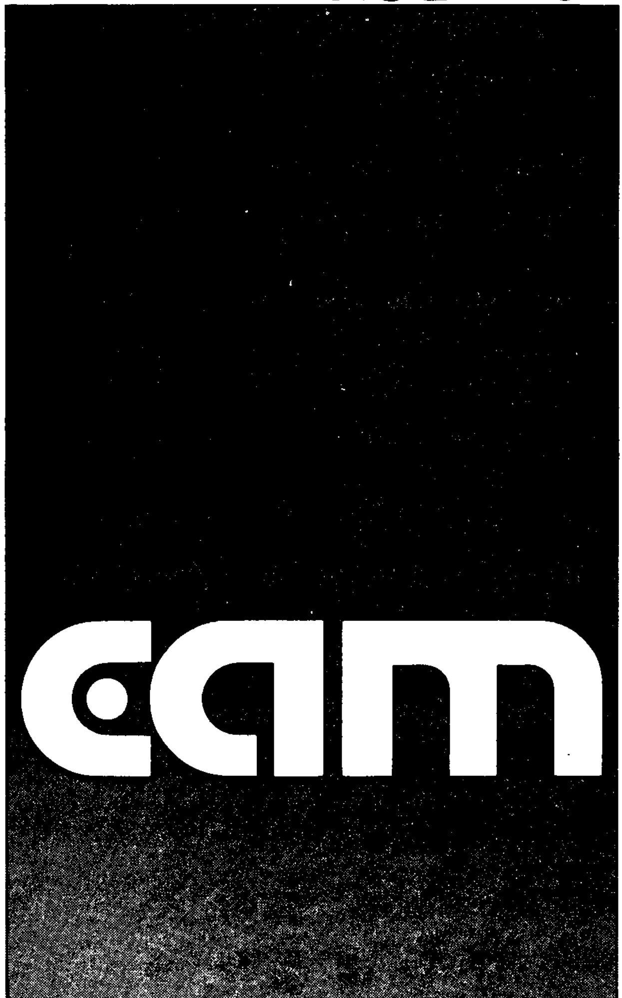
September 1986



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A TEM Study of Precipitates in As-grown Semi-insulating Indium-doped GaAs

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Abstract Precipitation in as-grown semi-insulating In-doped GaAs crystal has been studied using transmission electron microscopy. Hexagonal As precipitates that exhibit a very simple orientation relationship with the GaAs matrix were found, although the crystal showed no evidence of In-containing particles. Precipitates of quite different phase(s), very likely a new As-rich Ga-As phase, have also been observed with very large interplanar spacings. The number density of these particles is estimated to be approximately $1.5 \times 10^{8}/cm^{3}$.

1. Introduction

Precipitates in as-grown GaAs are believed to affect the properties of GaAs both structurally and electronically. Often they are studied in relation to the behavior of grown-in dislocations (Stirland et al, 1984, for example) and in fact have been suspected to be a potential source of dislocations (Cornier et al, 1984A). They are also believed to be important to the homogeneity of crystals, related in general to the distribution of point defects. In fact, the precipitates are suspected to be responsible, at least partially, for the fact that the EL_2 concentration in a GaAs crystal becomes much more homogeneous after annealing at certain temperatures (Holmes et al, 1984).

Observations of precipitates have been reported in

several articles (Markov et al, 1984, for example). A few TEM studies to characterize the particles have been also published, generally identifying them as hexagonal arsenic phase (Cullis et al, 1980; Lodge et al, 1985). No detailed study, however, has been done on precipitation in In-doped crystals despite the important fact that In-doping reduces dislocation density drastically without apparent change in electronic properties (VonNeida and Jordan, 1986). In the present research program, a battery of TEM techniques has been applied in an effort to more completely characterize the precipitates and to extend the analysis to the doped crystals. Results on precipitates in the In-doped materials are presented and discussed here.

2. Experimental

The crystal investigated in this work was grown by an LEC technique at a low axial thermal gradient of about 6°C/cm, fully encapsulated in boric oxide. Indium concentration in the melt was $2.8\times10^{19}/cm^3$. The crystal was mainly dislocation-free except an annular region of about 10mm at the periphery where the dislocation density was about $5000/cm^2$. It was also semi-insulating with resistivity of $10^7\,\Omega cm$. Further details of the growth conditions and results of macroscopic characterization have been reported elsewhere (Elliot et al, 1984). Both chemical thinning (chlorine in methanol) and ion milling were used to prepare suitable TEM samples and no significant differences were found between samples made by these different techniques. Prepared samples were first observed and screened using a Philips EM301 TEM followed by more detailed analysis in a JEOL 200CX TEM equipped with ultrahigh resolution goniometer. A Philips EM400 TEM/STEM was used for most of the chemical analysis although a JEOL 200CX AEM with an ultra-thin window detector was also employed for light element Energy Dispersive X-ray Spectrometry (EDXS) analysis (Z>5).

Due to their low density and relatively large size, the precipitates presented many experimental difficulties. In particular, two conflicting

conditions had to be satisfied at the same time: the specimen had to be thin enough to give meaningful results and yet had to contain the precipitate within the probed volume. Fortunately, when the precipitates were coupled to dislocations, they were more readily found in the thicker regions of the sample, allowing "controlled thinning" with the ion mill while monitoring the thickness periodically in the TEM. Figure 1 is an example of this procedure, where the decreasing length of the dislocation clearly shows the decrease in thickness of the sample.

3. Results of General Observation

About 65 TEM samples were prepared from various parts of an In-doped GaAs crystal. By surveying this large number of specimens, it was estimated that the precipitate number density is approximately $1.5 \times 10^8/cm^3$, which is slightly lower than but comparable to the value reported for dislocated undoped crystals (Cornier et al, 1984B). Most of the precipitates were found in the dislocated regions of the crystal and were coupled with nominally straight dislocations (see Fig. 1 for example). Isolated precipitates, however, were also found in the relatively dislocation-free regions. They were all observed to have a tetrahedral shape bounded by {111} matrix planes and to vary in size from a few tens to over two hundred nanometers. Their tetrahedral shape can be easily visualized from the fact that their projected shape on the {110} matrix plane is an isosceles triangle with two inside angles of 55° and one of 70° (Fig. 2(a) and Fig. 3(a)) and that the projected shape on the {111} matrix plane is an equilateral triangle (Fig. 4(a)).

4. Characterization of Observed Precipitates

Figure 2(a) shows a multibeam image of a typical precipitate found in In-doped GaAs and Figs. 2(b) and (c) are corresponding selected area diffraction patterns (SADP) with extra spots indicated and indexed. Notice the two SADP's were taken from slightly different crystallographic orientations near a same <110> matrix pole. This ap-

proach was necessary to accentuate weak diffraction spots associated with the particle. Measured interplanar spacings and angles, summarized and compared with the theoretical values in Table 1, clearly indicate that this is a hexagonal arsenic precipitate.

In agreement with this conclusion, results of the chemical analysis by EDXS in TEM, Fig. 2(d) show excess As compared to the matrix but no major element other than Ga and As in the precipitate. It should be stressed that the EDXS spectra presented in this work may not represent quantitative values because of the likelihood that the precipitates are completely surrounded by the GaAs matrix. It is very interesting that a simple orientation relationship exists between this particle and matrix GaAs and this point will be discussed in more detail in next section.

Figures 3 and 4 contain information obtained from other particles. Four interplanar spacings and two included angles measured from the diffraction patterns, Figs. 3(c) and 4(b), are summarized in Table 1. Note that an interplanar spacing as large as 1.9 nm is detected. The two patterns also show that a certain orientation relationship exists between the matrix and precipitates although there is no apparent consistency between them. The observed variation in intensities of the diffracted spots furthermore suggests an ordering in a direction parallel to the <112> matrix direction. This is also apparent in the high resolution image, Fig. 4(b). Precipitate EDX spectra, Figs. 3(b), 3(d) and 4(c), show that the precipitates are As-rich and do not contain any other major elements with $Z>10$, except Ga and As. The spectrum in Fig. 3(d) shows an indium peak, but it is too small in amplitude to be related to any kind of compound. Figures 3(b) and 3(d) show the results of an EDX analysis with an ultra-thin window detector and Fig. 4(d) the result of Electron Energy Loss Spectrometry (EELS) analysis employed to detect the existence of light elements. It is clear from these data that large amounts of light elements are not present in the precipitates. A thorough search has been performed but

no good match with all the information given has yet been found. It is suggested that the precipitates are an ordered compound of Ga and As which is As-rich. Although no such compound has been reported in the literature, the formation of a metastable phase may be possible under the high local pressure and high temperature growth conditions experienced by the crystal. Such a metastable phase may also be stabilized by a very small amount of impurities, possibly below the detectability limits of EDXS or EELS.

5. Discussion

There are very few reports of precipitates in In-doped GaAs except one of As-rich particles in In-doped crystals grown from an As-rich melt (Barrett et al, 1984). Since no In-bearing phase has been found even in this work, it may be concluded that indium is not involved in formation of precipitates in GaAs at the concentration level studied in this work and precipitation hardening is not a major mechanism for the observed reduction in dislocation density caused by In doping. However, it is still very interesting that a number of precipitates, all of them related to excess As, have been observed because this can give clues to the behavior of As-related defects in a growing crystal, for example to agglomeration phenomena of the defects. Most of all, the existence of unidentified complex phases which would not be formed at the normal environment illustrates the complicated behavior of these defects.

A very simple orientation relationship can be deduced from the SADP's in Fig. 2 between the As precipitate and matrix, namely $(001)_{As}//(111)_{GaAs}$ and $(\bar{1}20)_{As}//(\bar{2}02)_{GaAs}$. Note that the position of the 003 As spot can be estimated to be on the line connecting the transmitted beam and the 111 GaAs spot, even though the spot does not appear very bright under these diffracting conditions. Table 2 shows that differences in planar spacings, or lattice mismatch, are quite small in both directions suggesting that this orientation relationship is energetically favorable. In fact the As atoms in the (001) plane of arsenic are in an ar-

rangement similar to that of As atoms in the (111)B plane of GaAs. Since the same orientation relationship has been observed by Sands et al(1985) between the matrix and hexagonal As precipitates formed by the thermal oxidation of GaAs, it is believed that this kind of orientation relationship is generally taken by a hexagonal As precipitate in GaAs although Cullis et al (1980) reported they observed no simple orientation relationship between an As particle and its undoped GaAs matrix.

It is also interesting that the precipitates have a tetrahedral shape while particles in undoped GaAs reported previously show round or somewhat cylindrical shape (Cullis et al, 1980; Cornier et al, 1984A), suggesting that the interfacial energies and/or formation mechanism is altered by In-doping. Experiments to obtain more precise information on the precipitation phenomena in GaAs and to clarify uncertainties remaining in this work are in progress.

6. Conclusions

As a result of an extensive TEM work, a low density -about $1.5\times10^{8}/cm^{3}$- of precipitates has been observed in In-doped GaAs crystals. None of particles was found to contain significant amount of In, however all were found to be As-rich. One phase in particular was identified as hexagonal As. Analysis of diffraction patterns from these precipitates shows a very simple orientation relationship between the precipitates and matrix. Unidentified As-rich particles, with an interplanar spacing as large as 1.9 nm, have been also observed.

7. Acknowledgement

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Table 1 Analysis of diffraction patterns.

	Measured Spacings (nm)	Included Angles Meas.	Included Angles Theor.	Theor. Spgs (nm)	Planes in Hex. As
Fig. 2(b) & (c)	0.31	131°	131°	0.311	$(\underline{1}01)$
	0.275			0.277	$(\bar{1}02)$
Fig. 3(c)	1.9	91°			
	0.68				
Fig. 4(b)	0.58	94°			
	0.67				

Table 2 Lattice mismatch between hexagonal As and matrix.

Planes	d_{hkl} (nm)	Mismatch (%)
$(003)_{As}$	0.352	7.7
$(111)_{GaAS}$	0.326	
$(\bar{1}20)_{As}$	0.188	6.2
$(\bar{2}20)_{GaAS}$	0.1998	

Fig.1 Series of images of same precipitate illustrating the sample preparation procedure to result in a precipitate in the thin area of sample. Decrease in the length of dislocation lines reflects the reduction in thickness.

Fig.2 Multibeam image, (a), and SADP's, (b) and (c), obtained from a hexagonal As precipitate in In-doped GaAs. Foil planes are $(\bar{1}20)_{As}$ and $(\bar{2}20)_{GaAs}$. In (d) an EDXS spectrum from the precipitate is compared with one from nearby matrix.

Fig.3 Information from an unidentified precipitate; (a) BF image at 220 two beam condition, (b) corresponding SADP with extra spots arrowed, (b) EDXS spectrum from matrix and (d) EDXS spectrum from the precipitate (d). Note a very small spacing in SADP which corresponds to 1.9 nm of interplanar spacing in real space.

Fig.4 Microscopy data from another unidentified precipitate; (a) high resolution image, (c) EDXS spectra comparing particle and matrix and (d) EELS spectrum from precipitate. (b) shows magnified image of boxed part in (a) and SADP. Foil normal is $<111>_{GaAs}$.

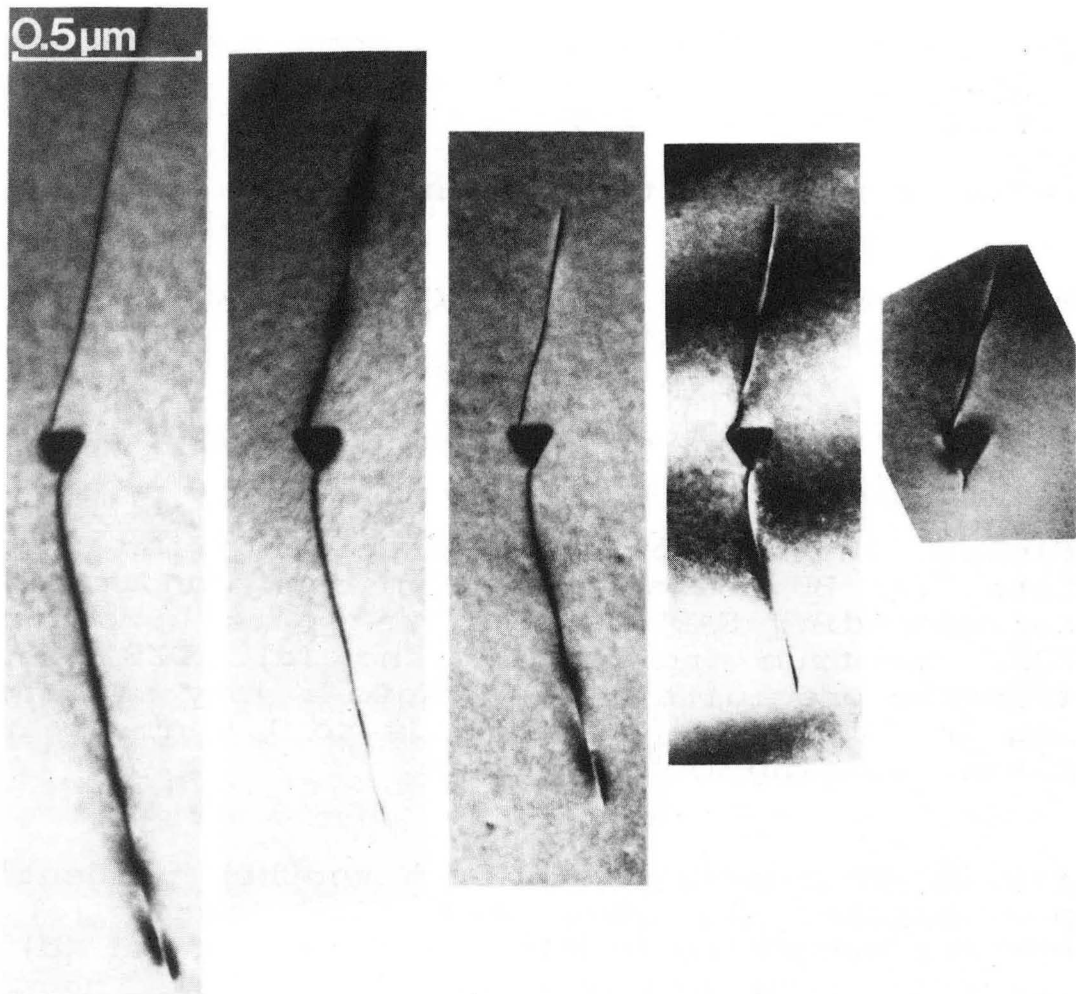

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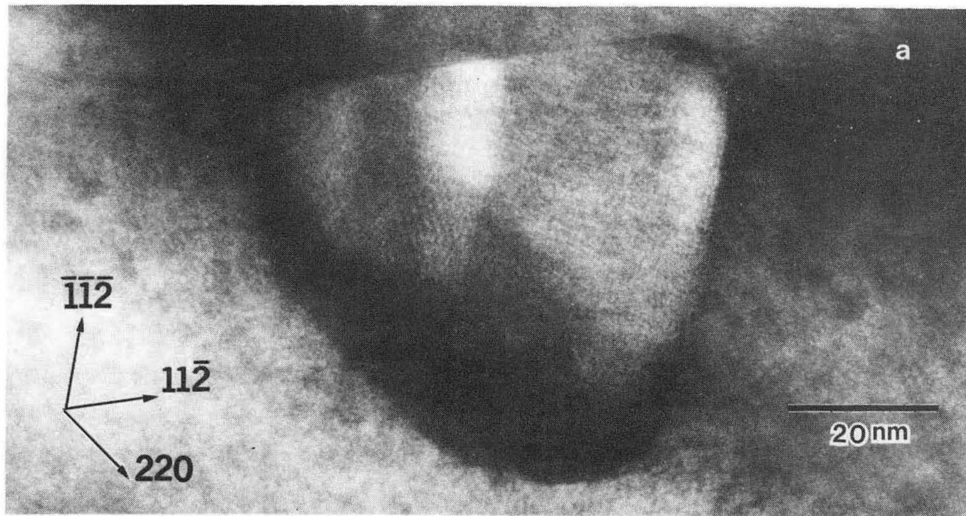
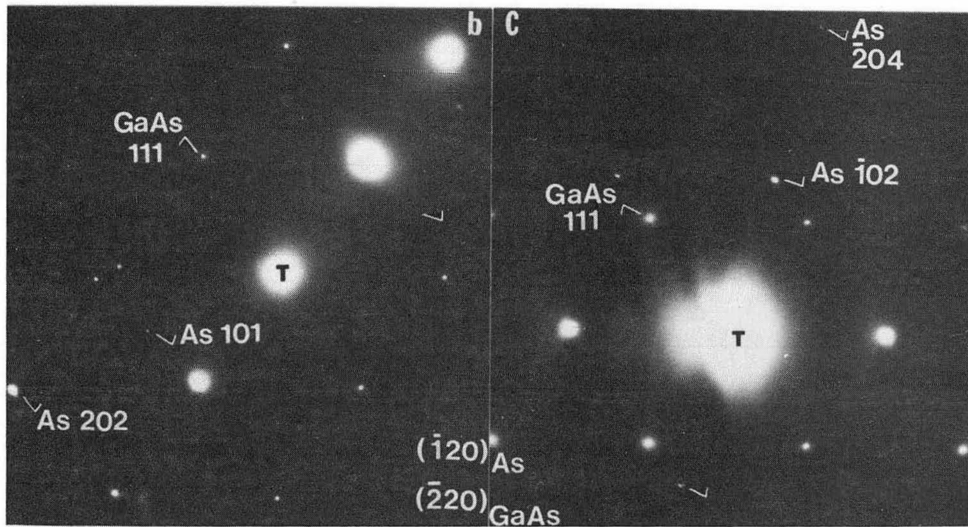
Figure 1.





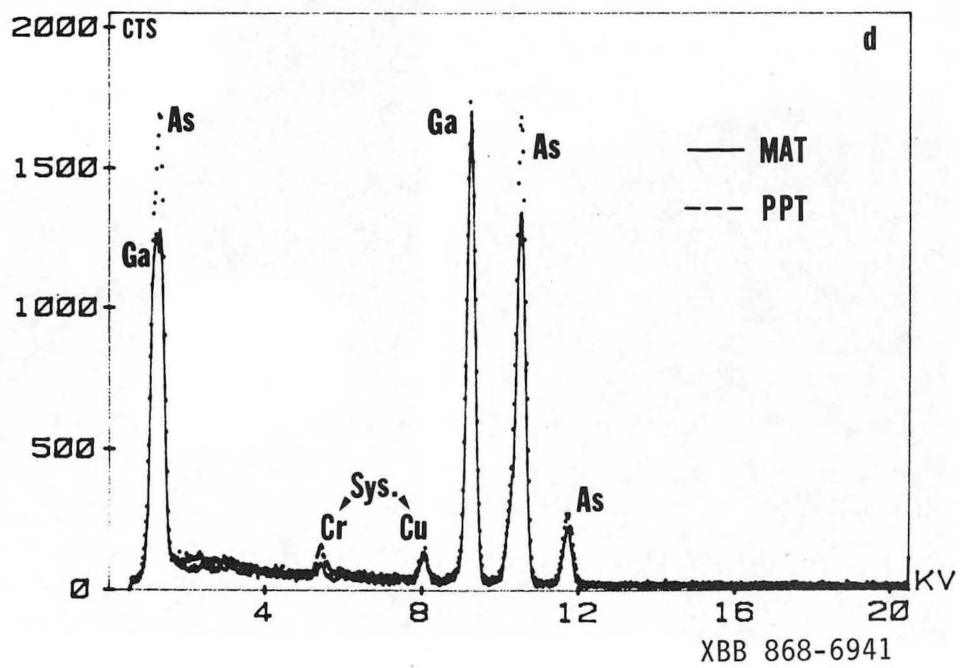


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Figure 2.

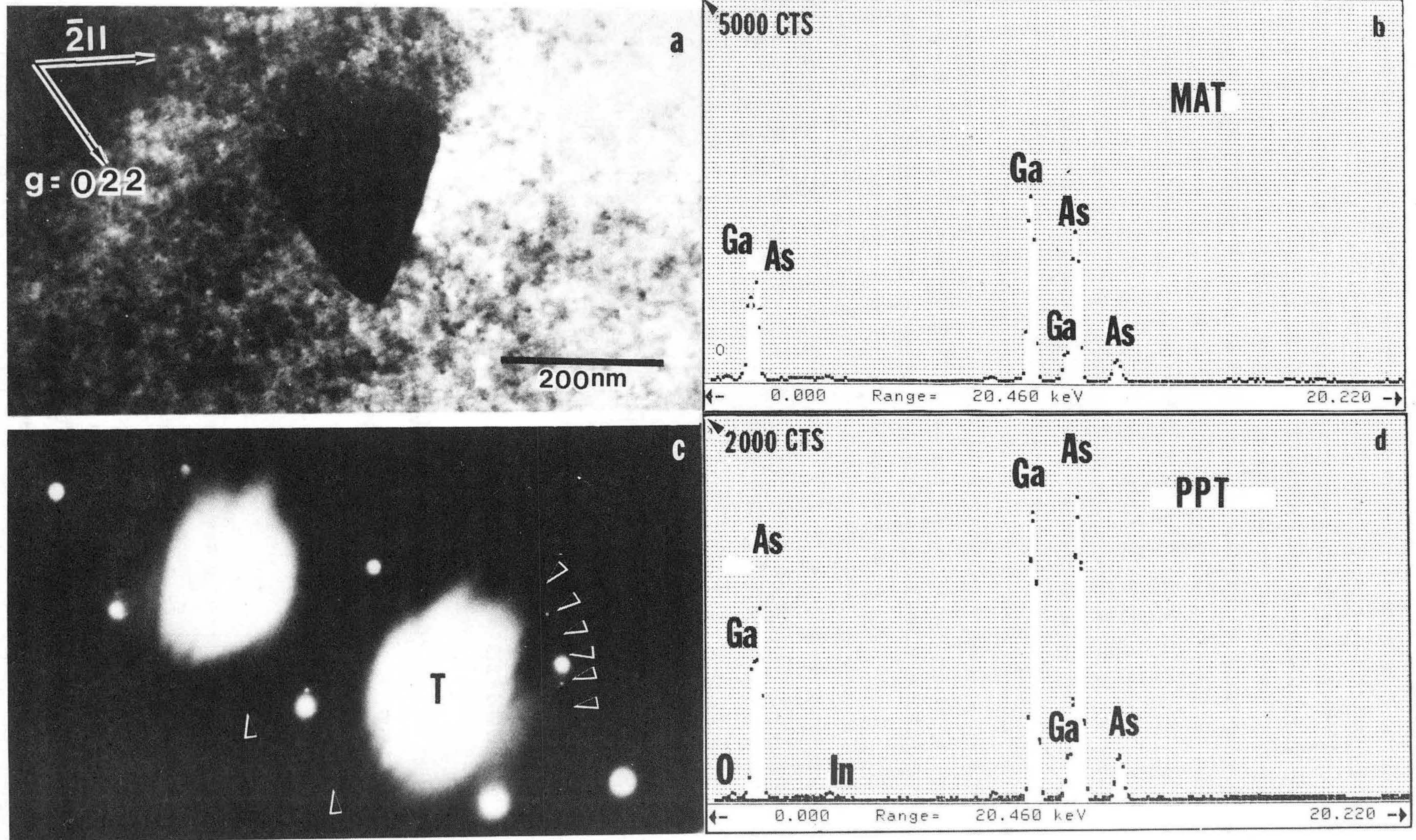

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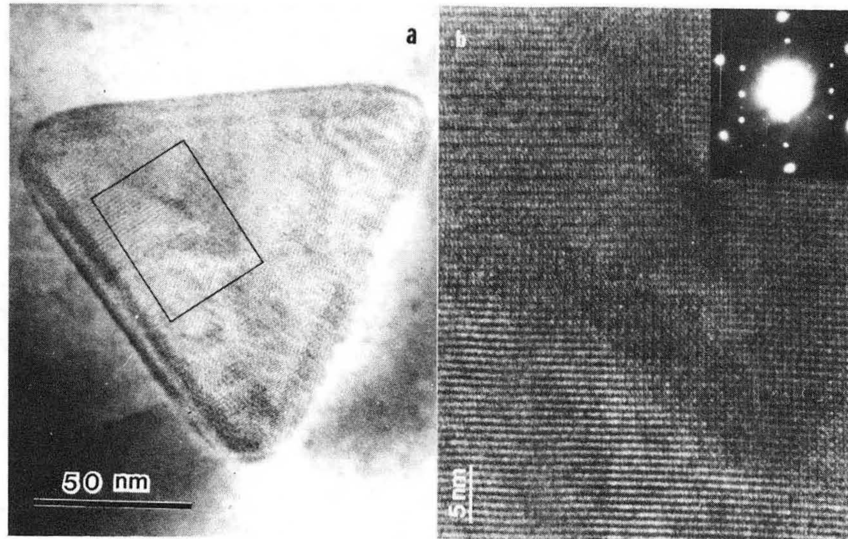
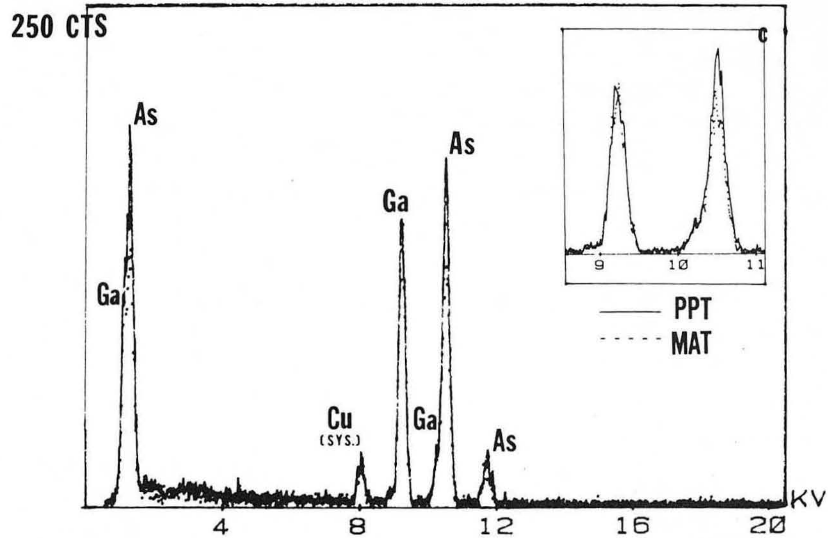
Figure 3.





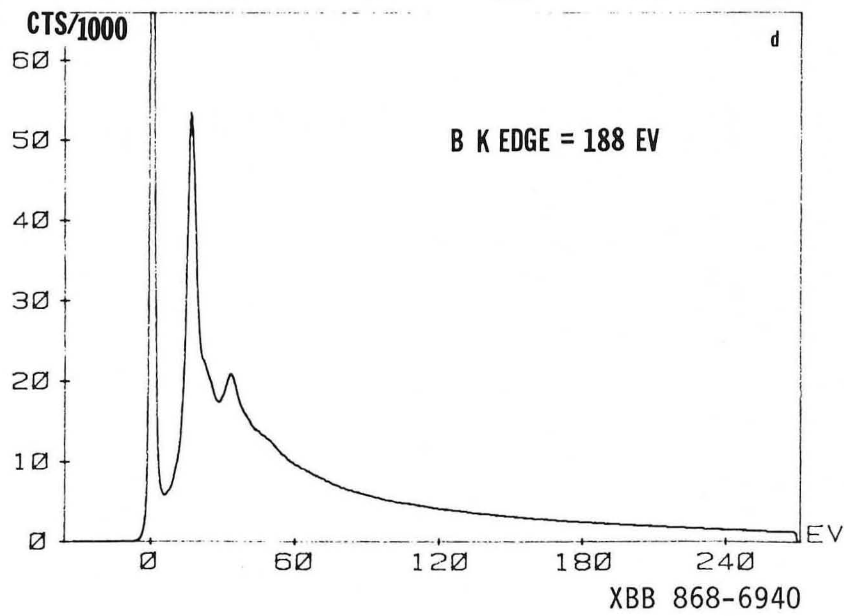


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Figure 4.

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