DETAILED 3D STRUCTURE OF {111} TETRAHEDRAL VOIDS AND ITS UNIDIRECTIONAL FORMATION IN CUBIC SIC —— S. Kondo, Y. Katoh, and L.L. Snead (Oak Ridge National Laboratory)

OBJECTIVES

We report the detailed shape and distribution of the tetrahedral voids in SiC neutron irradiated at 1460˚C, contributing significantly to irradiation-induced swelling. The specific rules for the selection of faceted void surfaces formed in crystals with polar surfaces are discussed.

SUMMARY

The {111} tetrahedral voids induced by neutron-irradiation in 3C-SiC were found to be spatially oriented in only one of two possible directions. The tetrahedral shape was unexpected as the surface-to-volume ratio is larger than the alternative {111} octahedral void common in both metals and ceramics. From a geometric viewpoint, all faces of the observed voids are either Si- or C-terminated surfaces. By comparing the surface area with the octahedral void (composed of the both Si- and C-surfaces) of the same volume, the considerable difference of surface energy between the Si(111) and C($\bar{1}\bar{1}\bar{1}$) was implicated.

INTRODUCTION

Microscopic voids, which are essentially three-dimensional aggregates of vacancies, have been the subject of study in several fields of material science. Significant effort has been directed to understanding the phenomena of the irradiation induced voids and the associated dimensional instability of nuclear materials [1,2]. In semiconductor devices, the distribution and elimination of grown-in voids, which are responsible for the reduction of carrier mobility, has also been extensively investigated [3,4]. On the other hand, engineered three dimensional periodic arrays of voids with a uniform geometric configuration in semiconductor crystals, often referred to as defect engineering, may enable optoelectronic, photonic, and/or quantum electronic functions. Knowing the material-specific three dimensional morphology is one of the key features of voids to help understand fundamental crystal properties and to control the void microstructures. For a given volume, voids generally take a shape that minimizes the total surface free energy [5,6]. If the surface energies of the different family planes are sufficiently close, more than one facet type may emerge. Void formation in face centered cubic (FCC) metals and alloys are generally classified as {111} truncated octahedra of {100} faceting (or tetrakaidecahedron) [7]. In body centered cubic (BCC) crystals there is no consistent void morphology. However, {011} faceted voids have been observed in iron [8] and other BCC metals [9].

Cubic silicon carbide (3C-SiC) is considered as a promising structural material for nuclear applications [10], and electronic and optoelectronic devices [11], because of the high thermal stability, excellent resistance to chemical attack, high thermal conductivity, and high electron saturation drift velocity. In the work by Kondo et al., likely production of {111} tetrahedral voids was reported in the irradiated β-phase SiC (3C crystallographic structure), contributing significantly to irradiation-induced volume expansion above ~1400˚C [12]. The faceted voids were previously observed in neutron-irradiated SiC by Price without detailed structural analysis [13], which is the only one other work implying the tetrahedral feature. In most materials having {111} faceted voids, the void shapes are octahedral and/or {110} truncated octahedra because of their lower surface area than the tetrahedra for a given volume. The formation of uncommon tetrahedral voids may result from the specific rules in this material made of two group IV elements of different electronegativities. In the present work, we report the detailed void shape in SiC and discuss the specific rules for the selection of faceted void surfaces formed in crystals with polar surfaces.

PROGRESS AND STATUS

Experimental

The material used for this work was poly crystalline β-SiC which was produced by chemically vapor deposition by Rohm and Haas Advanced Materials. The CVD material is extremely pure, with typical total impurity concentration of less than 5 wppm. The grain size is between 5 and 10 μm in the plane parallel to the deposition substrate, with the grains elongated in the <111> growth direction perpendicular to the substrate. The material is typically free of micro cracks or other large flaws, but atomic layer stacking faults on the {111} planes are common. There is no porosity in CVD SiC, and the material is generally considered to be of theoretical density (approximately 3.21 g/cm^3). The specimen was irradiated to 5.8 × 10^{25} n/m^2 (>0.1 MeV) at 1460 ± 100 ˚C in the HFIR, Oak Ridge National Laboratory in an ultrahigh purity inert gas environment. Due to the smaller atomic mass and the lower displacement threshold energy for C atoms on the C sublattice than those of Si atoms on the Si sublattice, there is about a factor of 3-4 higher number of C atoms displaced than Si atoms. A thin foil prepared in a commercial Ar-ion-milling unit (FISCHIONE model 1010) using 3-5 keV dual ion beam was examined in a transmission electron microscope (TEM/FEI Technai 20, 200 keV).

Results and discussion

Transmission electron images of the faceted voids created during irradiation are shown in Fig. 1(a)-(c). These images were taken utilizing different beam directions of B~$[0\bar{1}1]$, $[\bar{1}\bar{1}1]$, and [001], respectively (B; electron-beam direction). The {111} planes are indicated by the inset Thompson tetrahedron; four {111} faces named α to δ correspond to the observed crystal {111} planes and six edges correspond to the six <110> directions. The voids were imaged in slightly under-focused conditions, where the contrast arose from a weak absorption component and phase-contrast component due to defocus. Faceted voids are generally observed as polygonal shaped with dark peripheries in the under-focused condition. Through-focus and dark-field image analysis revealed that those polygonal defects were certainly voids without containing any stacking faults and dislocations. Stereo-micrograph analysis revealed that those defects were widely distributed over the specimen foil, distinguishable from surface pits.

In the B~$[0\bar{1}1]$ beam direction (Fig. 1 (a)), the projection view of voids appear as triangular shaped features containing two sides perpendicular to $[\bar{1}11]$ and [111] directions and a slight rounded side parallel to [011] direction. In comparison with a Thompson tetrahedron, the former two sides likely correspond to the edge-on β and δ surfaces, respectively. Meanwhile, the rounded side likely corresponds to α/γ edge, where vast majority of corners at the ends of the sides are rounded or truncated by the β or δ planes. Note that all the "triangular" voids formed in the same grain are oriented in the identical direction as shown in Fig. 1 (a). This feature will be discussed later. In the B~$[\bar{1}\bar{1}1]$ beam direction (Fig. 1 (b)), the projection view of voids appear as rounded triangles. Three bright lines connecting the triangle center with corners are generally seen inside the rounded triangle, each line is parallel to $[\bar{2}1\bar{1}]$, $[\bar{1}\bar{2}1]$, and [112] direction, respectively. The image contrast of inner edge of faceted voids was well simulated by theoretical calculation [14], where the intersecting faces was known to be shown as bright line. Orientation of these bright lines and periphery of the rounded triangle is well accorded with the projection view of the inset Thompson tetrahedron. Therefore, the bright lines most likely correspond to the surface intersecting edges at β/δ, α/δ, and α/β, respectively. In the B~ [001] beam direction (Fig. 1 (c)), the voids appear to be more rounded shape in projection. Two bright lines orthogonally crossed are observed inside some voids, where each line likely correspond to the α/β edge for the line perpendicular to [110] and γ/δ edge for the line perpendicular

to $[\bar{1}10]$. The rounded features observed in Fig 1 (c) indicate that most tetrahedral void edges would not be straight but slightly rounded toward the outside of the void. The curvature of the {111} surfaces, which are sufficiently away from edges, is supposed to be insignificant considering the relatively straight projection view of the edge-on surfaces (β, δ) as shown in Fig. 1 (a). By comparing the void images taken from three different directions with each corresponding Thompson tetrahedron, the shape of the voids is confidently determined to be near tetrahedral with {111} facets with vertices slightly truncated by {111} planes. Note that all the "triangular" voids formed in the same grain are identically oriented as clearly seen in Fig. 1 (a).

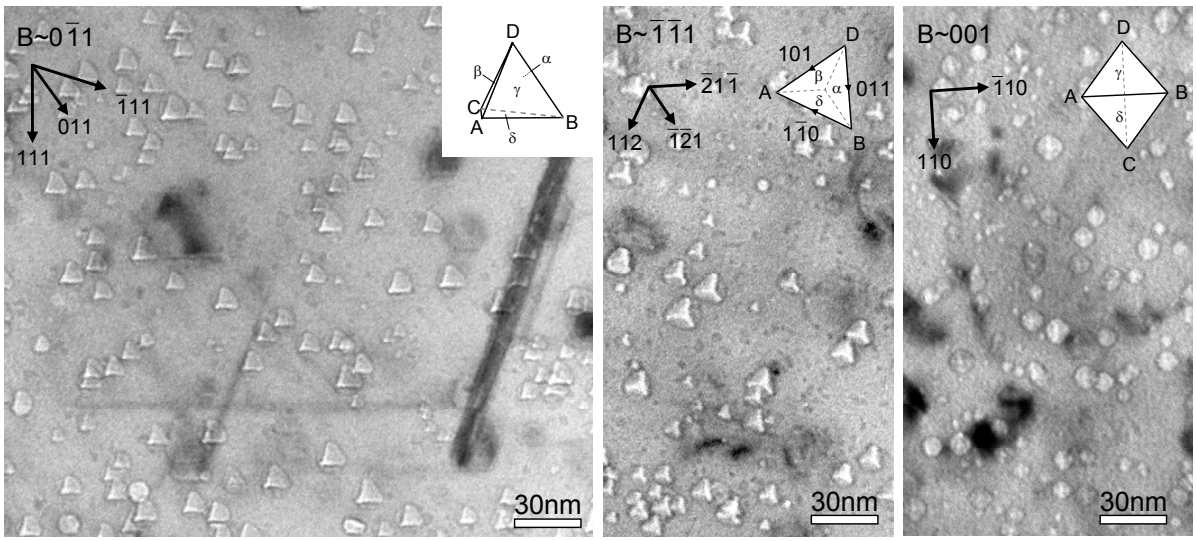

Fig. 1. Microstructure of tetrahedral voids in 3C-SiC after neutron irradiation at 1460˚C to 5.8 × 10^{25} n/m^2. The electron beam direction is close to; (a) $[0\bar{1}1]$, (b) $[\bar{1}\bar{1}1]$, and (c) [001] zone axis. The {111} planes are indicated by the inset Thompson tetrahedron; four {111} faces named *α* to *δ* correspond to the observed crystal {111} planes and six edges correspond to the six <110> directions.

Often in crystals with low stacking fault energy like SiC, stacking fault tetrahedra or Frank faulted loops are energetically preferred over voids when cluster size is relatively small [15, 16]. Presence of gas atoms (either pre-existing or created through nuclear transmutation) might prevent the collapse of a void in the early stage of the vacancy accumulation [17]. Such gas-stabilized voids tend to be in more spherical shapes, generically referred to in the literature as bubbles. However, it can be assumed that the voids examined here are not filled with gas at any significant pressure because of the very limited gas production rates for the highly pure SiC [18]. Therefore, the pressure of these gases is not a likely cause for the observed rounded features.

An important question is the underlying reason for the unidirectional distribution of the voids observed (see Fig. 1 (a)). In the usual case, the void surfaces may be randomly selected by offering equal opportunities to all {111} planes. Then, both types of "triangular" voids, which are symmetric to [011] or $[01\bar{1}]$, should be observed in B~$[0\bar{1}1]$ beam direction. However, that was not the case for 3C-SiC. This phenomenon has not been reported earlier. A possible explanation for such observation is that all the surfaces are either of the Si- or C-terminated {111} surface exclusively, as briefly described below.

The atomic surfaces can be created by bond cleavage at either widely spaced or narrowly spaced {111} interplanar binding; those are single-bond surface and triple-bond surfaces, respectively. For

the binary crystal with zinc blende structure, each ideal surface may be terminated at only one element (Si or C atomic layer for SiC). One can expect that the triple-bond surfaces are unfavorable for void surfaces because of its higher surface energy related to the higher dangling bond density [19]. Fig. 2 shows the schematic image of the tetrahedral voids in 3C-SiC, where voids are viewed from the $[0\bar{1}1]$ direction at the atomic level. Edge-on void surfaces are indicated by solid lines for the left-hand void and dashed lines for the right-hand void. Each open circle and closed circle can be either a Si atom or C atom. All four faces (two edge-on and the remaining two faces) of the left-handed void in the figure are made of only open circles. The faces of the right-handed void, which is [011] or $[01\bar{1}]$ symmetrical to the left-side void, are made of atoms indicated by closed circles. The unidirectionally-oriented tetrahedral voids indicate that all the surfaces of observed voids contain only one element of Si or C atoms as is clear from the Fig. 2. That is to say, the results indicate that either Si-single-bond-terminated or C-single-bond-terminated surfaces is favored as the void surface, and the other is unfavored.

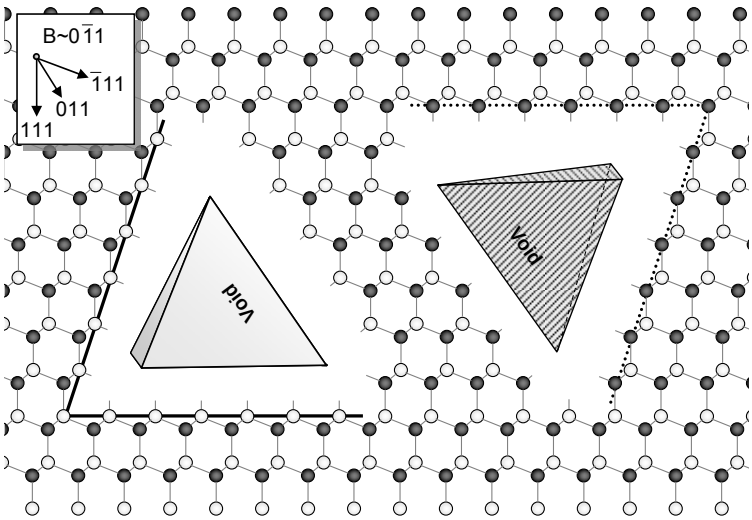

Fig. 2. Possible configurations of {111} tetrahedral voids in 3C-SiC. All four surfaces (two edge-on and the remaining two faces) are made of only open circles for the left-hand void, closed circles for the right-hand void. Each open and closed circle can be either a Si or C atom.

This rule may also affect the three dimensional void shape in this crystal. The void with {111} facets in cubic crystals can have the geometrically alternative shape of octahedron as well as the tetrahedral void shape, where the octahedron is generally preferred due to the lower total surface energy for a given volume in spite of the increase in edge and vertex energy at any TEM visible size. Lack of octahedral voids in 3C-SiC may be because the octahedral void geometrically needs both Si- and C-terminated {111} surfaces for its formation. If the surface energy still controls the equilibrium void shape and distribution in the irradiated SiC, and the energy is sufficiently different between Si- and C-terminated {111} surfaces, the unidirectional formation of tetrahedral voids may occur. The difference of surface energy between the two polar surfaces has not been clarified yet. However, the surface energy of the C-terminated (111) is considered likely to be significantly less than that of Si-terminated surface because of the faster growth rate of C-surfaces of 3C-SiC during the CVD process [20]. The lower surface energy for C-terminated surfaces resulting from stronger surface relaxation comparing to Si-surface has also been theoretically estimated [21-23], though theoretical values are widely scattered and depend strongly on the potential energy functions employed. The absence of octahedral voids indicates that the Si-terminated surface energy is at least 1.5 times greater than the C-terminated surface, by comparing total surface area between pure

tetrahedron and octahedron for the same number of contained vacancies. It is comparable to the theoretical simulations showing 1.3-3.4 times higher surface energy for Si-terminated surfaces. It should be pointed out that further study on other possible mechanisms that may be responsible for inducing the unidirectional formation of the tetrahedral voids may help to provide a more complete representation of the finding. Specifically, electronic structure, chemical properties of the void surface, and difference of the displacement damage rates between Si and C under neutron irradiation may be interrelated to the geometric aspects studied here.

In summary, irradiation-induced voids formed in irradiated SiC were tetrahedrally bounded by {111} lattice planes, and the distribution was unidirectionally-oriented in the each grain. Entire surfaces of the unidirectional voids are shown to be the same atomic layer (either Si {111} - or C $\{\bar{1}\bar{1}\bar{1}\}$ - surfaces) due to the crystallographic characteristics of zinc blende structure. This implies that the one of the two atomic surfaces is favored in forming void surfaces and the other is unfavorable. The absence of usual octahedral voids involving both surface types indicates at least 1.5 times higher surface energy for Si{111} than C$\{\bar{1}\bar{1}\bar{1}\}$ assuming the surface energy dominates the void shape.

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