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HIGH RESOLUTION ELECTRON MICROSCOPY OF INTERFACES IN CVD β-SiC

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Abstract Interfaces in CVD β-SiC have been analysed by high resolution electron microscopy. Models for the atomic structure of stacking faults, ζ3 and ζ9 twins in β SiC structure have been derived from the geometric approach of coincidence grain boundaries and symmetry considerations. These models have been checked and compared to the experimental results through high resolution image simulation.

1 - Introduction

Silicon carbide is a widely known technological material mainly used for its good thermomechanical properties. Its powders are very difficult to sinter without the help of additives but then, the grain boundaries often contain a second phase whose presence is detrimental to the properties. Chemical vapor deposition techniques can easily provide dense materials of high purity and, in the case of SiC, interfaces are well defined despite the high covalency of the structure. Moreover CVD specimens often exhibit a preferential orientation during the growth and this enhances the probability of occurrence of coincidence grain boundaries. In the case of the (110) orientation the specimen has a large choice of low energy boundaries: stacking faults, twins (ζ3), multiple twins (ζ9, 27, 81...) and others (ζ11, 19, 33...). In most cases, the orientation of the boundary plane (parallel to the direction of growth) is favourable to a complete high resolution imaging of the interfaces. Based on the classical theory of the geometry of coincidence grain boundaries and on the symmetry of dichromatic space groups, models of the atomic structure of the interfaces can be proposed and simulated images can be compared with the experimental results.

2 - Experimental procedures.

The samples of silicon carbide necessary for this study have been prepared by chemical vapor deposition (CVD) on a carbon substrate heated at 1500°C. The resulting platelet is polycrystalline with a cubic β structure and has an almost perfect (110) texture /1/. The specimen was mechanically polished down to 100 μm and 3 mm discs were cut by ultrasonic cutter. Final thinning was performed by an argon ion beam machine operating at 4.5 kV and 10 mA. High resolution images were obtained by a JEM 200CX with a point resolution of 0.23 nm allowing the imaging of the (110) plane of β SiC. Image simulation of the grain boundary was carried out based on the multislice dynamical equation. Periodic continuation approximation was used with the unit of the super-cell including the grain boundary. A large computer ACOS 2000 and an image processing system were used for the simulation of the high resolution images and the display of the images.
Silicon carbide exists mainly under the hexagonal form α or the cubic form β /2/. Using the Ramsdall notation the β form is noted 3C. SiC 3C has the zinc blende structure which consists of two interpenetrating fcc lattices (one for silicon, one for carbon) related by a displacement along the [111] direction through 1/4 [111]. The projection on the (110) plane is characterized by 6 atom rings which are similar to the rings of the diamond structure but with two different atoms (Fig. 1).

Figure 1. (110) projection of β SiC with silicon and carbon atoms noted respectively by large and small circles.

Figure 2. (110) projection of a unit cell of the Σ 3 coincidence orientation; crystals 1 and 2 are noted respectively by empty and full circles, the black dots represent the mid point in between silicon and carbon. The unit cell is built on (a) a silicon atom with one colored mirror m', (b) a carbon atom with one colored mirror m' and (c) on the mid point with two colored mirrors m', m*. Atoms in coincidence are pointed in white.

Figure 3. Atomic structure of the coherent 13 interface based on fig.2c with a boundary plane passing through a, b and c. (d) is equivalent to (c) but with silicon-carbon bondings at the interface.

4 - Interfaces in β SiC

We will describe all the relevant interfaces of this work within the framework of the model of the coincidence orientation. Moreover SiC having two atoms per unit cell, we will introduce the concept of dichromatic complexes, the set of the two crystal structures related by an orientation relationship. The symmetry of a complex, described by a colored space group, will be our guideline to classify the different possible structures /3/

For the simple case of the coherent (111) 23 boundary and considering that we have a [110] projection, the coincidence orientation can be described by the following rotation: 70.53° on the [110] rotation axis. A rotation of 109.47° on the same [110] axis would give for the fcc lattice an equivalent description /4/ but it has to be reminded that in the case of SiC (no center of symmetry due to the difference in chemistry between the atoms) the result will be different. Another parameter to be considered is the origin of the rotation. Figure 2 illustrates the importance of this choice for the case 70.53°, [110] and an origin on a silicon atom (a), a carbon atom (b) and a more "symmetrical" position (c). In the first two cases the complex has only one colored mirror, m', parallel to the direction of projection whereas in the last case the complex has two perpendicular mirrors, m' and m*. In this last case the unit cell has been built from an origin located on the site halfway between silicon and carbon along the [111] direction. In the case of diamond this site is the center of symmetry of the structure but even for silicon carbide it plays an important role in the choice of the dichromatic complex /5/. The three complexes represented in figure 2 are related by a simple translation of one crystal parallel to the projection plane.
The last step in order to build a representation of an interface is the choice of position for the boundary plane. Starting from the configuration with the highest symmetry and for a coherent boundary, the boundary plane, parallel to (111), can be positioned at different level in the unit cell. Figure 3 shows some of the possible choice (a, b or c) and the resulting interfaces. Figure 3c represents the most probable model for the structure of the coherent Σ3 but has at the interface a carbon-carbon bonding which does not exist in silicon carbide (a silicon-silicon bonding would have been obtained for a reverse choice of crystal 1 and crystal 2). For a different choice of rotation angle (109.47° instead of 70.53°) figure 3d can be proposed, all other parameters being identical with figure 3c. In this case a silicon-carbon bonding characterizes the interfaces and can be considered as a perfect interface. It has to be noticed that figures 3c and 3d are not related by a simple translation of one crystal but describe two structurally different orientation relationships.

In order to find the best model describing the structure of a grain boundary we will have to consider all the different possibilities offered by the various dichromatic complexes. Then the choice will be based on the highest symmetry and the less distorted atomic configuration. In the case of structures with more than one atom per unit cell the best choice will often come from the sites with the highest symmetry and a boundary plane at or in between mirror positions.

5 - Experimental results

Figure 6a is a HREM micrograph showing several interfaces in β SiC. All the grains have an almost common [110] direction parallel to the electron beam allowing simultaneous point resolution. The strong white contrast running across the picture can be described as a coincidence grain boundary whose orientation is modified by incoming twins lying in either grain I and grain II. Describing the micrograph from the top, the Σ27 boundary changes briefly for Σ81 when reacting with a microtwin lying in grain I. Then one twin boundary in grain I transforms it into a Σ9 boundary with a relatively planar interface. Again a microtwin laying in grain II generates a coherent Σ3 boundary. In grain I (top left) a stacking fault appears clearly between two Σ3 twin boundaries.

Generally speaking all the Σ3 boundaries have a coherent (111) planar interface. But in the case of grains I they are separated by two types of Σ3 boundaries: the first type is simply coherent, parallel to (111), whereas the second type has a marked contrast and lies perpendicular to the first. The boundary plane of the Σ9 can be in a symmetrical orientation: (221) in most cases but also (411); it can be also random. The boundary plane of Σ27 does not exhibit any preferential orientation. For the short segment of Σ81 boundary the boundary plane appears to lie very close to a (111) plane; it is, in fact, parallel to (877), one of the two twinning planes of the orientation.

We will analyse hereafter in details some of these interfaces.
Intrinsic stacking faults

Figure 7a is an enlargement of the area of figure 6a containing an intrinsic stacking fault (fig. 4). It lies on a (111) plane of grain I and is limited by two partial dislocations. The shift of the (111) planes is clearly seen on the micrograph and involves only two rows of white dots. As demonstrated on figure 5 this contrast is characteristic of an intrinsic stacking fault when the white dots of the HREM image are associated with the channels of the structure. This result will allow us to assume for the whole of figure 6a that white dots have to be associated to the channels of the structure.

The two partial dislocations are easily detected at the intersection of the stacking fault and the adjoining Σ3 boundaries. For the partial on the upper side the dislocation core is in the boundary plane and its strain field is homogeneously distributed in grain I and thus not affecting greatly the structure of the boundary. The other partial is located at the corner of two Σ3 boundaries and its strain field strongly modifies the contrast, and probably the boundary plane orientation, of one of the Σ3 boundary.

Sigma 3 boundaries, boundary plane orientation.

All of the grains in our specimens contain twin boundaries coming mainly from the deposition technique used for their preparation. A vast majority of them are Σ3 coherent twins lying on a (111) plane showing a sharp and well defined contrast at the interface. Due to the preferential orientation (110) of the foil they can be viewed directly edge-on. In some rare cases the boundary plane lies on an incoherent plane; that was the case in the preceding paragraph for one of the boundary limiting the intrinsic stacking fault.

Figure 7b shows a faceted Σ3 boundary with two facets along the (111) plane while the central one lies on the (211) plane perpendicular to the first two facets. The (211) plane is not a coherent twin plane of the Σ3 orientation and the contrast of this interface is very broad compared to the coherent twin. A possible model of such boundary is presented in figure 7c; another model involving a z relaxation of atoms exists also in the literature /6/ but it remains difficult to choose between the models.
Sigma 9 boundaries

In figure 8a, two coherent Σ3 boundaries (lower left) interact to give a Σ9 boundary with the boundary plane parallel to (221), one of the two twin planes with (114) of the orientation. However the contrast at the interface is slightly altered by the minute misorientation (note the difference in precision for the contrast between the two grains). Therefore it is difficult to judge if the periodicity is characteristic of a pure mirror with a flat interface or of a glide mirror with a zigzag interface.

In figure 8b the same coincidence orientation produces a clearer contrast at the interface indicating a shift of one half of the coincidence unit cell.

Figure 9 proposes two structure models of the Σ9 coincidence orientation with (a) no shift and (b) one crystal shifted by half parallel to the boundary plane. One can notice, for the latter case, the high coherency of the interface and the apparent doubling of the periodicity. The five and seven atom rings are now every half unit cell. The same effect is observed definitively on figure 8b, with alternately, on both side of the boundary, a strong dark contrast ("black atoms"). The model presented in figure 9b is the one generally adopted for the diamond structure.

Figure 8. HREM images of (a) two coherent Σ3 and one Σ9 boundaries, (b) one Σ9 boundary
We have simulated the contrast of such coincidence boundaries for the two models presented in Figure 9. For the image simulation we used a periodic continuation approximation with the unit of 9.25 Å x 13.08 Å. Figure 10a shows, for the model 9a, the simulated images. Although 500 Å defocus value is an optimum focus (Scherzer focus), the high resolution images with high contrast were usually taken with higher defocus values. For a crystal thickness of 140 Å, a defocus value of 750 Å and white dots associated with the channels of the structure there is a possible correlation between experiment and calculation. For the same crystal condition the reverse contrast ("white atoms") has been obtained for a defocus of 500 Å. However the quality of the contrast on the experimental image presented in Figure 8a makes any conclusion doubtful.

For the model presented in Figure 9b, the simulated images (Fig.10b) clearly show a shift of one half of the coincidence unit cell. For the reversed contrast and under the same crystal conditions as previously pertained, the five rings atoms appear now as very bright white spots. The contrast agrees well with the observed image in Figure 8a where we can find such alternating white dots at the boundary.

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