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# EBIC/TEM INVESTIGATIONS OF PROCESS-INDUCED DEFECTS IN EFG SILICON RIBBON

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by

Brian Cunningham and D.G.Ast

Materials Science and Engineering

Bard Hall, Cornell University

Ithaca NY, 14853

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## ABSTRACT

EBIC and STEM observations on unprocessed and processed EFG ribbon show that the phosphorus diffused junction depth is not uniform, and that a variety of chemical impurities precipitate out during processing. Two kinds of precipitates are found i) 10 nm or less in size, located at the dislocation nodes in sub-boundary like dislocation arrangements formed during processing and ii) large precipitates, the chemical composition of which has been partially identified. These large precipitates emit dense dislocations tangles into the adjacent crystal volume.

## INTRODUCTION

Many of the growth methods which produce silicon material for the fabrication of inexpensive solar cells yield material which contains a relative high density of structural defects, such as grain boundaries. twin boundaries and dislocations. Additional defects may be introduced during processing of the material. Because such defects will, in general. reduce the efficiency of a solar cell, there is a technological incentive to study the formation and structure of such defects, and their influence on the minority carrier lifetime.

In the following section. we will discuss the applications of TEM and EBIC to determine the defect structure of processed and unprocessed EFG ribbons. The defect structure of unprocessed EFG has been studied in considerable detail [1,2 3]. The majority of defects are coherent twins. some of which are only a few nm thick [1]. The electrical activity at these coherent twins varies considerably depending on the dislocation content.

Fig. 1 is a cross-sectional EBIC micrograph of an EFG ribbon after formation of a p-n junction by the diffusion of phosphorus. This micrograph was obtained by first cutting and polishing a ribbon perpendicular to the surface. A Schottky diode was then formed on the cross section by evaporation of aluminum. Because of the large difference in work function of Al on n and p type silicon [4] the p-n junction is clearly delineated. That the observed contrast is due to work function differences, and not to defects is indicated by the sign of the contrast. which is bright (i.e. high collected current) in the n-type region and low in the p-type region. If the contrast was due to (diffusion induced) defects, a reversal of the contrast would occur.

Inspection of Fig.1 shows that the depth of the p-n junction varies with position. Similar variations in junction position are observed in other polycrystalline materials [5]. The variation can be explained by assuming that there is enhanced diffusion along grain boundaries. In the case of EFG, the enhanced diffusion must be due to higher order twin boundaries. since coherent first order twin boundaries do not contribute to grain boundary diffusion [6].


Fig.1. Lateral EBIC image of a p-n junction in EFG silicon.


Fig.2. Helical dislocation in in junction region.


Fig.3. Sub-boundary in EFG silicon formed during processing.


Fig.4. Small precipitates located at dislocation nodes.

Fig.2 shows a dislocation helix in the base material adjacent to the junction. Such helical dislocations are never observed in unprocessed EFG, but have been observed previously in other phosphorus diffused junctions [7] and have been ascribed to the absorption of diffusion created interstial point defects.

Fig.3 shows a dislocation network formed in the base of processed EFG ribbons. Since such networks are never observed in unprocessed EFG the formation of the network must occur during the high temperature processing of the material. As Fig.3 shows, the dislocation network forms a planar boundary which takes up a small misfit between adjacent crystals. The dislocation nodes in this network act as heterogenous nucleation centers for very small precipitates (about 10 nm) one of which is shown in Fig.4. The chemical nature of these precipitates has not yet been identified.

The formation of the network is most likely due to stress relief which takes place in the material during high temperature processing. EFG ribbons are rapidly cooled during processing, and contain large internal stresses as indicated by the frequent breakage of unprocessed EFG ribbons during the thinning of TEM specimens.

In addition to the small precipitates described above processed EFG specimens contain large precipitates. These precipitates also form during processsing, since they are absent in unprocessed EFG material. During the preparation of the TEM specimen by ion milling, the matrix and the precipitates are sputtered at different rates. This difference in removal rates preferentially removes the precipitates from those (electron transparent) areas which are equal to or thinner than the diameter of the precipitate. For this reason, the precipitates were not seen in a conventional high resolution instrument and were only found when the material was inspected in a scanning transmission electron microscope operating at 200 KeV. This instrument has a higher penetration power due to the higher accelerating voltage and, more importantly, to the fact, that the instrument can form a contrast from electrons which have undergone several scattering events. (In a conventional microscope. such electrons are eliminated from contrast formation by the objective aperture).

Fig.5. Stem micrograph of processed EFG.


Fig.6. Same area imaged in the secondary electron mode.

Fig.5 shows a series of precipitates imaged in the scanning transmission mode. These precipitates are incoherent and emit dense dislocation networks which likely act as strong recombination centers. Fig.6 shows the same area in the secondary electron image (SEI) contrast mode. Comparison of the contrast of the arrowed particle in Fig.5 and Fig.6 shows that the precipitates, even when not intersecting the surface, cause variations in the secondary electron yield. This feature allows precipitates near the surface to be detected anywhere on the specimen. since the SEI mode, unlike the scanning transmission mode , is not restricted to the electron transparent region in the vicinity of the hole.

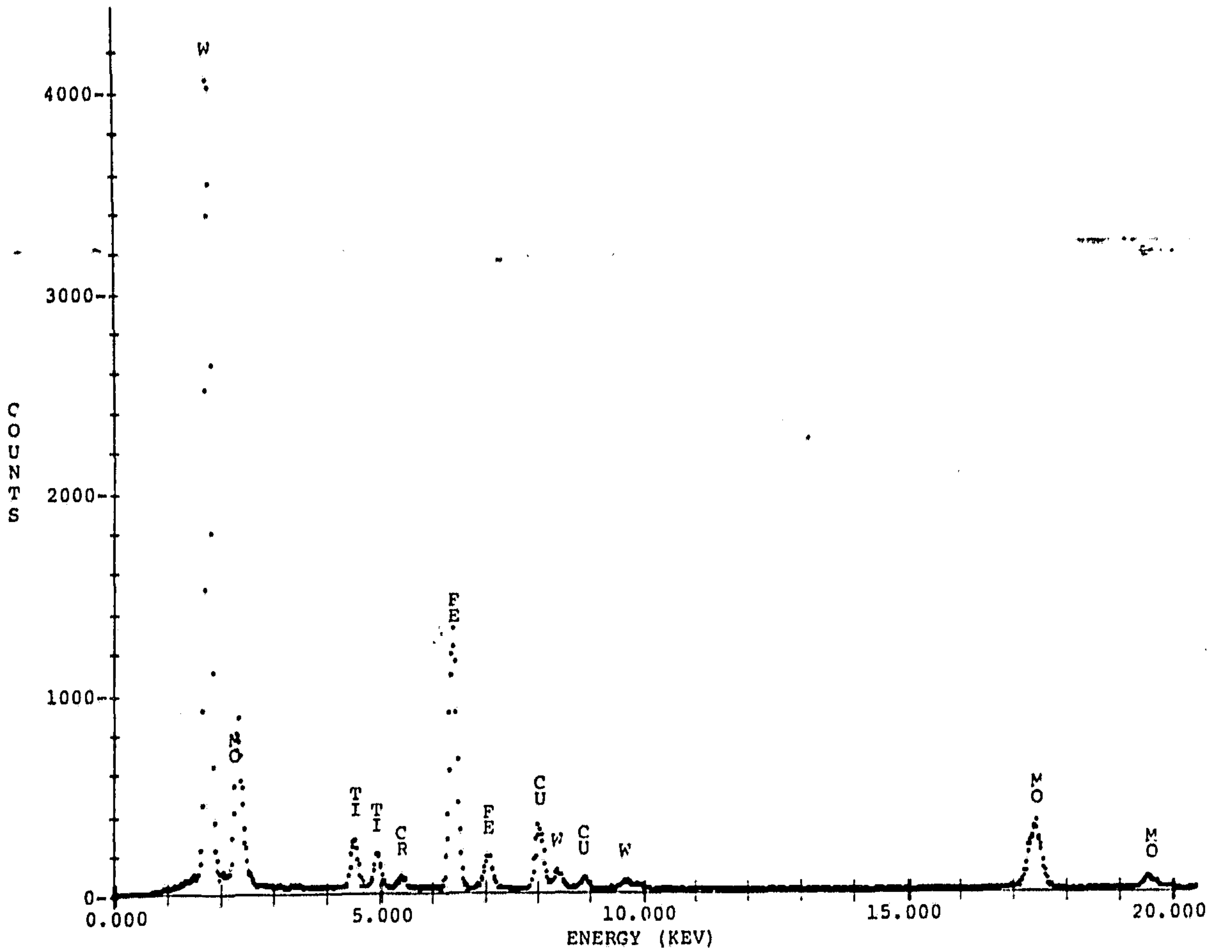


Fig.7. X-ray spectrum of precipitate A in Fig. 5.

The X-ray spectra from two of the precipitates shown in Figs. 5 and 6 are given in Figs 7 and 8. The large peak labeled W is a combined peak of both Si and W, whose peaks overlap within experimental resolution. For comparison, Fig. 9 shows a spectrum taken from the bulk of the sample. All spectra contain a weak Cu peak which is due to scattering from the Cu grid which supports the specimen. Several heavy metals are present in the precipitates, such as Fe, Mo and Ti. Metallic impurities, and in particular transition elements, reduce the efficiency of solar cells. A detailed study of the influence of impurities on solar cell performance can be found in ref. [8].

Other particles, (not shown) have been found to contain Ca. Cl and Au. It is likely that the Cl originates from the graphite elements in the EFG furnaces which are baked at high temperaures in Cl gas to remove impurities. Similarly, the most likely origin for the Mo are the heat shields in the furnace. Since the precipitates are not observed in the unprocessed material, it appears that these precipitates are dispersed in the as made material and precipitate out during processing. Empirically it is known that solar cells made from EFG material with a high oxygen content have a higher efficiency. It is possible, that the precipitates observed here are oxygen related gettering centers for impurities. The intensity of emitted x-rays decreases with atomic weight, and for low Z elements, most of the electronic excitations goes towards the production of Auger electrons. For this reason, low atomic number elements, such as oxygen, are very difficult to detect by their x-ray emission.

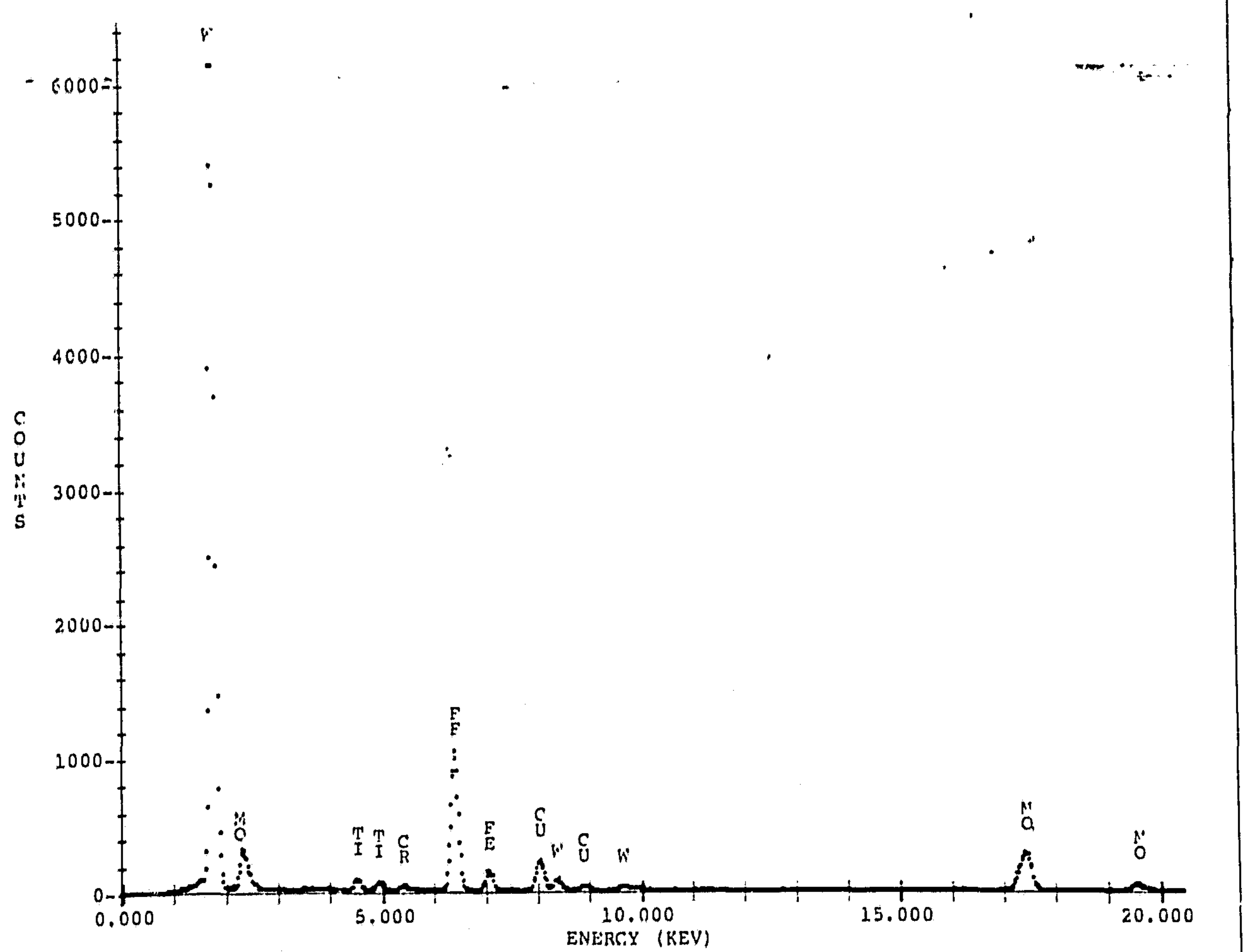


Fig.8. X-ray spectrum of precipitate B in Fig.5.

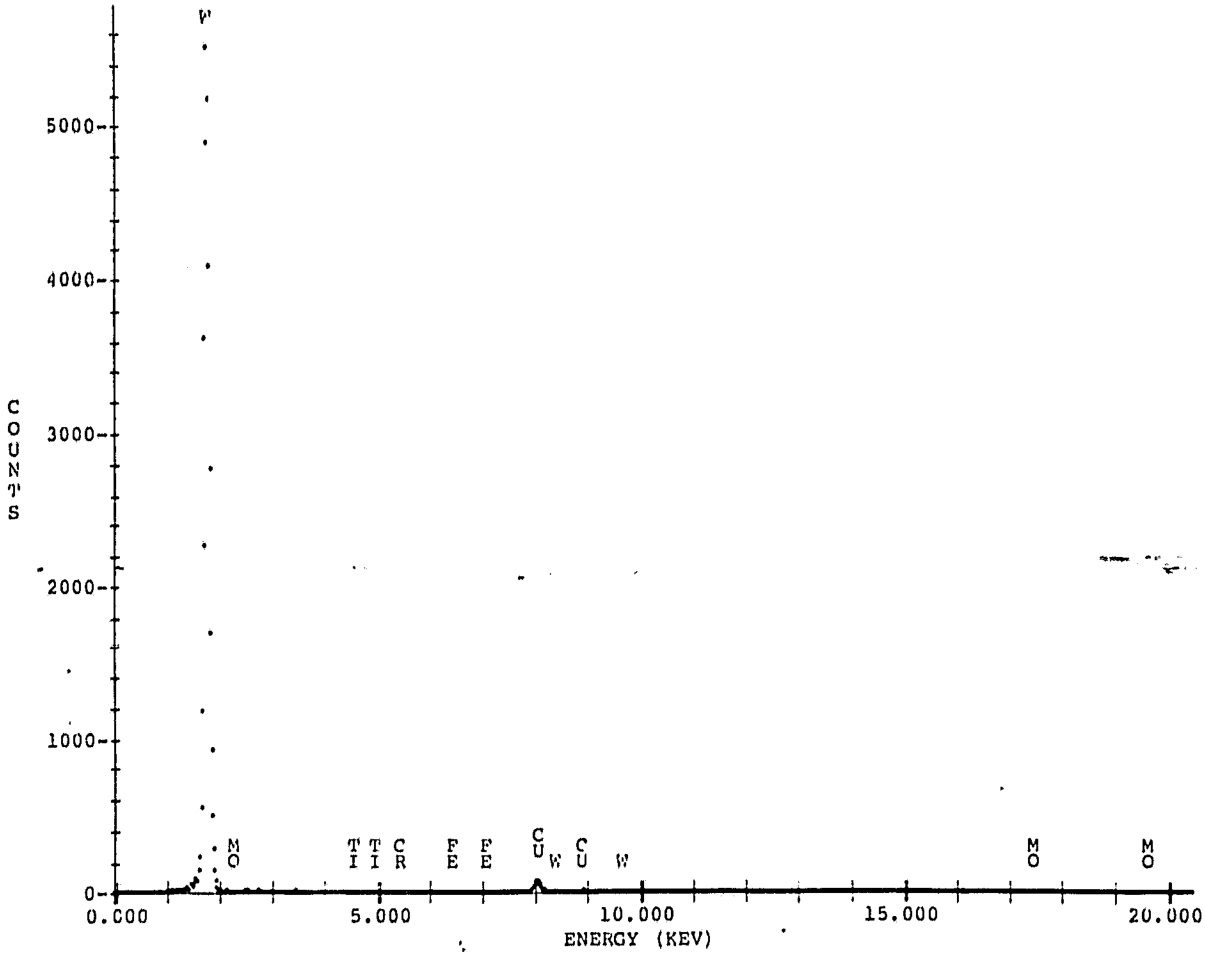


Fig.9. X-spectrum of matrix.

An analysis for carbon was carried out by examining the TEM specimen shown in Fig. 5 in a JEOL 733 SUPERPROBE scanning electron microprobe equipped with a 4 crystal dispersive x-ray system. This analysis showed that the precipitates contained a high amount of carbon. but calibration experiments are necessary to arrive at a quantitative number. Such experiments are being carried out.

SUMMARY

EBIC and STEM observations on unprocessed and processed EFG show that the junction depth is not uniform, and that a variety of chemical impurities precipitate out during processing. Two kind of precipitates have been identified i) precipitates of 10 nm or less, located at the dislocation nodes in sub-boundary like dislocation arrangements formed during processing and ii) large precipitates, containing several heavy elements impurities. These large precipitates emit dislocations and are , therefore. most likely strong recombination centers for minority carriers.

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REFERENCES

1. H. Foell and D. G. Ast, TEM and EBIC Observations on EFG, JPL/DOE Report No. 954852-1 (1978)

2. H. Strunk, B. Cunningham and D. G. Ast. Defect Structure of EFG Silicon. JPL/DOE Report No. 954852-6 (1980)

3. B. Cunningham, H. Strunk and D. G. Ast, Appl.Phys.Lett. in press.

4. E.H.Rhoderick, Metal Semiconductor Contacts, (Oxford University Press 1980)

5. N. M. Johnson, D. K. Biegelsen. M. D. Moyer. Appl.Phys.Lett. 38(1981) p.900

6. U. Goesele and H. Strunk, Appl.Phys. 20(1979)p.265; H. Strunk, U. Goesele and B. O. Kolbesen. J. Microscopy 118(1980)p.35

7. H. J. Queisser. Shockely Transistor Corp. Final Report. Contract AF30(602) 2556,1963.

8 R. H. Hopkins. J. R. Davis, A. Rohatgi. R. B. Campbell, P. D. Blais. P. Rai-Choudhury. R. E. Stapelton. H. C. Mollenkopf and J. R. Mc.Cormick, Effects of Impurities and Processing on Silicon Solar Cells, DOE/JPL Report No. 954331-9 Vol.2 (1980)