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INFLUENCE OF GRAIN BOUNDARIES ON THE ELECTRICAL
PROPERTIES OF POLYCRYSTALLINE-SILICON FILMS

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Abstract

Research in 1980/81 was carried out in three areas: i) diffraction experiments on diffusion bonded ("welded") boundaries; ii) combined EBIC and high voltage transmission electron microscopy in order to investigate the correlation between structure and electrical properties and iii) passivation of the electrical activity of crystal defects with hydrogen. The diffraction experiments did not furnish new information on the structure of grain boundaries in silicon, but were valuable as a check on the previous findings. In addition, they offered the possibility to separate double diffraction effects from boundary scattering.

ii) The combined EBIC and HVTEM experiments established (for the first time) unambiguously that coherent twin boundaries per se are not electrically active. The localized electrical activity observed in coherent twin boundaries is due to the presence of intrinsic dislocations, which are partial dislocations of the Schottky type. However, not all partial dislocations studied were electrically active, for reasons which are not completely understood. The combined EBIC and HVTEM investigations showed further (again for the first time) that many of the linear boundaries which were previously assumed to be coherent twin boundaries are second order twins, and that these twins are strongly electrically active.

iii) In passivation experiments, it is necessary to separate influence of the heat treatment from those of hydrogen. Passivation reduces the activity of some, but not of all defects. Passivation is particularly effective in reducing the electrical activity of deformation induced dislocations, which conceivably have a different core structure from grown-in dislocations.

1) Introduction

The object of our research is to understand the structure of linear and planar defects in silicon and the correlation between structure and the electrical properties.

The dominant planar defects in silicon are grain boundaries and coherent twins and stacking faults. The dominant linear defects are, of course, dislocations.

Most of the initial research under contract EY-76-02-2899 was concerned with the structure of grain boundaries. Specimens of controlled boundary geometry were prepared by diffusion bonding of two single crystals (so-called welded specimens). This technique has the advantage that any kind of boundary can be prepared (even unstable ones which are impossible to grow from the melt in bi-crystal form) but the disadvantage that the impurity content of the boundaries is currently not known. Because of a potential impurity problem and because we were initially not set up for electrical measurements, these earlier investigations were limited to structural characterization of boundaries.

The atomic structure of twist and mixed twist-tilt grain boundaries were studied in detail with high resolution transmission electron microscopy and with electron diffraction. As an additional benefit, we were able to determine very precisely the absolute values of the intrinsic and extrinsic stacking fault energy as well as their ratio from measurements on double ribbons. The good agreement with the literature values indicates that the boundaries were relatively clean. In addition, precipitates were never observed in welded boundaries which also indicates relatively clean boundaries.

With the addition of EBIC, we started to study the electrical activity of crystal defects; i.e., the effectiveness as recombination centers. These efforts benefited from a contract with JPL (supporting one postdoc) through which we obtained every new kind of novel silicon grown in the DOE/JPL LASS (large area silicon sheet) program. Many of these new growth methods produce poly-crystalline silicon with a high density of stacking faults, twins and dislocations. In electron microscopic investigations, one needs, because of the very high magnifications, a high density of defects in order to have a reasonable probability to find a defect within the field of view. Certain kinds of ribbon silicon, especially EFG silicon (edge defined film growth) contain a very high density of coherent twins. Such specimens are ideal in order to study the relation between the structure and electrical properties of simple line defects for reasons which are discussed later. In addition, these specimens, again because of their high density of crystal defects, offered a good opportunity to study the passivation of crystal defects with atomic hydrogen. Usually, several different defects are present within the area of one Schottky diode, a feature which makes it easy to study the relative degree of passivation which can be obtained on different defects.

2) Research in 1980/81

The research carried out in 1980/81 can be divided into three parts. The first part was essentially a completion of our work on the structure of diffusion bonded grain boundaries. Instead of direct imaging, we used electron diffraction techniques to investigate the boundaries. Although, in principle, no new information can be obtained (since there is no information in the diffractogram that is not contained in the image) diffraction has the advantage

that it has a better signal to noise ratio (since all the scattered information is collected and not just the part which is admitted through the objective aperture). Under certain conditions, this should outweigh the disadvantage of losing the phase information. Diffraction experiments on the welded boundaries also help to understand diffraction experiments on other materials. Basically, this is so, because in the welded specimens, the boundary plane is inclined to the foil normal. This feature makes it relatively easy to separate double diffraction effects (reciprocal streaks perpendicular to the foil normal) from true boundary diffraction effects (reciprocal streaks normal to the inclined boundary plane). In welded gold bi-crystals (which are by far the best investigated grain boundaries and which have been investigated in our department first by Balluffi) the grain-boundary plane is parallel to the foil plane, and the two effects cannot be separated. In the silicon work, an interesting and somewhat puzzling result was that direct imaging was able to show the presence of intrinsic (or DSC) dislocations in a $\Sigma 5$ boundary, but that this information could not be extracted from diffraction. For more information, the reader is referred to the first two of the attached publications, which discuss the diffraction experiment on silicon in more detail.

Another follow-up on our earlier work was an analysis of the weak beam contrast of stacking faults. This work exploits the fact that the relatively large lattice constant of silicon permits detailed structural imaging and therefore an unambiguous identification of the atomic structure of a defect. A study of the contrast behavior in the conventional imaging mode can, in conjunction with the known structure, be used to obtain insight into the contrast mechanism.

A second, and new area of research in 80/81 was an investigation of the relation between the structure and the electrical activity of defects in silicon. The system which we chose to study were partial dislocations in coherent twin boundaries. These partial dislocations are intrinsic grain boundary dislocations which accommodate small deviations from the ideal twin orientation. The electrical activity of these partials compared to complete lattice dislocations is relatively easy to study. Complete lattice dislocations in silicon may or may not be dissociated. (The factors which determine the dissociation width are not well understood. Furthermore the dissociation is double valued in the vicinity of the screw orientation for reasons which are also not understood^{*)}). It is likely that the electrical behavior of a complete dislocation depends on its dissociation width. A systematic study of the electrical activity of a dislocation would require a measurement of its dissociation which is not easily done. The study of partial dislocations avoids this difficulty. The localization of the partials in the boundary plane, which is easily traced in the image, facilitates a correlation between the EBIC and the TEM image. Finally, in most specimens the partials are well separated so that they can be resolved with EBIC.

In a typical experiment, we first fabricate a Schottky diode in the area of interest. Subsequently, we image the area in the EBIC mode inside a scanning electron microscope. The EBIC image supplies information on the local recombination of minority carriers at crystal defects. The resolution of the EBIC image is controlled by the generation volume (and not, as one might suspect, by the minority carrier diffusion length) and is typically in the order of 1 μm . After characterization of the electrical activity, the

^{*)} Hirsch et al. proposed that the double value arises from the presence of both intrinsic and extrinsic faults. This explanation is no longer tenable.

specimen is subsequently imaged in a high electron microscope. If the specimen was pre-thinned to about 2 μm thickness prior to EBIC, no specimen manipulation is required between the two steps. At such a thickness the specimen is opaque to the EBIC electrons (which typically have an energy of about 10 KeV) and transparent to TEM electrons (which have an energy of about 1 MeV). Correlation between the two images is a little bit complicated by the fact that the lowest magnification at which the TEM can be operated is typically one order of magnitude higher than the highest magnification achievable in the SEM, but otherwise straight forward.

In 1980/81 we applied the technique to partial dislocations, (111):(115) second order twins, and on a preliminary basis, on Lomer Cotrell dislocations. It appears that partial dislocations can be both electrically active and non-electrically active. There is some tentative evidence that the electrical activity is linked to the crystallographic orientation of the dislocations, i.e., curved dislocations which lie not (or only in a segmented fashion) in Peirls valleys, tend to be electrically active and straight dislocations tend to be inactive. Such a behavior, if it can be confirmed, would agree with models which ascribe the electrical activity of dislocations to kinks along the dislocation line. However, there are at least two more mechanisms which can account for the observations, which are i) a varying impurity content of the boundary, (possibly controlled by sinks formed by intersecting non-coherent grain boundaries) and ii) the difference between grown in (or at least formed at high temperatures) and deformation induced (low temperatures, during cool-down) dislocations.

At the moment the kink model appears to be the most likely explanation, but more work will be required before the two other mechanisms can be ruled out.

Next, we applied the technique to second order twins. These second order twins are formed when a material (say of orientation M) forms a coherent twin (of orientation T_1) which, in turn, forms a second coherent twin (of orientation T_2). If a common boundary exists between the original material and the second order twin (i.e., a boundary M/ T_2), its structure is that of a second order twin. Such twins have been studied theoretically already by Hornstra, but so far, had not been observed in silicon. They turn out, however, to be a relatively common defect in EFG silicon, where alternating twinning operations generate straight boundaries, which are alternatively made up of coherent and second order twins. Such boundaries are segmentally electrically active, and generate, when the twin spacing is on the order of the resolution of the EBIC mode, EBIC images which are quite similar to coherent twin boundaries containing electrically active partial dislocations. Because of the straight appearance, these boundaries were in the past, by all investigators, assumed to be coherent twin boundaries. More details on the technique and the results obtained can be found in the attached publications No. 4 and 5.

The third area of research in the 1980/81 year was the passivation of the electrical activity of crystal defects with hydrogen. We showed in 79/80 that hydrogen can decrease, but not totally eliminate the electrical activity of defects in silicon. In the 1980/81 period, we studied the passivation in a more systematic way in that we tried to separate the influence of heat treatment from that of hydrogen per se. Since in all hydrogen passivation treatment, the specimen is heated into the 450°C range, the two effects are usually intermixed^{*)}.

^{*)} We seem to be the only group which tries to separate these effects.

A 450°C vacuum anneal of silicon can increase the minority by a factor ten, and can further, if the starting material was slightly p-type, convert the material into n-type (this conversion is usually explained with the formation of the thermal donor complex SiO_4^{--}). Thus, large changes in the electrical properties can be introduced by heat treatment alone.

Hydrogenation passivates defects presumably by tying up dangling bonds. Since the Si-H bond strength is somewhat larger than the Si-Si bond-strength, the Si-H level lies below the top of the valence band. The bonded state is, therefore, removed from the band gap. The anti-bonding state (conduction band level) of the Si-H bond probably lies somewhat above the bottom of the Si-Si band, but the point is still controversial.

In a typical passivation experiment, we split a specimen containing continuous defects (grain boundaries, coherent twins with intrinsic dislocations) in three parts. After EBIC examination the pieces are stripped of their Schottky diodes. The left piece is left untreated, to serve as a control for the reproducibility with which the Schottky diode can be reapplied. The center piece is subjected to a glow discharge hydrogenation treatment at the temperature and duration of the vacuum anneal. The Schottky diodes are then reapplied and the diodes are examined in with EBIC to ascertain the changes in electrical activity which may have taken place.

The investigation showed that a thermal treatment alone can, as suspected, introduce large changes in the EBIC signal. Whether this is due to an increase in the minority carrier lifetime or some other effect (oxygen contamination, formation of MIS structures) has not been clarified. Deformation induced dislocations are about 1 order of magnitude more electrically active than ingrown dislocations. Hydrogen passivation reduces the electrical activity of these

dislocations to the level comparable to that of ingrown dislocations. The activity of ingrown dislocations does not appear to change markedly. These observations can be rationalized by assuming that the ingrown dislocation (which have been formed at high temperatures) have a reconstructed core with few or no dangling bonds. Such an interpretation has some support from ESR measurements which show that the spin signal of heavily deformed silicon disappears when the latter is heated above 700°C. The deformation induced dislocations, (which are presumably formed below 700°C) are assumed to have unreconstructed cores and are therefore expected to be more electrically active. However, more experiments will have to be carried out before such an explanation can be accepted. More details on the technique and the results obtained can be found in the attached publication No. 6.

Summary

Research in the period 1980/81 was carried out in three areas: diffraction experiments on diffusion bonded ("welded") grain boundaries, ii) combined EBIC and HVTEM experiments in order to correlate electrical and structural properties of simple defects and iii) passivation of crystal defects with hydrogen.

The results obtained from the diffraction experiment are in agreement with those obtained previously with conventional and high resolution (structural) transmission electron microscopy. Combined EBIC and HVTEM of partial dislocations and second order twins has clarified two causes of the electrical activity of coherent twin boundaries (which per se are not electrically active). This finding has technological implications for the improvement of poly or semi-crystalline materials for solar cells. Finally, the passivation experiments have demonstrated the need to separate thermal effects from passivation effects. Hydrogenation is found to reduce, but not to totally eliminate the electrical activity of crystal defects. Deformation induced dislocations can be passivated very effectively. This finding is of some interest for the production of solar

silicon material, which frequently is subjected to considerable deformation during the cool down cycle.

Report No. 1

GRAIN BOUNDARIES IN SILICON:
A STUDY BY ELECTRON DIFFRACTION AND MICROSCOPY

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When a periodic structure is present in a grain boundary it is expected to give rise to extra spots in the electron diffraction patterns(1). This was shown to be the case for manufactured grain boundaries at the midplane of gold bicrystals(1) and inclined boundaries in polycrystalline foils(2). The geometry of diffraction from an inclined boundary has now been discussed in detail(3); it is clear that diffraction information can be extremely valuable in identifying the periodic nature of many grain boundaries and in simplifying the interpretation of their images.

Silicon [001] twist grain boundaries were prepared by hot-pressing together single crystal chips of silicon and then cutting the resulting bicrystal at an angle to the boundary plane to give a specimen similar to that shown schematically in Fig. 1(a). The reciprocal lattice for such a boundary is shown schematically in Fig. 1(b): the matrix reflections (shown as squares) are elongated normal to both the foil surface and the boundary plane, while the extra reflections (shown as circles) are elongated normal to the boundary plane only. The appearance of the observed diffraction pattern is governed by how the Ewald sphere cuts the rods: thus for the $\bar{2}20$ region in Fig. 1(b) the diffraction pattern will show the array of spots in Fig. 1(c). The positions of the M (matrix) spots change in a systematic way as the sign and magnitude of s_g is varied. The extra (grain boundary) spots in Fig. 1(c) are not associated with M spots and it is the presence of these spots which show that a grain boundary has a periodic structure. Observations in agreement with Fig. 1(b,c) are illustrated in Fig. 2, which shows two regions of the same 3° boundary: in region A the bright lines correspond to a periodic array of screw dislocations, while in region B it is thought that the thin layer of amorphous SiO_2 initially present on the silicon surface has not been removed and thus prevents the formation of a grain boundary. The $\bar{2}20$ regions of the corresponding diffraction patterns are shown as insets and it can clearly be seen that extra spots are present in the diffraction pattern from region A, which do not occur in the pattern from region B. This confirms that extra spots will be present only when the grain boundary has a periodic structure. The occurrence of pairs of extra spots instead of the single spots predicted in Fig. 1(b,c), is due to the presence of a small tilt component superimposed on the twist boundary, which causes the offsetting of the bright lines in the image of region A.

Frequently the image can be quite complicated and in these circumstances it is found that the diffraction pattern provides unambiguous information on the periodic nature of the boundary. Fig. 3 shows the image of an 8° twist boundary which contains a coarse array of lines with 12 nm spacing and a fine fringe pattern (in the inset) with 1.3 nm spacing. The diffraction pattern from the $\bar{2}20$ region, for a slightly different orientation of the foil, shows the presence of a pair of extra spots midway between the M spots. These extra spots correspond to a twist component periodicity of 2.7 nm. Thus the 1.3 nm fringes must be due to a Moiré effect resulting from interference between strongly excited M spots and, therefore, provide no information about the actual boundary structure. The splitting of the spots suggests that a tilt component is present with a periodicity of 12.5 nm, which correlates well with the image.

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Figure 1. (a) Illustrating the geometry of a bicrystal containing a twist boundary which is inclined to the foil surface. The screw dislocation spacing is p , the foil normal is $\vec{m}$, and the grain boundary normal is $\vec{n}$. (b) The schematic reciprocal lattice for the bicrystal in (a). The extra grain boundary relrods are indicated by rods passing through filled-in spheres. (c) The electron diffraction patterns expected in the $2\bar{2}0$ region for opposite signs of s_g . The N spots result from the Ewald sphere cutting the relrods parallel to $\vec{n}$ which pass through the matrix reflections, while the M spots result from the Ewald sphere cutting the relrods parallel to $\vec{m}$.

Figure 2. Observations on a 3° [001] twist boundary. The weak-beam dark-field image was formed with $2\bar{2}0$ reflections. Note the presence of a pair of extra reflections (arrowed) from the region marked A, which shows periodic dislocation contrast. The direction of the arrowed pair of reflections is normal to the set of lines across which the screw dislocations are displaced.

Figure 3. Observations on an 8° [001] twist boundary. The bright field image shows a coarse array of lines with 12 nm spacing. The enlargement shows a fringe pattern with 1.3 nm spacing. The diffraction pattern from the $2\bar{2}0$ region shows the presence of a pair of extra spots (arrowed).

Report no. 2

Electron Diffraction and Microscopy Studies
of the Structure of Grain Boundaries in Silicon

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ABSTRACT

The diffraction effects expected from the periodic structure of twist boundaries in Si were determined by an examination of the reciprocal lattice of these boundaries. Methods of analysis were developed to distinguish between the real diffraction spots due to the periodic boundary structure and those due to double diffraction effects. The electron microscope images from the boundaries studied in Si bicrystals frequently were complex and contained Moiré fringes which provided no information on the actual boundary structure. By analyzing the electron diffraction patterns from these boundaries for the presence of new diffraction spots it was possible to show that all the $\Sigma 1$ [001], $\Sigma 1$ [111] and $\Sigma 3$ [111] twist boundaries examined have a periodic structure.

1. Introduction

Recently Föll and Ast (1979) reported the results of a transmission electron microscope study of the structure of twist and tilt boundaries in silicon bicrystals which had been produced by hot-pressing single crystal chips of silicon. The pressure-sintering technique allows systematic studies to be made of well-characterized boundaries where, for example, the boundary plane is fixed and the misorientation angle is varied. This technique was first developed for gold bicrystals by Schober and Balluffi (1969, 1970), but unlike the boundaries in gold which are parallel to the surface of the thin foil, those in silicon are cut to be inclined or normal to the foil surface. [The boundaries in gold can be made to rotate to the edge-on orientation (Schober and Balluffi (1971)) or be prepared in this orientation (Cosandey, Komem and Bauer (1978)).]

Föll and Ast showed that small angle twist boundaries in silicon consist of periodic arrays of screw dislocations as observed in the study of similar boundaries in gold. It was also observed that as the misorientation angle increased the visibility of the dislocation array decreased, as expected from diffraction contrast theory (Thölen 1970). Fringe contrast with spacings as small as 1.3 nm could be detected in the images of a $\Sigma 1$ [001] boundary. Lattice fringe imaging suggests that such images are due to a Moiré (interference) effect and not to the actual boundary structure.

Carter, Donald and Sass (1979) have recently examined the geometry of the reciprocal lattice associated with an inclined grain boundary in a thin foil and demonstrated that the diffraction pattern from the grain boundary region can provide unambiguous information on the periodic nature of the boundary. It was also shown that both the real extra reflections due to the boundary structure and the additional spots in the diffraction pattern arising from double diffraction could give rise to misleading artifacts in the image.

The present paper applies the electron diffraction technique to the study of the structure of three different types of twist grain boundaries in silicon, namely $\Sigma 1$ [001]; $\Sigma 1$ [111] and $\Sigma 3$ [111]. In addition the study provides a start to the cataloguing of diffraction effects characteristic of various types of known boundaries, for example, a twist boundary with a small superimposed tilt component. The aim of the latter part of this study is to facilitate the characterization of boundaries with unknown parameters using diffraction information.

2. Experimental Techniques

The bicrystals of silicon were manufactured using the hot-pressing technique described by Föll and Ast (1979). The technique is similar to that developed for gold by Schober and Balluffi and involves hot-pressing, at 1200°C and pressures of ~ 1 Mpa, two or more slices of silicon in a hydrogen atmosphere. The silicon used was n-type and the slices were polished to give a mirror finish. Specimens were prepared for electron microscopy by cutting the bicrystal(s) at an angle of 25° to the boundary plane. After chemical thinning or ion milling the specimens were examined using a Siemens Elmiskop 102 electron microscope operating at 125 kV.

The majority of the observations which will be discussed in this paper were made by tilting the specimen in the microscope so that the electron beam was nearly normal to the boundary plane. This is different from the approach used by Carter, Donald and Sass (1979), where the foil normal was kept almost parallel to the electron beam. The current procedure has the advantage that no correction need be made in order to relate the periodicities observed in the image with those present in the boundary. Throughout this work the boundaries will be referred to as [001] or [111] twist boundaries to signify that the boundary plane is very close to the (001) or (111) planes, respectively, although if a tilt component is present this will not strictly be the case.

3. Experimental Results and Discussion

3.1 [001] Twist boundaries

3.1.1 Geometry of the reciprocal lattice

The structure of a small angle [001] twist boundary is expected to consist of two sets of orthogonal screw dislocations with Burgers vector, $\vec{b} = a/2 \langle 110 \rangle$ and spacing, p , as shown schematically in Fig. 1 (a), where the foil has been tilted so that the electron beam is parallel to $\vec{n}$, the normal to the boundary plane. The reciprocal lattice associated with such a boundary, which is inclined to the foil surface, is shown schematically in Fig. 1 (b). The dislocation network gives rise to an array of relrods parallel to $\vec{n}$, on a square lattice with spacing $1/p$, which contains the matrix reflections [Guan and Sass (1973a,b)]. The boundary is the same as that considered by Guan and Sass (1973a,b) except that $\vec{m}$, the foil normal, is not coincident with $\vec{n}$. Regions of the diffraction pattern close to the pairs of $2\bar{2}0$ and 400 reflections are shown in Figs. 1 c and d respectively, for small values and different signs of the excitation error, s_g . The spots labelled M_1, M_2 are associated with the two crystals and their positions relative to the related N_1, N_2 spots depend on the magnitude and sign of s_g : if the sign of s_g is reversed the M spots will move to the other side of their respective N spots. (It should be noted that for this geometry it is the M spot which moves as s_g is varied and not the N spot [cf. Carter, Donald and Sass (1979)]). The misorientation angle is related to the spacing of primary dislocations in Fig. 1 (a) by the formula (Read 1953)

$$\sin \theta/2 = \frac{|\vec{b}|}{2p} \quad (1)$$

As the misorientation angle increases, the magnitude of p decreases, until it no longer is physically realistic to talk about individual primary dislocations and p will be the O-lattice spacing [Bollmann (1970)].

In the next section it will be demonstrated that the ability to separate the N and M spots allows the extra spots arising from the periodic structure of the boundary to be identified. In the case of the gold bicrystals,

where the grain boundary is parallel to the foil surface, the N_1 , N_2 and M_1 , M_2 spots always superimpose, and because of this it is difficult to eliminate all possibility of double diffraction causing additional spots (Sass, Tan and Balluffi, (1975); Sass and Balluffi, (1976)). Carter, Donald and Sass (1979) demonstrated that double diffraction can be a factor even for inclined boundaries and can lead to the presence of spurious spots in many regions of the diffraction pattern.

3.1.2 Double diffraction analysis

Double diffraction becomes important when a strong matrix reflection, excited in the upper crystal, is rescattered by the lower crystal. In order to determine the new spots that can result from this process, it is necessary to translate 000 to the positions of the strong matrix reflections, which act as new incident beams. When this is done, other matrix reflections can be moved close to the Ewald sphere, resulting in new diffraction spots. In order to determine the influence of this process on the observed diffraction pattern, it is necessary to examine the three dimensional representation of the reciprocal lattice for the inclined grain boundary shown in Fig. 2.

In this figure the geometry of diffraction is shown for the [001] twist boundary in Fig. 1 (a). The situation illustrated is with the pair of $2\bar{2}0$ reflections on the Ewald sphere ($s_g = 0$). If crystal 1 is the upper crystal then the $2\bar{2}0_1$ reflection can be rescattered by the lower crystal. To determine what new spots can result from double diffraction, translate 000 to position $2\bar{2}0_1$ as shown by the solid arrow; 040_1 then moves to superimpose on $2\bar{2}0_1$, while 040_2 moves to the position shown by the dashed arrow and yields spots M_D and N_D . Since the reflections from the two crystals and the grain boundary lie on the same reciprocal lattice (related to the coincidence site lattice [Sass, Tan and Balluffi (1975), Sass

and Balluffi (1976)]), reflection 040_2 is moved to a position that is on the square reciprocal lattice of the boundary. If that position is cut by the Ewald sphere such that $s_g \neq 0$ then it can easily be seen that if N_D and M_D are both present, it is not possible to decide if N_D is real. Also when $s_g = 0$, M_D and N_D superimpose and it is not possible to decide if the observed spot is real or due to double diffraction. If, however, when $s_g \neq 0$ the N_D spot is observed to occur without an accompanying M_D spot, then it must be real i.e. associated with the grain boundary structure. It can thus be seen that double diffraction can produce arrays of relrods parallel to $\vec{n}$ and $\vec{m}$, that yield spots lying on two lattices, one containing M_1 and M_2 (called the M lattice) and the other containing N_1 and N_2 (called the N lattice). The real grain boundary relrods, which are parallel to $\vec{n}$, will yield spots that lie on a lattice containing N_1 and N_2 . It is the presence of additional spots on the N lattice, *which are not paired to spots on the M lattice*, which is evidence for the periodic nature of the grain boundary structure. It can further be seen for the geometry of Fig. 2, that while the observed N lattice will be square, the observed M lattice will be distorted away from being square. However if the angle between $\vec{m}$ and $\vec{n}$ is relatively small, as is the case here, then it will not be possible to detect easily the deviation of the M lattice away from being square.

3.1.3 Observations

To illustrate the features observed from an actual boundary of the type discussed above, a nominally $\Sigma 1$ [001] twist boundary will be examined in some detail. All of the boundaries to be discussed here were slightly off the ideal boundary plane and thus contained a measurable tilt component. This was because the faces of the single crystals could not be polished to be exactly (001) or (111). The influence of the tilt component on the experimental observations will be discussed later in this section.

Fig. 3 is a bright-field multibeam image (Föll and Ast, 1979) of a nearly pure twist $\Sigma 1$ [001] boundary with a 2.0° misorientation angle, which shows a square network associated with the two sets of screw dislocations which have a 10 nm spacing. Frequently the bright field images are much more complicated, as is illustrated in Fig. 4 (a), which shows a complex array of fringes with 3.0 nm spacing from a 3.0° boundary. A weak-beam dark-field image of this same area, recorded using the $\bar{2}20$ region of the diffraction pattern, is shown in Fig. 4 (b): one set of screw dislocations appears as a series of narrow lines with 6.0 nm spacing while the other set is out of contrast. The screw dislocation lines in Fig. 4 (b) are occasionally displaced (every ~ 45 nm) and these shifts are believed due to dislocations with an edge component which accommodate a small tilt of $\sim 1/4^\circ$ in the boundary. The direction and magnitude of the tilt component can be accurately determined for small angles by recording the diffraction patterns of both crystals on the same photographic plate. Two electron diffraction patterns from this boundary, also recorded close to the nearly common 001 pole, are shown in Fig. 4 (c and d), together with enlarged insets of several areas of the patterns. (The two patterns are related by a tilt approximately about the $\bar{2}20$ axis.) Several of the insets in these figures are shown schematically and it can be seen that, in each case, the spots either lie on a fine lattice (o) or on a coarse lattice (•) and that the spacing of the coarse lattice is twice that of the fine lattice. The positions of the • spots relative to the o spots reverse when the sign of s_g is reversed (cf I and II) and this behavior agrees with the predictions in Fig. 1 (c and d): with the symbols o and • corresponding to the N and M lattices, respectively. The spacing of the N spots yields a twist angle of 3.1° which, according to equation 1, corresponds to an array of screw dislocations with spacing 7.1 nm, which is somewhat larger than the value of 6.0 nm measured from the dark field image in Fig. 4 (b).

It is frequently observed that spots on the N lattice do not have companion spots on the M lattice. This observation is in agreement with the predicted behavior of the extra spots from the grain boundary described in Fig. 2 and is direct evidence for the periodic nature of the boundary structure. The complex fringe pattern seen in Fig. 4 (a) is most likely the result of interference among the many reflections seen in the insets in Fig. 4 (c,d), which have been brought into the vicinity of the origin by double diffraction. Since many of the reflections in Fig. 4 (c,d) are the result of double diffraction, the image must contain Moiré fringes which provide no information about the boundary structure. It appears then that the diffraction pattern is the best source of unambiguous information about the actual boundary structure.

Conclusive proof that the extra spots on the N lattice result from relaxations in the grain boundary, and are not present when two single crystals are simply touching, can be obtained by studying the diffraction patterns from the interface shown in Fig. 5(a) which has a misorientation similar to those of the boundaries in Figs. 3 and 4. In the region shown, the area A of the interface is a grain boundary, since the weak-beam image shows images of one of the sets of screw dislocations with a measured separation of 7.0 nm; the dislocation line displacement occurs more frequently than in Fig. 4 (b) (~18 nm spacing) and must be associated with a larger tilt component. The neighboring area B shows no evidence for a dislocation array; with only a fine set of fringes typical of a Moiré effect present with a measured 3.5 nm periodicity. This value is half that of the expected dislocation spacing predicted from Eqn. 1 for this boundary. Superimposed on both areas are thickness fringes associated with the inclination of the interface to the foil surface. The observed features can be explained by noting that where dislocations are not present the two crystals do not actually touch but are separated by a thin amorphous or glassy phase which is presumably SiO_2 . The amorphous region

is an artifact produced by the sintering technique used to manufacture the bicrystal.

Figs. 5 (b and c) show selected area diffraction patterns taken from the grain boundary and amorphous interface regions, respectively. The misorientation angle determined from the diffraction pattern is 3.1° which, according to equation 1, is consistent with a dislocation spacing of 7.1 nm. By comparing the diffraction patterns in the vicinity of the same matrix reflections from the two regions, it can be seen that the area of structured grain boundary gives rise to pairs of closely-spaced extra spots (arrowed) in addition to N and M spots while the non-structured interface gives rise to no extra spots. This is a direct proof that the extra reflections result from the grain boundary region. This observation demonstrates that the detection of M and N spots by themselves only shows that an inclined interface is present and gives no information on the structure of the interface. The pair of extra reflections lie along a line which has a different direction than that of the line joining the M and N spots, and which is normal to the array of lines across which the screw dislocations are displaced.

The origin of the pairs of extra spots in Fig. 5 (b) can be most clearly demonstrated by examination of the boundary shown in Fig. 6 (a), which is a 220 weak-beam image of another region of the same nominally $\Sigma 1$ [001] twist boundary in Fig. 5, intercepted by an extremely low angle grain boundary. In area A the structure of the boundary is similar to that shown in Fig. 5 (a) with the set of screw dislocations in contrast being periodically displaced by a coarse set of dislocations; in area B the coarse network is now parallel to one set of screw dislocations.

The diffraction patterns from regions A and B are shown in Figs. 6 (b and c), respectively: in both cases in the 220 region a pair of extra spots is

present between the N spots, and the direction of the line joining the two spots is normal to the coarse dislocation array in the region from which the diffraction pattern is taken. The separation of both sets of spots corresponds to a distance in real space of ~ 19 nm. It can therefore be seen, in this example, that the occurrence of a pair of closely spaced grain boundary reflections is related to the presence of a periodic array of dislocations with partly edge character which accommodates a tilt component superimposed on the twist boundary. It is interesting to note that Guan and Sass (1979) made a similar observation, on a large angle tilt boundary upon which was superimposed a small twist component, of the splitting of single grain boundary reflections into pairs.

Both the twist and the tilt components impose their own periodicity on the boundary. If, as is likely, these are not simple multiples of one another, the true periodicity of the boundary may be very large (100 nm or more). It seems more meaningful then to separate out the different components when discussing such a boundary, instead of concentrating on the correct (and possibly large) unit cell. An example of just such a boundary with a large unit cell in a polycrystalline foil was discussed by Carter, Donald and Sass (1979a, Fig. 3).

With previous analyses and observations as background, attention can now be focussed on a larger angle ($\sim 8^\circ$) twist boundary where the structure cannot be determined from the image. A bright-field image of this boundary recorded with both crystals set close to the 001 pole, is shown in Fig. 7 (a), together with an enlarged area in Fig. 7 (b) to show the faint square fringe pattern present. The fringes lie along the mean $\langle 110 \rangle$ directions and have a spacing of 1.3 nm (another set of fine fringes parallel to the mean $[100]$ direction is also present with a spacing of 0.9 nm). Another image of this boundary recorded slightly off the 001 pole is shown in Fig. 7 (c) and one set of fringes with 1.3 nm spacing and another set with 12.5 nm spacing are observed. A diffraction pattern from this area of the boundary is shown in Fig. 7 (d) together with insets of selected areas at greater magnification. Once again it can be seen

that there are pairs of extra reflections present which are located midway between the two N spots and that the line connecting these extra pairs of spots is not parallel to the NM direction. From the diffraction pattern it can be seen that when s_g changes sign, the M spots move from one side of the N spots to the other, while the extra pair of spots remains midway between the N spots. As a result of the analyses based on Figs. 1 to 6, it can be concluded from the presence of the extra pairs of spots which are symmetrically located midway between the N spots, both that the 8° twist boundary has a periodic structure and that a tilt component is present. The angle of misorientation is determined from the diffraction pattern to be 8.2° and the periodicity of the relaxation is expected to be 2.6 nm according to equation 1 (where $\vec{b}$ is taken to be $a/2\langle 110 \rangle$). The 1.3 nm fringe spacing observed in Fig. 7 (a,b) must, therefore, be due to interference between the pair of M spots or the pair of N spots which are separated by a distance which is twice the spacing between an N spot and the midpoint of the pair of extra spots. The separation between the pair of extra spots corresponds to a periodicity of 12.8 nm which is close to the observed spacing of 12.5 nm. It is also observed that the direction of the line connecting the extra pair of spots is normal to the coarse fringe periodicity. For the boundary considered in Fig. 7 it can be concluded that, apart from the coarse fringe contrast associated with the tilt component, there is no other information in the image about the structure of the twist boundary.

It is interesting to note that the extra reflections from the 8° boundary are apparently much weaker relative to the matrix reflections than corresponding reflections from a similar boundary in Au [see Fig. 4 (b) of Guan and Sass (1973a)]. This difference may be due partly to the magnitude of the atomic displacements associated with the twist boundary in Si being smaller than in Au. Bristowe and Sass (1980) have found, from computer modelling studies, that the atomic displacements for twist boundaries with a given misorientation angle, vary

depending on the f.c.c. metal considered, and are particularly large for Au.

Au is a much stronger scatterer of electrons than is Si which may also explain why the grain boundary spots appear stronger in Au than in Si.

Attempts were made to examine a boundary in the vicinity of the $\Sigma 5$ [001] misorientation ($\theta = 36.87^\circ$), but although evidence for secondary dislocations and a tilt component was obtained from the image (Carter, Föll, Ast and Sass, 1979), the diffraction pattern showed no extra effects related to the presence of a periodic structure. The volume of the grain boundary region is expected to decrease with increasing misorientation, since its thickness is expected to decrease with increasing misorientation [Cottrell (1953)]. If this is the case then it might be expected that the magnitude of scattering from a large angle boundary would be less than that from a small angle boundary. Indeed it was noted above that the intensity of the grain boundary reflections was quite low for the 8° boundary and, therefore, it is reasonable to expect that the intensity from the $\sim 37^\circ$ boundary would be even lower, which may explain why it was not detected.

3.2 [111] Twist boundaries

3.2.1 Geometry of the reciprocal lattice

Three [111] twist boundaries are shown schematically in Figs. 8 (a, b, c.) Fig. 8 (a) shows a $\Sigma 1$ boundary consisting of an hexagonal array of pure screw dislocations with Burgers vector $a/2\langle 110 \rangle$ while Fig. 8 (b) shows the situation commonly observed in this boundary in silicon, which has a relatively low stacking fault energy; the configuration consists of nodes containing alternating extrinsic and intrinsic stacking faults. Fig. 8 (c) shows a $\Sigma 3$ [111] twist boundary with the same misorientation from exact coincidence as for the $\Sigma 1$ boundaries in Fig. 8 (a,b). This boundary can be formed by imagining the stacking fault energy to be zero in fig. 8 (b) and then adding a pure $\Sigma 3$ twin boundary to remove all the stacking faults.

Equation 1 can be used to relate the spacing of the dislocations shown in

Fig. 8 (a) to the angle of misorientation. In order to do this, two sets of orthogonal, pure screw dislocations must be chosen and these need have no relation to the actual dislocations present in the boundary. Equation 1 can be written as:

$$\sin \theta/2 = \frac{a}{y} \frac{\sqrt{3}}{4\sqrt{2}} \quad (2)$$

where a is the lattice constant, and y , the shortest periodicity for this boundary, is defined in Fig. 8 (a). The periodicity, y , is in the $\langle 110 \rangle$ direction and is thus expected to give rise to extra spots in the 220 region of the 111 plane in reciprocal space as shown in Fig. 8 (d). The extra spots will be a distance $1/y$ from the N spots and lie along $\langle 110 \rangle$ directions in a hexagonal array. The projected structure of the boundary has hexagonal symmetry and the formation of extended nodes will not alter this symmetry.

For the same misorientation the $\Sigma 3$ boundary will have a smaller unit cell *in projection* than the $\Sigma 1$ boundary as illustrated in Fig. 8 (c). Equation 2 will still hold but the shortest periodicity is now $x (=y/\sqrt{3})$ and is in the $\langle 112 \rangle$ direction. This structure will give rise to extra spots as shown in Fig. 8 (e); the distance between the extra spots is now equal to the distance between the N spots and the hexagonal array from the grain boundary structure is actually based on these N spots.

3.2.2 Observations

(a) $\Sigma 1$

Fig. 9 (a) shows a bright-field image from a $\theta=5.2^\circ$ boundary viewed at normal incidence; a fine hexagonal fringe pattern with spacing of 2.0 nm is clearly visible in the enlargement in Fig. 9 (b). The corresponding diffraction pattern is shown in Fig. 9 (c) where the approximately equal intensity of each spot of the pairs of 220 spots indicates that any tilt component which is present in this boundary is very small, as confirmed by observations on the Kikuchi lines. Examination of the enlarged 220 region in the inset shows that weak and strong extra spots are present close to the matrix spots but, because of the small value of s_g for the low index reflections, it is not possible to distinguish the M and N

spots. This information is necessary since the appearance of both strong and weak extra spots suggests that double diffraction may be influencing the diffraction pattern. The foil was then tilted away from the 111 orientation in order to weaken some of the matrix reflections, and the diffraction pattern shown in Fig. 9 (d) was recorded. In several of the enlarged insets the M spots can be clearly distinguished from the N spots and it can be seen that extra spots are present on the hexagonal N lattice in the positions predicted by Fig. 8 (d). The presence of these extra spots shows that the boundary has a periodic structure.

A 5.2° deviation from $\Sigma 1$ would give a Moiré fringe spacing of 2.2 nm for 220-type reflections, while the actual boundary periodicity is expected to be 3.7 nm. The appearance, direction and 2.0 nm spacing of the hexagonal fringe pattern in Fig. 9 (a,b) confirms that it is a Moiré effect resulting from the interference of pairs of 220-type reflections and other double diffraction spots with the same spacing. Thus the image contains no information on the structure of the boundary, which has been shown to be periodic from the diffraction pattern. It is interesting to note that many of the strong extra spots present in the vicinity of each pair of 220-type spots in Fig. 9 (c), disappear with the small tilt to Fig. 9 (d), indicating that they and similar reflections close to the origin are due largely to double diffraction. It is these reflections in the vicinity of the origin that are producing the strong fringe contrast in Fig. 9 (a,b).

In certain of the insets in Fig. 9 (d), where s_g is relatively large and the N spots are easily identified, the M_1 and M_2 spots are split into pairs (See the white arrows). Close examination shows that the M spots are actually split in two different directions. By comparing the diffraction patterns and the image it can be seen that the direction of the line joining a particular pair of spots is normal to the thickness fringes in the corresponding grain. This suggests that the splitting of the M spots is due to the foil not having parallel surfaces

but instead being wedge-shaped. Each matrix reflection can be considered to have two $\vec{m}$ relrods passing through it, with a relrod being normal to each of the foil surfaces (de Ridder, Van Landuyt, Gevers and Amelinckx 1970). This effect is only likely to be observed experimentally when both the wedge angle and s_g are relatively large. This observation does emphasize the importance of being able to identify the N spots which are not influenced by the surface of the thin foil but depend only on the plane of the boundary.

Careful examination of the diffraction patterns in Figs. 9 (c and d) shows the presence of forbidden spots (see F), which are indexed as $1/3(224)$ -type. These spots were not observed in the single crystal diffraction patterns taken from the Si crystals adjacent to the boundary and, therefore, they must be associated with the grain boundary region. These spots are also observed from the 1° twist boundary shown in Fig. 10 (a). This boundary shows a complex array of images of Shockley partial dislocations and Moiré fringes due to unsintered regions. In region A the boundary consists of extended nodes similar to those shown in Fig. 8 (b); one set of partial dislocations is out of contrast having $\vec{g} \cdot \vec{b} = 0$. Figure 10 (b) shows a tilt sequence of diffraction patterns going from (110) to (111) to (112). The forbidden spots are clearly seen in the (111) pattern (see white arrow) and after tilting through a large angle about the $2\bar{2}0$ axis to the (112) orientation, it can be seen that the forbidden spots are still present, though their positions have changed slightly. Further tilt to the (110) orientation causes the forbidden spots to move into the positions of Si reflections. Thus it is seen that the forbidden spots close to 000 are due to elongation into relrods of the 111-type reflections. Since the 111-type reflections above and below the (111) reciprocal lattice plane, lie on lines normal to this plane which pass through $1/3(224)$ -type positions, it can be deduced that the relrods are normal to the (111) plane.

Information on the origin of the forbidden $1/3(224)$ -type reflections was obtained from a study of the small angle twist boundary with a large tilt component in

Fig. 11 (a,b). The weak-beam image in Fig. 11 (a) clearly shows a rectangular network of dislocations and, in agreement with this, the extra diffraction spots present in Fig. 11 (b) lie on a rectangular lattice (which is slightly distorted). The rectangular network is apparently the result of the interaction of the edge dislocation array due to the tilt component with the hexagonal dislocation array of the twist boundary. In other twist boundaries which have only a small tilt component stacking faults are probably present at the dislocation nodes (see e.g. area A of Fig. 10 and Fig. 10 of Föll and Ast 1979). There is no evidence for stacking faults being present in the boundary in Fig. 11 while stacking faults were identified for the boundary in Fig. 10. The absence of both stacking faults and forbidden reflections for the boundary in Fig. 11 and their presence for the other (111) twist boundaries suggests that the presence of stacking faults and forbidden reflections from the boundaries are linked together [these forbidden reflections can also occur when the specimen is very thin (Lynch 1971)]. Since the stacking fault is extremely thin, it is expected that the Si reflections will be elongated to give relrods normal to the fault (see e.g. Clarebrough and Forwood 1976). Thus the relrods associated with forbidden spots in Figs. 9 and 10 are believed due to the elongation into relrods normal to the boundary plane, of the 111 Si reflections above and below the 111 reciprocal lattice plane. As further confirmation of the link between stacking fault and relrod, it should be noted that the forbidden reflections are absent from all the [100] observations in Figs. 3 to 7, where there is also no evidence in the image for the presence of stacking faults. As noted before, the grain boundary displacement field will give rise to relrods, whose length is inversely related to the magnitude of the thickness of the boundary (Carter, Donald and Sass, 1980). It can be concluded that the relrods due to the grain boundary are considerably shorter than the relrods due to the stacking faults, since in the case of the [001] twist boundary, the 111 reflections do not exhibit long relrods, while

in the case of the $[111]$ twist boundary with stacking faults present, the 111 reflections do exhibit long relrods. The observed diffraction patterns from the $[111]$ twist boundaries behave as if the effects due to the stacking faults are present in addition to the effects due to the grain boundary. This is an interesting experimental observation because the stacking faults are an integral periodic part of the grain boundary structure, and it might have been expected that the length of the relrods would be influenced by the overall displacement field of the boundary, not just the local effects at the stacking faults.

It is interesting to note in the (111) pattern in Fig. 10 (b) that, in addition to the forbidden spots, there are also diffuse spots in an approximately hexagonal array around the Si matrix spots. On tilting about the $2\bar{2}0$ axis it is seen that the diffuse spots along this axis remain, indicating that they do not result from double diffraction and must be real. The disappearance of the diffuse spots lying along other $\langle 110 \rangle$ directions in the 111 plane indicates that they are not due to relrods. It is suggested that these spots, which lie on a reciprocal lattice with one-quarter the spacing of the Si reciprocal lattice, may be associated with the coherent precipitates occasionally found in these boundaries (see Fig. 14 (b), Föll and Ast 1979).

(b) $\Sigma 3$

Fig. 12 (a,b) shows a weak-beam dark-field image and the diffraction pattern from a $\Sigma 3$ boundary with $\sim 1.7^\circ$ misorientation. The image shows a fine fringe pattern which exhibits hexagonal symmetry in different regions. The inset in the diffraction pattern shows an array of spots lying on the N lattice in the positions predicted in Fig. 8 (e). Since these extra spots are not associated in general with M spots, it can be concluded that they are not due to double diffraction (see section 3.1.2) and their presence, therefore, demonstrates that the boundary structure is periodic. Measurements on the diffraction pattern yield a spacing of 6.4 nm. It is difficult to determine the periodicity from the image,

since it is not uniform in appearance. The fringes running parallel to [220] appear to have a somewhat smaller spacing of 5.0 nm. An interesting point to note is that the Moiré fringes associated with a small deviation from exact $\Sigma 3$ coincidence will have the same spacing as the screw dislocations if these are present, although of course the presence of the Moiré fringes would not give any information on the structure of the boundary. The forbidden weak $1/3(224)$ -type spots are again observed (see white arrow), and in this case are believed to be related to the presence of the twin interface (see e.g. Clarebrough and Forwood 1976).

4. Conclusions

The images from twist grain boundaries contained in Si bicrystals are frequently complex and contain Moiré fringes that provide no information on the actual boundary structure. An analysis of the reciprocal lattice associated with these boundaries has made it possible to separate out real extra reflections resulting from the periodic structure of the boundary, from spurious effects due to double diffraction. It was possible to show that all the $\Sigma 1$ [001], $\Sigma 1$ [111] and $\Sigma 3$ [111] twist boundaries examined had periodic structures. The $\Sigma 5$ [001] boundary gave rise to no detectable diffraction effects, however, the presence in the image of a periodic array of secondary dislocations demonstrated the periodic nature of the boundary. It is possible to detect small tilt components in these boundaries by the splitting into pairs of the extra reflections from the boundary.

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List of Figure Captions

Figure 1

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- c) The electron diffraction patterns expected in the $2\bar{2}0$ region, for opposite signs of s_g .
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Figure 2

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Figure 3

Bright-field multibeam image of 2° $[001]$ twist boundary.

Figure 4

Observations on a $\sim 3^\circ$ $[001]$ twist boundary.

- a) Bright-field image
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c,d) Electron diffraction patterns from the boundary in (a,b).

The two patterns are related by a tilt about the $2\bar{2}0$ axis.

Figure 5

Observations on a $\sim 3^\circ$ $[001]$ twist boundary

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Figure 8

The geometry of three $[111]$ twist boundaries.

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- d) 220 region of the diffraction pattern expected for (a) and (b).

- e) 220 region of the diffraction pattern expected for (c).

Figure 9

Observations on a $\sim 5.2^\circ$ [111] $\Sigma 1$ twist boundary.

- a) Bright-field image.
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Figure 10

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Figure 11

Observations on a small angle [111] $\Sigma 1$ twist boundary with a large tilt component.

- a) Weak-beam dark-field image formed with $2\bar{2}0$ reflections.
- b) Diffraction pattern corresponding to (a).

Figure 12

Observations on a $\sim 1.7^\circ$ [111] $\Sigma 3$ twist boundary.

- a) Weak-beam dark-field image formed with $2\bar{2}0$ reflections.
- b) Diffraction pattern corresponding to (a).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 4(c)

Figure 4(d)

Figure 5(a)

(b)

(c)

Figure 5

Figure 6(a)

(b)

(c)

Figure 6

(a)

(b)

Figure 7

Figure 7

Figure 8

(a)

(b)

(c)

Figure 9

Figure 9(d)

Figure 10(a)

Figure 10

Figure 11

(a)

(b)

Figure 12

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Weak-Beam Contrast of Stacking Faults in Transmission Electron Microscopy

By

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Stacking faults (and other planar defects) imaged under weak-beam conditions can exhibit pronounced contrast changes if the sign of the diffraction vector or of the excitation error is changed. This contrast behaviour has not yet been understood. In this paper, the contrast of weak-beam images of stacking faults in silicon is studied systematically; the faults are subsequently unambiguously characterized by direct lattice imaging. Other related planar defects in silicon, stainless steel, and a copper alloy are also investigated. Extrinsic stacking faults are found to show significant contrast asymmetries while intrinsic faults did not. A simple theory is presented which taking into account the finite thickness of an extrinsic stacking fault can explain most of the observed contrast phenomena.

Stapelfehler (und andere planare Defekte), die unter „weak-beam“-Bedingungen abgebildet werden, können ausgeprägte Änderungen im Kontrastverhalten zeigen, falls das Vorzeichen des Beugungsvektors oder des Anregungsfehlers geändert wird. Dieses Kontrastverhalten konnte bisher nicht erklärt werden. In dieser Arbeit wird der „weak-beam“-Kontrast von Stapelfehlern in Silizium systematisch untersucht; die Defekte werden anschließend durch direkte Kristallgitterabbildung eindeutig charakterisiert. Andere planare Defekte in Silizium, rostfreiem Stahl und einer Kupfer-Aluminium-Legierung werden ebenfalls untersucht. Extrinsische Stapelfehler zeigen, im Gegensatz zu intrinsischen Stapelfehlern, beträchtliche Kontrastasymmetrien. Eine einfache Theorie wird erläutert, die durch Berücksichtigung der endlichen Dicke eines extrinsischen Stapelfehlers die meisten der beobachteten Kontrastercheinungen erklären kann.

1. Introduction

The contrast of transmission electron microscope (TEM) images of stacking faults has been studied in great detail for the case of dynamical or kinematical two-beam conditions; for reviews see [1 to 3]. Under these conditions the contrast is well understood and can be accurately simulated using standard computing methods [4]. The principal parameters entering the calculations are $\mathbf{R}$, the displacement vector of the fault, $\mathbf{g}$, the diffraction vector, s , the excitation error, d , the depth position of the fault in the foil, and T , the foil thickness. It is found that the contrast varies periodically with both d and T , giving rise to the well known stacking-fault fringes observed for a stacking fault inclined in the foil. A basic result of previous calculations is that the intensity of the fringes is independent of the sign of the product $(\mathbf{g} \cdot \mathbf{R}) \cdot s$ (apart from the change of black fringes to white ones and vice versa). However, when the weak-beam technique [5] is used it has been shown that this need not be the case for stacking faults in silicon [6, 7].

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Fig. 1. Low magnification micrograph of the stacking faults in silicon which are studied in detail in Fig. 2 to 5 incl.

The experimental observation is that reversing the sign of g may change the over-all intensity of the stacking fault image from relatively high to very low [6, 7]. A similar observation has recently been made [8] for the related case of incoherent twin boundaries in both silicon and stainless steel where R then refers to the so-called rigid-body translation [9]. No explanation for the observed contrast anomaly has been offered in the literature, it therefore appeared worthwhile to re-investigate the contrast of stacking faults using weak-beam imaging conditions. Preliminary result of this study were given in [10] and the details of this investigation are the subject of this paper.

2. Extrinsic and Intrinsic Stacking Faults in Silicon

2.1 The geometry of the stacking faults investigated

The configuration of the stacking faults investigated in Si is shown in Fig. 1. The stacking faults form two truncated pyramids which appear to have one side in common. The defects occurred in the epitaxial silicon layer deposited on a $\{111\}$ oriented substrate. This process frequently results in the formation of very large stacking faults [11], in this case the faults were nucleated at the end points of dislocations which moved into the substrate during the epitaxial process due to thermal stresses [11]. A short Sirtl etch treatment [12] was applied in order to identify stacking-fault rich areas; specimens of suitable size were then taken from these areas. Chemical-mechanical polishing in silica-gel was used to remove the etched layer and the specimens were then chemically thinned from the backside. The mechanical-chemical polishing however did not remove the entire etch structure and the faults thus lie in groves which outline their shape (Fig. 1). Before this investigation it had already been established that the

Fig. 2. Lattice image of stacking faults at area B in Fig. 1. Arrows denote traces of $\{111\}$ planes

stacking faults in these samples were exclusively intrinsic in nature if they occurred as single faults or as single fault pyramids. It thus could be safely assumed that the faults forming the defect of interest were of the intrinsic type, too — except for the portion AB. This could be an intrinsic fault, an extrinsic fault, two intrinsic faults overlapping on non-adjacent planes or even a microtwin (the existence of microtwins in connection with stacking faults in epitaxial layers of Si has been demonstrated in [13]). An unambiguous distinction between these possibilities with conventional (“first-fringe”) methods proved to be impossible, partly because the specimen was too thin for these methods to be applied reliably [4] and partly because a distinction between the possible defect configurations mentioned above is very difficult even under favorable conditions.

The nature of the defect was therefore ascertained by further thinning the sample using an ion-beam thinner (after the weak-beam images discussed in the next section had been taken) and then studying the area of interest using lattice imaging techniques [14, 15]. Axial illumination was used after tilting the specimen approximately 35° to the $\{110\}$ pole so that the particular stacking faults could be viewed edge-on. The specimen was somewhat buckled after the ion-milling; a determination of the actual orientation within the accuracy needed for “true” structural images [14] was therefore

Fig. 3. Weak-beam image of area B. Arrows in this and in the following pictures indicate diffraction vectors. $g = \{220\}$ in this case

not possible. In order to overcome this difficulty several sets of pictures have been taken with slightly modified imaging conditions. The microscope used was an Elmiskop 102 equipped with a tilt stage and operated at 125 keV. Fig. 2 shows the lattice image of the defect (area B); the inserts 1 and 2 are from sets of images taken under slightly different imaging conditions, insert 3 is an enlargement from this image. These images (and some twenty others not shown here) demonstrate conclusively that the defect between A and B on Fig. 1 is an extrinsic stacking fault while the other faults are intrinsic. The contrast irregularities along parts of the stacking faults in the lower magnification image of Fig. 2 are most likely due to very small tilts away from the ideal diffraction conditions and not due to the presence of impurities in the fault. This is concluded from the observation that the expected lattice image can be obtained by a small change in the diffraction conditions.

2.2 Weak-beam contrast from stacking faults in silicon

Fig. 3 shows weak-beam images of the same area shown in Fig. 2 which were obtained using $\{220\}$ reflections close to the $\{111\}$ pole. A large change in contrast on reversing g can be seen for the extrinsic stacking fault (E), while little change occurs for the intrinsic faults (I). The change in contrast of the extrinsic fault was found to be relatively insensitive to the magnitude of the excitation error s , provided this was not too small. Fig. 4 a, b shows a similar pair of weak-beam images from area A, together with an image for a larger value of s (Fig. 4f), two images using $\{111\}$ reflections and a strong-beam image. The actual diffraction conditions used are indicated in the figures. Fig. 4f does not show the intensity modulation of the stacking fault fringes visible in Fig. 3 and Fig. 4 a, b which are due to the strong coupling of g and $2g$ [16]. Fig. 4 a, b also demonstrates that the asymmetry in the contrast is not due to particular values of the foil thickness because they show the same asymmetry as Fig. 3 a and b, although the specimen is thicker here.

From Fig. 4 c and d it appears that the contrast asymmetry does not occur, or is much less pronounced for the $\{111\}$ reflections.

Fig. 4. Area A imaged with different diffraction vectors. a), b), e), f): $g = \{220\}$, c), d): $g = \{111\}$. For details see text

Fig. 5. Area C imaged with different diffraction vectors. a), b): $g = \{111\}$; c), d): $g = \{220\}$

Fig. 5 shows similar weak-beam images from area C. In this case, which is for a much thicker foil, the possibility cannot be excluded that the $\{111\}$ images show some asymmetry if g is reversed (Fig. 5 a and b) even though both faults are intrinsic in nature. In contrast, the $\{220\}$ reflections (Fig. 5 c and d) do not show a detectable effect. These images also show that impurity segregation has occurred along the stair-rod dislocation at the junction of the stacking faults.

Clearly, the contrast mechanism is complicated, but it can be concluded from these observations that

(i) the contrast of an extrinsic stacking fault in Si inclined with an angle of $\approx 70^\circ$ in the foil shows a large contrast asymmetry with respect to the sign of g if weak-beam diffraction conditions and a $\{220\}$ reflection is used. The contrast of an intrinsic stacking fault under identical conditions does not appreciably change;

(ii) the contrast of an extrinsic stacking fault in Si inclined with an angle of $\approx 60^\circ$ in the foil shows no detectable contrast asymmetry with respect to the sign of g if weak-beam diffraction conditions and a $\{111\}$ reflection is used. The contrast of an intrinsic fault under identical conditions may show a small asymmetry.

3. Additional Experimental Results

Contrast asymmetries from planar defects other than intrinsic and extrinsic stacking faults in silicon have also been observed. Although the geometry of these defects was not as well established as that of the stacking faults discussed above, it is worthwhile to show some examples.

Fig. 6 shows a number of overlapping stacking faults in stainless steel (the defect could be a microtwin; this is however not known with certainty) imaged using dynamical two-beam conditions and weak-beam conditions. No change in the average

Fig. 6. Overlapping stacking faults in stainless steel a), b): strong-beam images; c), d) weak-beam images; $g = \{111\}$

Fig. 7. Overlapping stacking faults in stainless steel. The small arrows mark identical areas; $g = \{111\}$

contrast is observed with reversing g in the strong-beam pictures (Fig. 6 a and b); at "A" an area showing little contrast is present. This would usually be attributed to a total displacement vector $R = \sum R_{in} = 3nR_{in}$ with $n = 1, 2, 3, \dots$, so that $\alpha = 2\pi gR$ is a multiple of 2π . The same defect imaged using weak-beam conditions (Fig. 6 c and d) not only shows strong contrast in area A (changing when g is reversed) but also shows no contrast in areas where a strong contrast was observed in the strong-beam images. A particular striking example of contrast asymmetries in the case of many overlapping faults is shown in Fig. 7, this is a different region of the defect shown in Fig. 6.

Micrographs of overlapping stacking faults separated by a larger distance (≈ 4 nm as estimated from the fringe offset) in a CuAl alloy are shown in Fig. 8. These images were recorded using a $\{111\}$ reflection and three different (positive) values of the excitation error s . It can be seen very clearly that with increasing s the contrast goes through a minimum.

Finally, Fig. 9 shows kinematical bright-field images of overlapping stacking faults in silicon. These faults have been shown not to be microtwins [17]; the distance between the faults is thought to be a few nanometers. A clear asymmetry of the contrast upon reversing g is observed in parts of the fault area.

4. Theoretical Considerations

In this section the experimental observations will be discussed both from an analytical point of view and using the concept of amplitude-phase diagrams. For simplicity the kinematical contrast theory [1 to 3] will be used; this can be justified as a first approximation when the experiments were performed using weak-beam conditions and, although particularly for the $\{220\}$ reflections dynamical effects can be strong [16], it has been found (e.g. Fig. 4) that these cannot explain the contrast asymmetry.

Fig. 8. Overlapping stacking faults in CuAl alloy. The magnitude of the excitation error s increases from a) to c); $g = \{111\}$

In standard calculations [1 to 3] intrinsic or extrinsic faults are described by one translation vector $\mathbf{R}_{\text{int}}$ and $-\mathbf{R}_{\text{int}}$ (where it is assumed that $\mathbf{R}_{\text{ext}} = 2\mathbf{R}_{\text{int}}$ — lattice vector $-\mathbf{R}_{\text{int}}$) respectively, i.e. by *one* “cut” and a corresponding translation for either fault. This is not correct for the extrinsic fault because it consists of two *separate* translations both with magnitude $\mathbf{R}_{\text{int}}$ on adjacent $\{111\}$ planes. An extrinsic fault can therefore be considered to consist of two overlapping intrinsic faults on adjacent $\{111\}$ planes, Fig. 10 illustrates this. In what follows we therefore consider the general case of two overlapping intrinsic stacking faults, separated by a distance d_n (taken along the electron beam, see Fig. 10)

$$d_n = nd_{111}/\cos \theta \quad (1)$$

with d_{111} distance between adjacent $\{111\}$ planes, n number of $\{111\}$ layers between the two faults ($n = 1$ for an extrinsic fault), and θ angle of inclination of the faults with respect to the electron beam. Only if d_1 is very small compared to the effective extinction distance [1], can the extrinsic fault be described for contrast purposes by

Fig. 9. Overlapping stacking faults in Si. A significant contrast change is visible upon reversing the sign of $g = \{220\}$ as shown in the inserts

Fig. 10. Geometry of an extrinsic (or two overlapping intrinsic) stacking faults. For the column shown phase shifts occur at a depth z_0 and $z_0 + d_1$

a translation $-\mathbf{R}$ in one plane. This clearly is not the case for weak-beam diffraction conditions where typical values for the effective extinction distance ξ_g are $\xi_g \approx 5$ nm [5] and, for an extrinsic fault, $d_1 \approx 0.9$ nm.

With the phase shift α_{in} at an intrinsic fault

$$\alpha_{in} = 2\pi(\mathbf{g} \cdot \mathbf{R}) = \pm 120^\circ \quad (2)$$

occurring at a depth z_0 for an intrinsic fault and at a depth z_0 and $z_0 + d_1$ for an extrinsic fault, the amplitude of the diffracted beam is given by (apart from preexponential factors)

$$A_{in}(z_0, T) = \int_0^{z_0} \exp 2\pi i s z \, dz + \exp i\alpha_{in} \int_{z_0}^T \exp 2\pi i s z \, dz, \quad (3)$$

$$A_{ex}(z_0, T) = \int_0^{z_0} \exp 2\pi i s z \, dz + \exp i\alpha_{in} \int_{z_0}^{z_0+d_1} \exp 2\pi i s z \, dz + \exp 2i\alpha_{in} \int_{z_0+d_1}^T \exp 2\pi i s z \, dz. \quad (4)$$

The intensities are obtained by multiplying the amplitudes with their conjugate complexes in the usual way. The results are easily obtained, however lengthy. Since only the over-all contrast features are required the average over z_0 and T is taken and gives the average intensities $\langle I \rangle_{z,T}$

$$\langle I_{in} \rangle_{z,T} = 2 - \cos \alpha_{in}, \quad (5)$$

$$\langle I_{ex} \rangle_{z,T} = 3 - 2 \cos \alpha_{in} + 4 \sin^2(\alpha_{in}/2) \cos(D_1 + \alpha_{in}), \quad (6)$$

where $D_1 = 2\pi s d_1$ is the magnitude of the phase shift between the faulted layers. $\alpha_{in} = 0$ gives the average background intensity (unity) and subtracting this from the above expressions, the average contrast, $\langle C \rangle$, is given by

$$\langle C_{in} \rangle = 1 - \cos \alpha_{in} = 1 - \cos(\pm 120^\circ) = 1.5, \quad (7)$$

$$\langle C_{ex} \rangle = 3 + 3 \cos(D_1 + \alpha_{in}). \quad (8)$$

Fig. 11 shows $\langle C_{ex} \rangle^4$ for $\alpha_{in} = \pm 120^\circ$ as a function of D_n ; the ratio of the average contrasts is also given. Clearly, the contrast of overlapping stacking faults, including extrinsic faults, is expected to show large asymmetries with respect to the sign of the phase shift α_{in} , or, more generally, with respect to the sign of $(\mathbf{g} \cdot \mathbf{R}) \cdot s$, within the framework of the kinematical two-beam theory.

It will be shown in the discussion that this theory cannot account for all the observed contrast phenomena. Nevertheless, in the belief that it provides at least the

Fig. 11. The average contrast of an extrinsic stacking fault as a function of the phase shift between the two faulted planes. Curves are shown for a positive and a negative sign of the phase shift and for the ratio of the average contrast. (a) $\langle C \rangle_-$, (b) $\langle C \rangle_+$, (c) $\langle C \rangle_- / \langle C \rangle_+$

⁴) In this and in the preceding formulae the subscript "ex" stands not only for an extrinsic stacking fault but for any two overlapping faults if D_1 is replaced by the appropriate D_n .

Fig. 12. Amplitude-phase diagram for zero contrast of an extrinsic stacking fault for one sign of the phase shift a) and for strong contrast for reversed phase shift b). S starting point; I, II points of first and second phase shift; E end point for fault; B end point for background contrast

correct starting point for a better understanding of the observed contrast asymmetries, the following conclusions can be drawn:

(i) If $d_n/\xi_g \gtrsim 1/30$ (corresponding to a phase shift D_n between the two faults of $\gtrsim 12^\circ$), the contrast difference between two micrographs taken with $+g$ and $-g$, respectively, should be noticeable, (see Fig. 11) for weak-beam and strong-beam conditions.

(ii) Total contrast extinction should be observed for $D_n = 60^\circ$ (corresponding to $d_n/\xi_g = 1/6$) and for one sign of g , whereas a strong contrast should be obtained for the other sign of g . This is approximately true for $45^\circ \lesssim D_n \lesssim 75^\circ$.

(iii) Contrast asymmetries similar to those discussed for two overlapping faults can be expected for more than two overlapping faults, for microtwins (more than two overlapping faults on adjacent $\{111\}$ planes) and for coherent twin boundaries (an infinite number of overlapping faults on adjacent $\{111\}$ planes).

(iv) If the ratio d_n/ξ_g is sufficiently large, there should always be a contrast asymmetry for two or more overlapping faults and no contrast asymmetry for planar defects with only one translation on one plane such as intrinsic stacking faults.

The perhaps surprising prediction of essentially zero contrast under certain conditions can be best illustrated with an amplitude phase diagram, drawn for $D_n = 60^\circ$, Fig. 12. In this case, the amplitude vector, after suffering the two phase shifts of 120° (Fig. 12a) again ends on the original (background) circle, but it is delayed somewhat in comparison to the background amplitude. The only contrast effect of the stacking fault under those conditions therefore would be to shift the thickness fringes in its area as projected on the image plane. Changing the sign of α_{in} (Fig. 12b) leads to a circle for the end points of the amplitude vector of the stacking fault which is distinctly different from the background circle and a good contrast is expected. This contrast behavior appears to be experimentally confirmed by the micrographs shown in Fig. 3 (in this case D_1 was approximately 37° ; i.e. almost within the zero contrast region) and in Fig. 6, 7, and 8.

5. Discussion

It has been shown in the preceding section that if more than one phase shift is introduced along the path of the electron beams, i.e. if an extrinsic stacking fault, overlapping stacking faults or twin boundaries are present, a general asymmetry in the contrast can result when the sign of $(g \cdot R) \cdot s$ is changed if the distance between the planes of successive phase-shifts is larger than a few percent of the extinction distance.

This contrast effect is neither limited to weak-beam diffraction conditions nor to silicon or germanium as specimens, but should always occur if the above conditions are met. In particular, overlapping faults imaged with strong-beam conditions should show a contrast asymmetry if they are either rather widely spaced or very steeply inclined so that d_n becomes very large. Contrast asymmetries of overlapping stacking faults have indeed been observed (Fig. 9), consequently great care has to be taken as to the sign of α_{in} if real micrographs are to be compared to computed ones, as, e.g., in [4].

Quite dramatic contrast changes are predicted and have been observed, especially the disappearance of the fault contrast under certain conditions. The simple theory presented in the preceding section however cannot account for all the observed phenomena. Major difficulties which remain to be solved are

- (i) the absence of contrast asymmetries in cases where it might be expected, e.g. for the extrinsic fault in Fig. 4 imaged with a $\{111\}$ diffraction vector,
- (ii) the contrast asymmetry with respect to the sign of g which may be concluded for intrinsic stacking faults from Fig. 5.

The striking absence of any detectable contrast asymmetry in the case of the extrinsic stacking faults imaged with an $\{111\}$ diffraction vector (Fig. 4) might be due to shortcomings of the simple theory presented in this paper. These are neglect of segregation effects, i.e., concentration of impurity atoms at the stacking fault which may modify the local atomic scattering factors; break-down of the column approximation for steeply inclined stacked faults, and the assumption that the phase shift of the electron waves between the two faulted layers of an extrinsic stacking fault can be represented by the second integral in (3); i.e. in a continuum approximation. For a more accurate calculation this integral should be replaced by a summation over all the atoms between the faulted layers which would automatically take into account possible effects of higher order Laue zones (HOLZ). This could well lead to a total phase shift D_n substantially different from that derived here using the integral expression and also to differences between different diffraction vectors. Multi-beam effects might also influence the contrast and give rise to contrasts different for different kinds of diffraction vectors. Multi-beam effects have been shown, indeed, to produce contrast asymmetries at high accelerating voltages (600 kV) for intrinsic and extrinsic stacking faults [18].

The contrast asymmetries for intrinsic faults cannot be explained by the possible effects of HOLZ contributions or multi-beam effects. More involved dynamical multi-beam calculations [19] indeed do not predict any asymmetries. In principle an asymmetry of the contrast of intrinsic faults lying inclined to the image plane is expected if the finite Bragg angle is taken into account appropriately, i.e., if the column approximation is avoided. Such an asymmetry is due to the inherent asymmetry in the diffraction condition as illustrated in Fig. 13. However, corresponding contrast cal-

Fig. 13. Ewald sphere construction showing the inherent asymmetry in diffraction conditions upon reversing the sign of g ; a) position of the stacking fault in the foil, b) construction for $g/3g$ conditions, c) construction for $-g/-3g$ conditions. The Ewald sphere cuts the spike in reciprocal lattice caused by the stacking fault in different positions

culations (Wilkins unpublished) have shown that this effect gives contrast asymmetries of the order of, or less than, 1% under the image conditions applied in this paper. Another possibility is that a stacking fault is not adequately described by a translation vector $(a/6)\langle 112 \rangle$ but that a small component perpendicular to the fault might be present, which either may be due to the presence of impurities in the fault [20] or may be an intrinsic property of stacking faults [21, 22]. Within the framework of two-beam theory this would not lead to a contrast asymmetry since α_{in} only changes in sign, but not in magnitude (which no longer would be 120°) with a sign change of g . Multi-beam effects however may introduce an asymmetry in this case.

A situation similar to an intrinsic fault is the case of "special" grain boundaries (so-called coincidence or near-coincidence boundaries [23]) if they are imaged with a diffraction vector which is common to both crystals. In this case a rigid-body translation [9] (which may have several, symmetry related values) is thought to be present in the plane of the boundary [9]. The electron beams thus would suffer a phase shift related to the magnitude of the rigid-body translation vector. The boundary is therefore visible if imaged with a diffraction vector common to both crystals and exhibits a contrast very similar to that of an intrinsic stacking fault. Boundaries showing this particular behavior have been observed [8, 9] and it has been demonstrated that using weak-beam conditions they show a large contrast asymmetry if the sign of the diffraction vector is changed [8]. This is, as in the case of an intrinsic stacking fault, not in accordance with the theory presented. However, in this special case it is possible that the rigid-body translation is not entirely located at the interface but rather spread out over several lattice planes, i.e. the lattice planes perpendicular to the boundary are bent. Such an effect may occur in relatively low stacking fault energy materials as, e.g., silicon and stainless steel. It would introduce a fundamental asymmetry and could very well explain the contrast asymmetries in this case.

A similar explanation for intrinsic stacking faults seems to be less likely since any "spreading" of the translation vector would destroy the three-fold symmetry in the stacking fault plane.

Despite the serious problem which still remain to be solved, it is clear that great care has to be taken in the interpretation of weak-beam images of planar defects. Moreover, even conventional strong-beam images are not always free of contrast asymmetries and the detailed structure of planar defects as well as a proper consideration of the sign of $(g \cdot R) \cdot s$ has to be taken into account if erroneous conclusions are to be avoided.

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COMBINED HVTEM AND EBIC STUDIES IN EFG SILICON.

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The structure and electrical activity of defects in thin Si ribbons prepared by Edge (Defined) Film Growth (EFG) are of current technological interest because they influence the efficiency of low cost solar cells. In addition, the material is highly suited for basic studies on the relation between structure and electrical activity since it contains a high density of simple defects.

The dominant defects in EFG Si are coherent twin boundaries and dislocations. (Incoherent twin boundaries and high angle grain boundaries are only rarely seen). An optically sharp twin boundary usually consists of bundles of microtwins a few nm thick. Fig. 1 shows a DF image of such an array. The electrical activity of twin boundaries as measured by EBIC (i.e. resolution in the μ range) varies widely. Intrinsic point defects (dangling bonds), impurities, grain boundary dislocations, and termination of microtwins all may play a role.

Presently, we are trying to relate the electrical activity of twin boundary dislocations to their geometric parameters (burgers vector and line direction; kink density). These intrinsic grain boundary dislocations are single Shockley partials, which eliminates the problem of dissociation encountered in corresponding studies of lattice dislocations. Booker et al. have shown that the dissociation width has a strong influence on the electrical activity (1).

The experimental approach is identical to that of Heydenreich et al. (2). It requires a specimen transfer from the SEM to the HVTEM but avoids manipulation of the specimen (thinning) between the two observations. Petroff et al. have shown that simultaneous EBIC and structural analysis can be carried out in a HVSTEM (200 KeV) at the expense of a decreased EBIC current (3). This fall off is more easily tolerated in GaAs where the dislocations are very efficient recombination centers. In Si, where the electrical activity of dislocations varies widely (see below) separate observations are probably preferable.

A first example of the technique is shown in Figs. 2 and 3 which show HVTEM and EBIC images of the same area. (The EBIC image was taken first to avoid spurious electronic effects by radiation induced recombination centers). Fig. 2a shows the microtwin in contrast. The microtwin is out of contrast in Fig. 2 but its outline can be traced by the presence of dislocations in both boundary planes. Fig. 3a shows the corresponding EBIC image and Fig 3b is a schematic sketch of the observed EBIC contrast. A comparison between Figs. 2 and 3 suggests that dislocations may show no, weak, or strong EBIC contrast, and that in general only a fraction of the dislocations are electrically active. These results are currently being analysed with a model that assumes that the kink density

controls the electrical activity.

The strength of the present approach is that it applies both structural and electronic studies to a particularly simple defect system. So far we have demonstrated the feasibility of the approach. Initial results appear to be promising enough to pursue further studies of these defects.

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Fig. 1 DF image of microtwins in Si ribbon material.

Fig. 2a BF image of microtwin with dislocations. The coarse feature at left and lower right are surface scratches.

Fig. 2b Same area as Fig. 2a, with twin out of contrast.

Fig. 3a EBIC image of area of Fig. 2. The EBIC image is inverted upside down.

Fig. 3b Schematic sketch of EBIC contrast. Large, medium and small circles correspond to strong, medium and low EBIC contrast.

Report No 5

DEFECT STRUCTURE OF EFG SILICON RIBBON

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ABSTRACT

The defect structure of EFG ribbons has been studied using EBIC, TEM and HVEM. By imaging the same areas in EBIC and HVEM a direct correlation between the crystallographic nature of defects and their electrical properties has been obtained. (i) Partial dislocations at coherent twin boundaries may or may not be electrically active. Since no microprecipitates were observed at these dislocations it is likely that the different electrical activity is a consequence of the different dislocation core structures. (ii) 2nd order twin joins were observed which followed the same direction as the coherent first order twins normally associated with EFG ribbons. These 2nd order twin joins are in all cases strongly electrically active.

EFG ribbons contain high concentrations of carbon. Since no evidence of precipitation was found with TEM it is suggested that the carbon may be incorporated into the higher order twin boundaries now known to exist in EFG ribbons.

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1. INTRODUCTION

Rapid progress has recently been made in the production process of edge defined film-fed growth (EFG) silicon /1/. EFG ribbon is a promising material for the production of inexpensive solar cells and therefore an understanding of the relationship between the crystallographic nature of the defects and their electrical properties is desirable. This information can then hopefully be used to modify the ribbon growth process to reduce the density of defects which decrease the efficiencies of solar cells.

After a summary of the characteristic defect structure of various EFG silicon ribbons, results are presented which were obtained by correlating EBIC measurements and HVEM observations on selected defects.

2. EXPERIMENTAL TECHNIQUES

The electrical properties (i.e. enhanced minority carrier recombination) were investigated in the scanning electron microscope (SEM) operated in the electron beam-induced current (EBIC) mode. Schottky diodes were produced by evaporating a thin film of Al($\sim 500\text{\AA}$) onto one surface /2/. EBIC images exhibit dark contrast at defects which act as recombination sites for minority carriers, with an EBIC resolution of $\sim 1\text{-}2\mu\text{m}$. The EBIC technique can be extended to obtain quantitative information. The collected current can be measured as a function of specimen co-ordinates allowing the determination of 'recombination efficiencies' of specific defects /3/, minority carrier lifetime /4/ and trap level measurements /5/ are possible using high speed beam blanking techniques. These extensions of the EBIC technique are currently being introduced.

Defect structures were investigated by transmission electron microscopy (TEM). To obtain unbiased observations, specimens were broken off the ribbons at random, ground to a thickness of $\sim 50\mu\text{m}$ and thinned for TEM examination by ion beam milling. Subsequent investigations were carried out in a Siemens Elmiskop 102 operating at an accelerating voltage of 125 kv (conventional TEM, CTEM).

To correlate electrical and structural properties of defects, areas were selected and mapped out in EBIC. Specimens 3mm in diameter were then cut out from the ribbon and ion-milled from the back-side (with the Schottky-diodes still at the surface) until the areas of interest were contained in the electron transparent regions. These specimens were subsequently examined in a high-voltage electron microscope (HVEM) operating at an accelerating voltage of 1MV. HVEM has the following advantages over CTEM because of the high penetration power of highly accelerated electrons (several μm as compared to 0.5 μm in CTEM):

- (i) The probability of finding the defects, previously mapped by EBIC, in the large transmittable area is high.
- (ii) Extended defects such as twin or other grain boundaries can easily be traced over long distances.
- (iii) The volumes investigated by HVEM and by EBIC are comparable.

Difficulties arise when comparing EBIC and HVEM micrographs because of the large difference in working magnifications (SEM-EBIC typically 1,000x, HVEM typically 10,000x). The comparison is facilitated by utilizing permanent surface marks, such as scratches, or etched topological features. In addition a series of low magnification EBIC micrographs (10x, 50x, 200x) helps to locate the areas of interest.

A brief discussion of the advantages of the present technique for the electrical characterization of defects, may be found in /6/.

3. INVESTIGATED EFG RIBBONS

The ribbons investigated in the present study are briefly described below:

- 1) JPL identification #5-871 run 18-112-1, 'small grain'. Displaced die, growth speed 3.0-3.4 cm/min. Undoped.
- 2) JPL identification #5-866 run 16-163, 'small grain'. Displaced bulbous ended die, growth speed 3.1 cm/min. Boron doped, resistivity 1 Ωcm .
- 3) JPL identification #5-1158. 'Large grain'. (reduced AT flow).
- 4) Mobil Tyco supplied... 'large grain' ribbon. (reduced AT flow).

4. CHARACTERISTIC DEFECT STRUCTURE OF EFG SILICON RIBBONS

4.1. Etch

Similar features were observed in all of the EFG ribbons examined, the only difference being the scale of the defects (e.g. 'large' and 'small' grain). Figs. 1(a) and (b) show typical etch patterns, which have already been described (e.g. /7/to/10/). Only a brief description will therefore be given here, with emphasis on features which are interesting in connection with the correlation work reported in Section 5.

On a large scale the observed pattern is generally inhomogeneous, on a small scale, however, frequently homogeneous. Figure 1(a) shows an area of parallel striations, which are generally attributed to the presence of twin boundaries. (see Section 5 for a detailed discussion). At the top of Figure 1(a) is a region containing a high density of dislocation etch pits. It should be noted that the density of dislocations varies appreciably from region to region. Whereas Figure 1(a) represents the 'standard' defect structure (i.e. equilibrium structure', e.g. /11/) which is frequently discussed, Figure 1(b) shows an example of a more complicated pattern. Areas such as this were found on all of the ribbons and covered appreciable areas of the surface. The irregularity in Figure 1(b) is caused by reactions between grain and/or twin boundaries and by an inhomogeneous distribution of dislocations. In several regions the dislocation etch pits are aligned along crystallographic directions suggesting that the dislocations had been generated by plastic processes (See Section 5).

The orientation of the grains at the surface varies; in order of falling frequency $\{110\}$, $\{112\}$ have been found, in partial agreement with earlier work /12,13/. An example of the variation in grain orientation is shown in Figure 2. Orientations are given with respect to the growth direction.

4.2. EBIC

Figure 3 is a low magnification EBIC micrograph showing the distribution of electrically active defects. In the upper part of the micrograph contrast lines apparently due to grain boundaries are visible. In addition black dots due to active dislocations are randomly distributed throughout the matrix. [Figure 4 is a higher magnification micrograph of the area described above.] Most of Figure 3 consists of almost horizontally aligned boundaries, some of these very dark (showing strong electrical activity), some weak in contrast or exhibiting 'dotted' contrast. Figure 5 shows an-

other example of dotted EBIC contrast where the effect is more pronounced. We will show in Section 5 that this pattern is related to the twinned structure of the material. Such a relationship was earlier inferred from comparison of etched surfaces and EBIC micrographs /3/ and by independent observations of twins in TEM /10/. An exact analysis, however, requires direct correlation between EBIC and TEM, as presented in Section 5.

4.3. TEM

Twins with a {111} habit plane occur with a high frequency and are therefore generally observed by TEM. A typical twinned structure is shown in Figure 6. The thicknesses of micro-twins may vary from a few layers of {111} planes up to tens of microns (which of course means single twin boundaries are observed in TEM). A micro-twin five layers thick is revealed by structural imaging in Figure 7. The 'small grain' ribbons contain a high density of microtwins (e.g. Figure 6) with thicknesses up to several 100 nm. 'Large grain' material contains isolated twin boundaries spaced several μm apart, resulting in a more proportionate distribution of 'twinned' and 'matrix' material.

Twin boundaries may contain partial dislocations (twin boundary dislocations) the density of which can vary from boundary to boundary. No relationship between twin boundary dislocation density and ribbon type has been found.

4.4. Results concerning the carbon content

Graphite dies are used in EFG ribbon growth. Two consequences result from this technique: (i) SiC - particles are present at the ribbon surface (e.g. /3/) and (ii) a high density of carbon ($\sim 10^{18} - 10^{19} \text{ cm}^{-3}$ /14/) is incorporated into the silicon material.

EBIC has been used to investigate the electrical activity of the defect structure nucleated at SiC particles. Figure 8 shows a typical arrangement with a high density of black dots, corresponding to dislocations, and a number of twin boundaries. Except for this high density of defects no other unusual effects were observed. This is particularly interesting since an excess of carbon may be expected near a SiC particle, thereby enhancing any carbon-induced impurity segregation. Such a segre-

gation is expected to cause increased minority carrier recombination. However, in the present study, the electrical activities of the defect structure near SiC particles, and of the 'equilibrium structure' are not noticeably different.

Recently a ribbon growth model was proposed to account for carbon concentrations above the solubility limit /15/. The model assumes eutectic growth and directional solidification of the ribbon, which leads to lamellae of a silicon-carbon 'phase' embedded in a carbon rich silicon matrix. Such a structure should give rise to special contrast effects in TEM. If the silicon-carbon phase is not coherent with the silicon matrix, which is likely due to the difference in the bond lengths of silicon and carbon atoms, strain contrast effects should be observed, at least at irregularities of the lamellae. Moreover, interference patterns, e.g. Moiré fringes, and/or, in the case of a long range order, diffraction effects would be expected. None of these effects has been observed in this study.

5. CORRELATION OF EBIC WITH HVEM OBSERVATIONS

Figure 9(c) shows part of an EBIC micrograph exhibiting a row of dots similar to those seen in Figure 3. Figure 9 (a) is a HVEM micrograph of the same area. A comparison of Figure 9 (a) and (c) confirms that the dots mark the trace of a microtwin approximately 200 nm thick, the boundaries of which are visible in fringe contrast. This microtwin is imaged in Figure 9 (b) with its boundaries invisible, revealing that partial dislocations are contained in both boundaries. A comparison of EBIC and HVEM micrographs shows a one to one correspondence between dots and dislocations. Ignoring the central spot for the moment, the EBIC dots have similar contrast and correspond to individual, slightly curved dislocations. Diffraction contrast analysis reveals that the dislocations differ in Burgers vector (of type $1/6 \langle 112 \rangle$), and that their character is not of simple 30° or 90° type. These observations suggest that the dislocations are comparably effective sites for the recombination of minority carriers, irrespective of their crystallographic character. The central dot in Figure 9 (c) arises from the combined effect of a group of 3 partial dislocations which are too closely spaced to be resolved by EBIC. ($\sim 1-2 \mu\text{m}$).

Figure 10 (a) shows another example of dots in EBIC contrast. These dots, though similar to those shown in Figure 9 (c) are caused by a totally different structure. Figure 10 (b) is an etch pattern from the same area, showing that the observed contrast in Figure 10 (a) is due to the interaction of boundaries. The nature of the boundaries was determined by HVEM. As an example the area encircled in Figure 10 is shown in Figure 11. A three dimensional sketch of this area clarifying the relationships between the different areas is given in Figure 12. Analysis shows that T_1 is a microtwin $\sim 100\text{nm}$ thick, lying in the matrix M perpendicular to the growth surface. T_2 is in a different twin orientation to the matrix M with an inclined $\{111\}$ - habit plane. Thus the boundary between T_1 and T_2 joins two crystal grains with a misorientation caused by two non-parallel twinning operations. The geometric construction is depicted in Figure 13, projected along the $\langle 110 \rangle$ direction common to all three grains. Boundaries of this type have been termed 'second order twin joins' by Kohn /16/ and are $\Sigma 9$ boundaries in the CSL model /17/. In the present case the $\{111\}$ plane of T_1 matches a $\{115\}$ plane of T_2 . This unsymmetric configuration has been modelled by Kohn /18/, yet has not been observed so far to the author's knowledge. The dislocation model discussed by Hornstra /19/ could also be extended to describe this unsymmetric case, but would require a very high density such that the dislocation core regions would overlap. In Figure 11 (b) the specimen was tilted to show the boundaries of the microtwin T_1 . Dislocations that are contained in the $\{111\}/\{115\}$ boundary are clearly visible. These dislocations accommodate a small deviation from the $\{111\}/\{115\}$ orientation relationship and are commonly referred to as extrinsic boundary dislocations /20/. The Burgers vectors of these dislocations have not been analyzed.

Figure 14 shows a contrast experiment to determine the character of the partial dislocations present in the boundaries T_2/M . The specimen was tilted until these boundaries were almost perpendicular to the incident electron beam, allowing an easy determination of the crystallographic direction of the straight dislocation lines. The Burgers vectors were found from standard contrast analysis /21/. The dislocations

analyzed were Shockley partials of either 30° or 90° type, examples are indicated in Figure 14 (c).

The comparison of the HVEM micrographs (Figures 11 and 14) with the corresponding EBIC pattern (Figure 10) gives the following result: (i) The black dots in Figure 10 (a) correspond to the $\{111\}/\{11\bar{5}\}$ second order twin joins, which therefore represent efficient sites for minority carrier recombination. (ii) The straight 30° and 90° partial dislocations show no contrast in EBIC (although etched in Figure 10 (b)) and thus are virtually electrically inactive.

6. DISCUSSION

In recent years a large number of experimental results on the dislocation core structure in tetrahedrally co-ordinated semiconductors has appeared (e.g. /22/). High resolution electron microscopy has revealed the presence of dissociated and constricted perfect dislocations (e.g. /23, 24/). Dislocations introduced by plastic processes are generally dissociated /22/ and are, since dissociation is difficult to envisage on the shuffle-set, therefore assigned to the glide set (e.g. /22/). Indications for the existence of "shuffle set" dislocations /25/ in Ge, suggest that such dislocations also may exist in Si. Transformation from one set to the other can occur by the addition or removal of rows of point defects /26/; experimental evidence for such a process exists (e.g. /24/).

Theoretical models for dislocation core structures were first developed by Hornstra /27/, and these models have been extended and refined to include bond reconstruction (e.g. /23/). The electrical properties of dislocations with different core structures are likely to be different.

Experimental results obtained by combining EBIC with HVTEM will contribute to the discussion of these various models.

6.1. Dislocations at coherent twin boundaries

In the present investigations dislocations were observed with apparently two different levels of electrical activity: dislocations giving rise to an EBIC contrast, Figure 9 (c), and dislocations with no, or at least considerably lower electrical activity, Figure 11. Confirmation of these observations is required before a detailed inter-

pretation of the nature of dislocations can be presented. It is however interesting to speculate about the possible significance of the present results, with regard to the formation and core structures of dislocations.

The simplest approach to correlating crystallographic and electrical properties is to reduce the number of applicable models. To this end the present investigation is concerned with single partial dislocations and therefore the question of whether the dislocation is dissociated or constricted (as present with perfect dislocations) does not arise.

It is conceivable that the core structure of a dislocation will depend on how the dislocation is generated. The present observations, that the electrically active dislocations do not follow $\langle 110 \rangle$ directions, and are in fact sometimes curved, and that the non-active dislocations are aligned along a $\langle 110 \rangle$ Peierls valley, tends to support this view. During growth of EFG ribbons there are two temperature ranges in which dislocation generation processes may occur. During solidification, when diffusion can occur, twin boundaries grow and can accommodate partial dislocations by atomic steps in the boundaries. At lower temperatures thermal stresses are relieved by plastic processes and these dislocations can react with twin boundaries, in which case the lattice dislocations dissociate into twin-boundary partial dislocations. Diffusion plays only a minor role in this case. Whether a distinction between grown-in and deformation induced dislocations is possible and what type of dislocations are formed by each process has yet to be determined.

6.2. The $\{111\}$ $\{115\}$ second order twin join

The present study has shown that the detected $\{111\}$ $\{115\}$ second order twin join is strongly electrically active. Since extrinsic dislocations are contained in the investigated boundary it cannot be explicitly stated that the electrical activity is an intrinsic property of the boundary. However considering the complicated arrangement of atoms and bonds at the boundary (e.g. Figure 13) it is likely that the extrinsic dislocations have only an additional effect, if at all, on the electrical activity.

Since the second order twin join is confined to the $\{111\}$ matrix planes it is of

considerable interest in the discussion of the so-called equilibrium structure /11/ of EFG (and comparably grown) ribbons. This structure has been identified from etch investigations to be generally present in EFG ribbons and to consist of parallel coherent twin boundaries which extend on {111} matrix planes along the growth direction. Consequently, once a second order twin join is formed on a {111} matrix plane it can extend over long distances parallel to the equilibrium structure without further reactions. Second order twin join therefore have to be regarded as an inherent part of the defect structure of EFG ribbons. Thus the equilibrium structure consists of a large number of electrically inactive coherent twin boundaries intermingled with electrically active second (or even higher) order twin joins. This conclusion is consistent with thus far unexplained EBIC observations (e.g. /3, 10/, that only some of the linear boundaries revealed by etching are electrically active.

6.3. CARBON DISTRIBUTION IN EFG-RIBBONS

It has been found that the grain size of EFG ribbons generally decreases with increasing (overall) carbon concentration /15/. Since this concentration is beyond the carbon solubility limit in silicon the distribution of C has to be considered. The present experiments give no indication for a lamellae two-phase structure as suggested in the eutectic growth model /15/. The TEM observation of {115} {111} second order twin joins suggests the possibility that the carbon is preferentially incorporated into such joins, as well as into higher order twin and other grain boundaries. This explanation seems reasonable since the atomic arrangement at these boundaries is considerably disturbed (independent of the model used to describe the joins) thereby allowing the incorporation of a high density of carbon atoms. The correlation-higher carbon concentration smaller grain size is natural in this context since decreasing grain size increases the possibility of twin boundary interactions. How an intentional increase in the concentration of incorporated carbon atoms (by changing the growth conditions of the EFG ribbon) causes more boundaries to form, and how the carbon atoms influence the electrical activity of the higher order twin joins are topics of future research.

CONCLUSIONS

1. The correlation of HVTEM and EBIC is a valuable tool for the investigation of the defect structure of semiconducting materials, e.g. EFG ribbons.
2. The existence of the $\{115\}$ $\{111\}$ second order twin join has been proven for the first time. It may occur relatively frequently in the ribbon due to twin boundary interactions and lies along the same direction as the first order twin boundaries.
3. The $\{115\}$ $\{111\}$ twin joins were observed to be electrically active, whereas coherent $\{111\}$ $\{111\}$ twin boundaries were inactive.
4. Partial dislocations at coherent twin boundary can be electrically active. No microprecipitates were observed at these dislocations suggesting that the electrical activity is not impurity controlled but a consequence of the dislocation core structure per se.
5. It is suggested that the carbon atoms present in EFG ribbons in high concentrations are preferentially adsorbed to the higher order twin joins.

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FIGURE CAPTIONS

1. Optical micrographs of etched ribbon surface Ribbon #2.
2. Optical micrograph of ribbon surface showing variation in grain orientations. Open circles mark areas analyzed by Laue X-ray and also orientations with respect to standard 001 stereographic projection (Courtesy of F. Stafford).
3. EBIC micrograph of typical EFG structure. Ribbon #2.
4. Higher magnification EBIC micrograph of area at top right of Figure 3.
5. EBIC micrograph showing dotted contrast along linear boundaries. Ribbon #3.
6. TEM micrograph (125 kv) of microtwins in E.F.G. ribbon. Ribbon #1.
7. High resolution structural image of a microtwin five atomic layers thick. (125 kv).
8. EBIC micrograph showing contrast near a SiC particle. Ribbon #4.
9. a) Bright field HVEM image of a microtwin containing dislocations. b) Same area with twin out of contrast. c) EBIC micrograph from the same area. g = diffraction vector - Ribbon #4.
10. a) EBIC micrograph showing dotted contrast. b) Optical micrograph of the same area showing interaction of microtwins. Ribbon #2.
11. a) Bright field HVEM micrograph of twin boundaries shown in Figure 10. b) Same area with one set of twin boundaries out of contrast.
12. Schematic sketch of the arrangement of twin boundaries shown in Figure 11.
13. Projection along the common $\langle 110 \rangle$ direction of twins indicated in Figure 12 showing the arrangement of atoms at the (111) (115) twin join.
14. HVEM micrographs of the same area as Figure 11. These were used to determine the nature of the dislocations in the twin boundaries, examples of which are marked in c).

200 μ m

Figure. 1

400 μ m

Figure. 2

Figure. 3

Figure. 4

Figure. 5

Figure. 6

Figure. 7

Figure. 8

Figure. 9

Figure. 10

Figure.11

Figure.12

Figure.13

Figure.14

CHARACTERIZATION OF DEFECTS IN SILICON RIBBONS BY COMBINED EBIC AND HVEM

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ABSTRACT

The electrical properties and crystallographic nature of linear and planar defects in EFG silicon ribbons were studied. A direct correlation between electrical and mechanical properties was obtained by imaging the same areas first with EBIC and then with HVEM. Coherent twin boundaries were found to be electrically inactive, but higher order twins and other grain boundaries generally enhanced minority carrier recombination. Partial dislocations confined to coherent twin boundaries were usually electrically active, but in certain instances partial dislocations were observed which had no apparent EBIC contrast.

INTRODUCTION

Rapid progress has recently been made in the production process of edge defined film-fed grown (EFG) silicon ribbon, a description of which can be found in ref. [1]. EFG ribbon is a promising material for the production of inexpensive solar cells and therefore an understanding of the relationship between the crystallographic nature of the defects and their electrical activity is desirable. This information can then hopefully be used to modify the ribbon growth process to reduce the density of electrically active defects which detract from solar cell efficiency.

EFG ribbons typically contain a large number of linear boundaries, the majority of which is parallel to the growth direction. The electrical activity observed at these boundaries can vary greatly. Linear boundaries can be electrically active along their entire length, or show no detectable activity. A large number of boundaries show enhanced carrier recombination only along certain sections, resulting in a "dotted" appearance in EBIC. The differing electrical activity of these linear boundaries has previously been ascribed to the dislocation content of the boundaries [2] or to the amount of impurity decoration at boundary dislocations [3]. In the present study two cases of dotted EBIC contrast are considered. Although the EBIC appearance of both is similar it will be shown that the defects producing the effect are markedly different.

EXPERIMENTAL

The electrical properties of EFG silicon ribbons were investigated in the scanning electron microscope (SEM) operated in the electron-beam induced current (EBIC) mode. Schottky diodes were produced by evaporating a thin film ($\sim 500 \text{ \AA}$) of Al onto the surface. A high voltage electron microscope (HVEM)

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operating at an accelerating voltage of 1 MV was used to study the crystallographic nature of the defects in the ribbons.

To correlate the electrical and structural properties of defects, areas were selected and mapped out in EBIC. Specimens 3 mm in diameter were then cut out from the ribbon and ion-milled from the back side until the EBIC mapped areas were contained in electron transparent regions. These specimens were subsequently examined by HVEM.

In the present study HVEM has the following advantages over conventional TEM.

- (i) Specimens with thicknesses of up to several μm can be examined, providing large electron transparent regions.
- (ii) Extended defects such as twin or other grain boundaries can easily be analyzed.
- (iii) The volumes investigated by HVEM and EBIC are comparable.

RESULTS

Case I

Figure 1(c) is part of an EBIC micrograph showing dotted contrast. The same area imaged by HVEM, Figure 1(a), reveals that the EBIC active areas, or "dots," mark the trace of a microtwin with a thickness of ~ 200 nm. The twin boundaries in Figure 1(a) are visible through fringe contrast. Figure 1(b) shows the same microtwin with the twin boundaries out of contrast. Partial dislocations with different crystallographic character are contained in both twin boundaries, and a comparison with Figure 1(c) shows a one to one correspondence between the position of dots and the position of dislocations. Except for the central spot, the EBIC dots have similar contrast and correspond to individual dislocations. This observation suggests that the dislocations have comparable electrical activities despite having different crystallographic character. HVEM shows that the central dot corresponds to a group of dislocations which are too closely spaced to be individually resolved by EBIC ($\sim 1-2$ μm). The EBIC signal in this case is therefore the sum of the signals from the individual dislocations.

Case II

The second example of dotted EBIC contrast is shown in Figure 2(a). An optical micrograph of the etched surface, Figure 2(b), shows that the EBIC contrast results from the interaction of linear boundaries. HVEM micrographs of part of the dotted row are shown in Figure 3. Figure 4 is a sketch showing the geometrical relationship between the different areas. Analysis shows that T_1 is a microtwin ~ 100 nm thick. T_2 is also twinned with respect to the matrix M but with a different $\{111\}$ twinning plane. The heavy lines in Figure 4 therefore represent traces of boundaries separating grains with a misorientation resulting from two non-parallel twinning operations. Boundaries of this type have been termed "second order twin joins" by Kohn [4]. In the present case a $\{111\}$ plane of T_1 matches a $\{115\}$ plane of T_2 . To the authors knowledge this $\{111\}/\{115\}$ second order twin has not previously been observed: a coincidence lattice model for this boundary was proposed by Kohn [5]. The dislocation model proposed by Hornstra [6] for twin boundaries resulting from tilts about $\langle 110 \rangle$ can also be extended to describe the present case.

Twin boundary dislocations were revealed by tilting the specimen, Figure 3(b). Using a reflection common to grains T_2 and M , the boundaries T_2/M are rendered invisible, whereas the boundaries of the microtwin T_1 are visible in fringe contrast. The dislocations in the T_2/M twin boundary were determined to be Schockley partials lying along a $\langle 110 \rangle$ direction and with either 30° or 90° character. The character of the dislocations in the $\{111\}/\{115\}$ twin boundaries has not been completely determined so far since these boundaries are steeply inclined in the foil.

Correlation between EBIC and HVEM shows that the areas of high recombination in Figure 2(a) correspond to the $\{111\}/\{115\}$ twin boundary joins. The most interesting features however are the partial dislocations in the T_2/M boundaries which are apparently nonactive.

DISCUSSION

The first point to note is that similar features observed in EBIC can result from different crystallographic structures. Care must therefore be exercised when interpreting EBIC micrographs. Direct correlations between EBIC and TEM are required until statistically significant results can be obtained.

Partial dislocations have been observed with apparently two different levels of electrical activity: dislocations giving rise to a dotted EBIC contrast, Figure 1(c), and dislocations with no, or at least considerably lower electrical activity, Figure 3(b). Although a detailed discussion relating the activity of dislocations to their core structures requires a large number of observations at crystallographically identical defects, it is interesting to speculate about the possible significance of the present results. Dislocations introduced by plastic processes are regarded as glide dislocations and are therefore assigned to the "glide set" [7]. In addition the "shuffle set" dislocations [8] must also be considered. The core structure of a dislocation will depend on whether it belongs to the glide or shuffle and on the way the dangling bonds reconstruct [9]. It is conceivable that the core structure of a dislocation will depend on how the dislocation is generated. The present observations, that the electrically active dislocations do not follow $\langle 110 \rangle$ directions, and are in fact sometimes curved, and that the non-active dislocations tend to be aligned along a $\langle 110 \rangle$ Peierls valley tends to support this view. EFG ribbons contain both ingrown dislocations formed during solidification and dislocations generated by thermal stresses during cooling. It is possible, although not proven, that these two types of dislocations correspond to the non-active and active dislocations observed by EBIC.

Since the present experiments investigate single partial dislocations, measurements are not complicated by dissociation and constriction which occur at single perfect dislocations. If dissociated the two partials cannot be resolved by EBIC, thereby impeding the correlation with HVEM.

The effects of impurity atoms has not been considered explicitly since the present results can be discussed in geometrical terms alone. Both carbon and oxygen are present in varying quantities in EFG ribbons, however decoration of defects by precipitates was not observed in the EFG ribbons examined. Since the carbon content in ribbons is high but cannot be found as precipitates it is possible that the carbon is incorporated into the higher order twins and general grain boundaries. This model is consistent with the observation that an increase in carbon content leads to a decrease in grain size and an increase in the number of electrically active boundaries. A detailed investigation of the role of carbon would require doping of the ribbon during growth with C^{13} to allow the use of detection methods such as SIMS without interference from the C^{12} background.

Fig. 1. a) Bright field HVEM image of a microtwin containing dislocations, b) Same area with twin out of contrast, c) EBIC image of the same area.

Fig. 2. a) EBIC image showing dotted contrast, b) Optical image of the same area showing interaction of microtwins.

Fig. 3. a) Bright field HVEM image of twin boundaries shown in Fig. 2, b) same area with one set of twin boundaries out of contrast.

Fig. 4. Schematic sketch of the twin boundaries in Fig. 3 showing the geometrical relationship between the different areas.

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Report No. 7

EBIC INVESTIGATION OF HYDROGEN PASSIVATED STRUCTURAL DEFECTS IN EFG SILICON RIBBON

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ABSTRACT

EBIC contrast of structural defects in as-received and hydrogen passivated polysilicon ribbon is studied using aluminum Schottky barrier diodes. Enhanced charge collection after passivation is demonstrated by comparing the EBIC signal from two sections of a split ribbon, one half of which was passivated. Electrical activity of specific linear defects before and after passivation is examined by recording charge collection profiles across these defects under standardized conditions of beam voltage and current. Such measurements show that passivation does reduce the electrical activity of selected defects. Possible reasons for this behavior will be discussed.

INTRODUCTION

Hydrogen passivation of electrically active defects in silicon has been studied by a variety of techniques [1-4] including electron-beam-induced-current (EBIC) microscopy [5,6]. The present authors [5] observed that hydrogenation passivated some but not all defects. Seager et al. [6] report that practically all grain boundaries were passivated. Whether this difference is due to different hydrogenation procedures or a result of the specimens used (EFG, SOC) is not known.

In ref. 5 hydrogenation reduced the electrical activity of certain defect structures relative to surrounding features. These EBIC images had low magnification (X100) and several relevant parameters (incident beam current, signal amplification, DC level, etc.) which influence the image were not quantified. Hence the question remained whether the reduced contrast was due to hydrogenation or merely reflected the difficulty to detect the defect against a brighter background.

The present work was undertaken to

- (i) develop quantitative techniques for assessment of the electrical activity of defects observed in EBIC,
- (ii) compare high-resolution-EBIC micrographs with charge collection profiles before and after the hydrogenation of selected defects,
- (iii) image split specimen in order to compare contiguous defects before and after hydrogenation and to evaluate matrix activity.

EXPERIMENTAL PROCEDURES AND RESULTS

300 Å thick aluminum (Al) Schottky barrier diodes were evaporated onto as-grown undoped (205 Ωcm) EFG ribbon which had been mechanically ground flat, syton polished and HF etched. Suitable areas were selected for EBIC studies and the specimen was divided into three pieces (Fig. 1): piece (1) remained untreated except for Schottky barrier formation and removal, piece (2) was vacuum annealed, and piece (3) was hydrogenated in a plasma. Diodes 1a and 2a

were positioned such that adjacent areas of pieces (1) and (2) could be imaged simultaneously; similarly diodes 2b and 3b covered both pieces (2) and (3). An additional diode 3a was placed on piece (3) to study specific defect structures. Diodes were always removed prior to vacuum or plasma annealing and redeposited afterwards.

Both pieces (2) and (3) were first vacuum annealed at 200 °C for 8 hours at 8×10^{-5} torr. An EBIC comparison of pieces (1) and (2) (Fig. 2) clearly shows enhanced charge collection in the annealed specimen. The charge collection profile indicates that the collected current is about 75% higher in the annealed specimen. No significant difference was observed in the EBIC image of piece (2) and (3) (not shown). The observed increase in diode efficiency most probably reflects an increase in carrier lifetime, possibly due to the formation of oxygen donor complexes [7].

Piece (3) was then annealed at 200 °C in hydrogen plasma (2×10^{-3} torr for 8 hr. then 0.7 torr for 15 min). This treatment increased the charge collection by about 30% relative to piece (2) (Fig. 3). The effect is clearly seen in the charge collection profile, but is less obvious in the micrograph. Note that piece (3) was held at 200 °C for a total of 16 hr as compared to 8 hr for piece (2). Whether the observed increase is due to hydrogenation alone is therefore not known, since the length of heat treatment also affects carrier lifetime.

Next, piece (3) was annealed at 350 °C for 16 hr. in a 1.5 torr hydrogen plasma. This treatment produced an additional 60% increase in collection, relative to the 200 °C plasma anneal (Fig. 4). As above, thermal effects and hydrogenation cannot be separated.

In an attempt to drive off the hydrogen, piece (3) was annealed at 500 °C in an 8×10^{-5} torr vacuum for 12 hr. Charge collection increased by an additional 70%, to a total of 160% relative to piece (2) after the 200 °C vacuum anneal (Fig. 5). The large increase in collection efficiency could be in part due to the increase in carrier lifetime which reaches a maximum near 500 °C [7]. In addition, Fig. 5 shows some EBIC contrast outside the diode area conceivably due to surface conversion of the lightly p-doped matrix by thermal donors.

One particular defect structure in the ribbon is shown at higher magnification (1000X) in Figs. 6, which compare corresponding sections in pieces (2) and (3). The parallel lines are probably composed of closely spaced twin boundaries the majority of which are coherent, and contain partial dislocations. The EBIC contrast of these defects varies considerably with annealing and the influence of hydrogenation will now be examined in more detail.

We first compare the defect contrast in piece (2) after the 200 °C vacuum anneal and piece (3) after the 350 °C hydrogenation (Fig. 6a and b). The profile depth of the darker right-hand boundary is similar in both pieces, even though the matrix level in piece (3) is higher. The contrast of the dislocation-like defects is less than that of the boundaries in piece (2), but is comparable to that of the boundaries in piece (3) after hydrogenation. Hence hydrogenation appears to reduce the electrical activity of the boundaries, but not of the dislocation-like defects (although it does tend to localize them more). The 500 °C vacuum anneal of piece (3) (Fig. 6c) greatly increased the contrast of both boundaries, but again did not significantly alter that of the other defects. Evolution of hydrogen from the boundaries seems the most plausible explanation.

Finally, profile minima corresponding to the dislocation-like defects in all three figures 6a-6c are of similar depth while the DC response (the absolute value of the current collected) varies nearly 300%. A possible interpretation is that these defects have a maximum recombination rate which is saturated at relatively low levels of DC response. Hence as the DC response increases, the relative depth of the minima decreases, rendering it progressively less detectable. Interestingly, no defects initially observed disappeared in toto after any later treatment; indeed defects not initially observed later became visible.

On diode 3a (Fig. 1), a scratch was observed to alter appearance after the 350 °C hydrogenation. Examination revealed a family of structures oriented perpendicular to the scratch which appeared to be deformation induced dislocations (Fig. 7a). Prior to the last hydrogenation, these structures, while photographed, were not examined because of their unresolved appearance. High magnification micrographs (5400X) (Fig. 8) at 5 KV exhibit a nominal width of 0.2 μ and a collection profile depth similar to that of other dislocation-like defects. The width and shape of corresponding change collection profiles are consistent with those theoretically predicted for dislocations [8]. After the 500 °C vacuum anneal, associated profile minima increased their depth by a factor of 4, appearing once again rather diffuse (Fig. 7b), presumably due to removal of hydrogen.

The apparent increase in resolution upon hydrogenation is an artifact of the narrow range of contrast which can be displayed in a micrograph. We could image the unpassivated dislocations, at the expense of back ground details, by deviating from our standard imaging conditions.

SUMMARY

A quantitative study of the EBIC contrast of linear defects in annealed, unannealed, and hydrogenated EFG silicon ribbons was carried out using split specimens. The major results are :

- (i) heat treatment, per se, increases collection efficiency.
- (ii) plasma hydrogenation reduces the contrast of some defects. However, none of the observed defects showed a total loss of EBIC contrast.
- (iii) Hydrogenation is useful to resolve tightly spaced arrangements of strongly active dislocations without loss of background details.

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Fig. 1. EFG ribbon, polished and split, with evaporated aluminum diodes..

Fig. 2. EBIC image with charge collection profile; piece (1) left, no treatment; piece (2) right, 200°C vacuum anneal.

Fig. 3. EBIC image with charge collection profile; piece (2) left, no treatment; piece (3) right, 200°C hydrogenation.

Fig. 4. EBIC image with charge collection profile; piece (2) left, 200°C anneal in vacuum; piece (3) right, 350°C hydrogenation.

Fig. 5. EBIC image with charge collection profile; piece (2) left, 200°C vacuum anneal; piece (3) right, 500°C vacuum anneal.

Fig. 6. EBIC images with charge collection profiles. (a) piece (2), 200°C vacuum anneal; (b) piece (3), 350°C hydrogenation; (c) piece (3), 500°C anneal in vacuum.

(a)

(b)

Fig. 7. EBIC image with charge collection profile of scratched region. (a) after 350°C hydrogenation; (b) after 500°C vacuum anneal. Note relative contrast of deformation induced and grown in dislocations.

Fig. 8. Section of Fig. 7(a).