

On the stability of 3C-SiC single crystals at high temperatures

D. Dompoin^{1, a}, I. G. Galben-Sandulache^{2, b}, A. Boulle^{1, c}, D. Chaussende^{2, d, *},
D. Eyidi^{3, e}, J. -L. Demenet^{3, f}, M. -F. Beaufort^{3, g} and J. Rabier^{3, h}

¹ Science des Procédés Céramiques et de Traitements de Surface (SPCTS), CNRS UMR 6638, Centre Européen de la Céramique, 12, rue Atlantis 87068 LIMOGES, France

² Laboratoire des Matériaux et du Génie Physique (LMGP), CNRS UMR 5628, Grenoble INP, Minatec, 3 parvis Louis Néel, BP 257, 38016 Grenoble Cedex 01, France

³ Institut Pprime, CNRS UPR 3346, Département Physique et Mécanique des Matériaux, SP2MI-Téléport 2-Bd Marie et Pierre Curie, BP 30179, 86962 Futuroscope-Chasseneuil Cedex, France

^adeborah.dompoin@etu.unilim.fr, ^birina.galben@grenoble-inp.fr, ^calexandre.boulle@unilim.fr, ^ddidier.chaussende@grenoble-inp.fr, ^edominique.eyidi@univ-poitiers.fr, ^fjean.luc.demenet@univ-poitiers.fr, ^gmarie.france.beaufort@univ-poitiers.fr, ^hjacques.rabier@univ-poitiers.fr, *corresponding author

Keywords: 3C-SiC, 3C-6H transition, stacking faults, dislocations.

Abstract. The 3C-6H polytypic transition in 3C-SiC single crystals is studied by means of diffuse X-ray scattering (DXS) coupled with transmission electron microscopy (TEM). TEM reveals that the partially transformed SiC crystals contain regions of significantly transformed SiC (characterized by a high density of stacking faults) co-existing with regions of pure 3C-SiC. The simulation of the diffuse intensity allows to determine both the volume fraction of transformed material and the transformation level within these regions. It is further shown that the evolution with time and temperature of the transition implies the multiplication and glide of partial dislocations, the kinetics of which are quantified by means of DXS.

Introduction

The question of the relative stability of the different polytypes is a longstanding issue in the studies of SiC materials. In the case of 3C-SiC this point is of special importance since this polytype is believed to be unstable and transforms into 6H-SiC at the temperatures usually required to grow SiC single crystals from the vapor phase [1,2]. As a consequence, the crystals grown are in general of poor crystalline quality, characterized by a high density of stacking faults (SFs) and/or 6H inclusions. The improvement of the overall crystalline quality of 3C-SiC single crystals hence requires a significant optimization of the growth conditions. Along this line, a better understanding of the stability of 3C-SiC at high temperatures, for instance in terms of the 3C-6H transformation kinetics and the mechanisms involved, would provide an invaluable help. This is the topic of the present article.

Because of the rarity of 3C-SiC single crystals, the 3C-6H transition in SiC has only been scarcely studied (see Ref. [1] and references therein) and the transformation kinetics are yet unknown. Up until recently even the transformation mechanism was not clearly identified. A previous study using diffuse X-ray scattering (DXS) revealed that the transformation implies the glide of partial dislocations [3], probably according to a mechanism first described by Pirouz (Ref. [4] and references therein). In the present work, we pursue these DXS experiments, combined with transmission electron microscopy (TEM), in order to analyse the 3C-6H polytypic transition on both a qualitative (i.e. what are the mechanisms involved) and quantitative (i.e. the transformation kinetics) standpoint.

Experimental details

In this work we used (001)-oriented 3C-SiC single crystals produced by Hoya Corp. by chemical vapor deposition on “undulant” (001) Si substrates [5]. It is known that the SF distribution in these samples is anisotropic [5]: the (-111) and (1-11) planes exhibit a high SF density, whereas the (111) and (-1-11) planes exhibit a low SF density. In the following we shall only consider the planes exhibiting a high SF density, since the 3C-6H transition mainly takes place in the direction normal to these planes. In order to determine the transformation kinetics, a first set of crystals have been annealed at 2000°C for a time ranging between 1 h and 8 h. A second set of crystals annealed 5 h for temperatures ranging between 1700 and 2100°C allows us to assess the activation energy of the transformation. All crystals have been characterized by DXS on a high-resolution laboratory diffractometer. This technique allows to determine, in a non-destructive way, the mechanism involved in the transformation, the level of transformation (i.e. disorder), the nature of the polytypes and their relative amount. Full details concerning the DXS technique can be found in Ref. [6]. Plane-view and cross-section samples have also been prepared from a crystal annealed at 1800°C for TEM observations.

Results and discussion

Microstructure of the annealed crystals. A plane-view of a typical microstructure formed in the annealed crystals is shown in Fig. 1(a). There are regions extending parallel to the $\{111\}$ planes, of several micrometers wide, characterized by a high density of SFs. The volume fraction of these regions is denoted x_i and the level of transformation in these regions is denoted τ ($\tau = 0$ for the 3C phase and $\tau = 1$ for the 6H phase). Between these regions, the 3C-SiC (with volume fraction $1 - x_i$) is unaffected by the transformation. A zoom on an isolated SF terminating within the crystal, Fig. 1(b), shows that it is bounded by a dislocation whose Burgers vector was determined to be $1/6[2-1-1]$, which correspond to the Burgers vector of partial dislocations in 3C-SiC. Such partial dislocations result from the dissociation of a perfect basal plane dislocation according to $1/2\langle 1-10 \rangle \rightarrow 1/6\langle 2-1-1 \rangle + 1/6\langle 1-21 \rangle$. A basal plane dislocation undergoing that type of dissociation is clearly visible in Fig. 1(c) (see arrowheads). Since the two partials are characterized by different mobilities [4], the expansion of one of the partial forms a loop that produces a SF in the entire lattice plane. Double cross-slipping then allows successive lattice planes to be faulted (according to a mechanism proposed in [4]) so as to, starting from the 3C stacking, form the final 6H sequence.

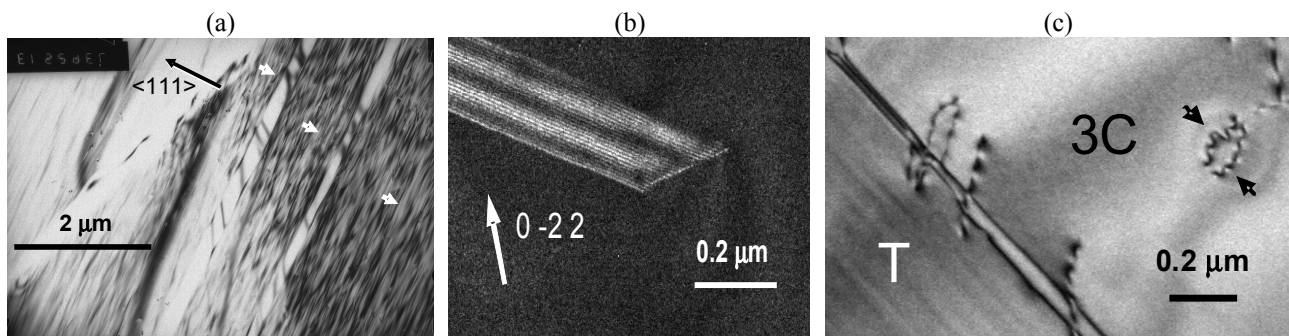


Fig. 1: TEM observations of a 3C-SiC crystal annealed at 1800°C. (a) overview showing transformed, stacking-fault-rich bands (arrowheads) between pure 3C-SiC areas. (b) weak-beam image of a typical stacking fault and a bounding dislocation. (c) Bright-field image of short partial dislocations and long dislocations lying at the interface between transformed areas (T) and 3C-SiC. Two dissociated partials in pure 3C-SiC are also visible (arrowheads).

Transformation kinetics. All DXS experiments reveal that, upon high temperature annealing, 3C-SiC systematically transforms into the 6H polytype [3,6,7]. The presence of SFs produce extended diffuse X-ray scattering, the simulation of which allows to determine the volume fraction of transformed material x_i and the transformation level within the partially transformed regions τ . The

model used for the simulation is built on the following findings obtained by TEM: (i) the SiC crystals contain regions of heavily transformed SiC co-existing with regions of perfect 3C-SiC, so that the overall scattered intensity is written as a volume average of the intensities scattered from each type of region, and (ii) the transformed regions contain SFs which are bounded by partial dislocations which result from the dissociation of basal plane dislocations (for details see [6]).

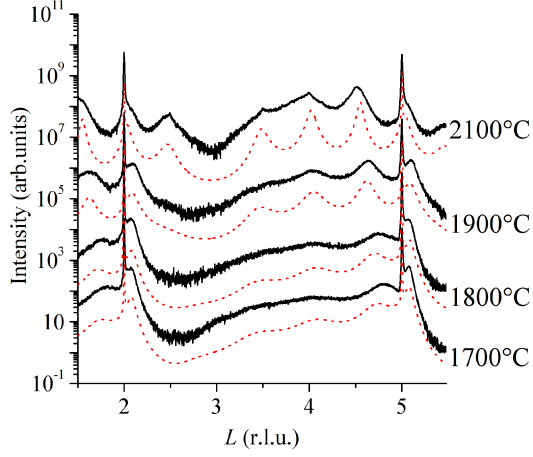


Fig. 2: DXS curves (black line) and simulation (red dotted line) corresponding to SiC crystals annealed 5h for increasing temperatures.

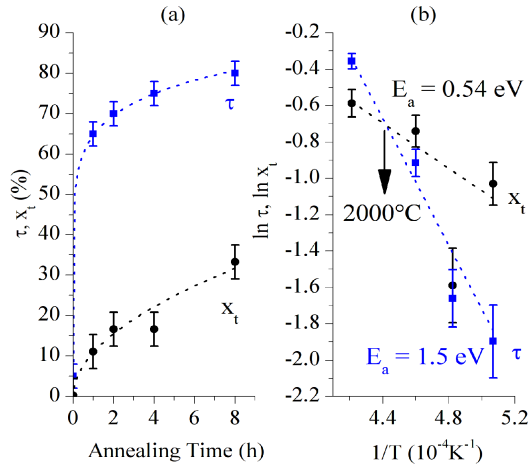


Fig. 3: (a) kinetics and (b) Arrhenius plot corresponding to the transformation level τ and the volume fraction x_t .

creation of new SFs: the glide of partial dislocations in their planes produces an extension of the SFs that increases the volume fraction of transformed material. However, in order to fault significant regions of the crystal, these dislocations have to glide over several tens of micrometers, a path along which they might be pinned by structural defects. Moreover, two dislocations, gliding in two different glide planes (say (-111) and (1-11)) can not cross each other (since they correspond to two different orientations of the upcoming 6H phase) so that the motion of one of the dislocation is stopped. These arguments might explain why the corresponding kinetic is much slower and does not reach very high values (contrarily to τ).

More can be learned from the activation energies corresponding to each mechanism, Fig. 3(b). The increase of τ is characterized by an activation energy $E_a = 1.5$ eV. Since the increase of τ

The DXS curves (together with the simulations) recorded along the $[10L]_h$ row corresponding to the second set of crystals is shown in Fig. 2 (the subscript 'h' stands for hexagonal). The index L corresponds to the Miller index in a three-layer hexagonal unit cell, *i.e.* the Bragg peaks occurring at $L = 2$ and 5 correspond to the (002) and (-113) Bragg peaks of 3C or, alternatively, to the (104) and (10 10) peaks of 6H [6]. Upon increasing temperature the diffuse intensity located between the Bragg peaks increases and forms broad pseudo-peaks (corresponding to the Bragg peaks of the forthcoming 6H phase) indicating the progress of the transformation.

The volume fraction x_t and the transformation level τ deduced from the simulations for all investigated crystals are displayed in Fig. 3. Fig. 3(a) represents the evolution with time of τ and x_t at a temperature of 2000°C. Fig. 3(b) represents the evolution of τ and x_t as a function of temperature in the form of an Arrhenius plot. Let us first consider the evolution with annealing time. The first striking observation is that the transformation level and the volume fraction are characterized by two very distinct kinetics. Whereas the transformation level exhibits a fast kinetic and reaches a value of 80 % after 8 hours, the volume fraction exhibits a much slower kinetic and only reaches 33 % after 8 hours. This observation suggests that these two evolutions imply two distinct mechanisms. The increase of the transformation level necessarily implies the creation of new SFs. As mentioned earlier, new SFs can be created in SiC by the multiplication of partial dislocations using the double cross-slip mechanism [4]. On the contrary, the increase of the volume fraction does not necessarily imply the

necessarily implies the creation of new SFs, this activation energy simply correspond to the energy required to activate double cross-slip. This value is in excellent agreement with the value ($E_a = 1.54$ eV) deduced from *ab initio* calculations [8]. The increase of x_t is characterized by an activation energy approximately three time smaller ($E_a = 0.54$ eV). This demonstrates that it indeed implies a distinct mechanism than τ , and in particular a mechanism that requires a much smaller activation energy. This value might hence correspond to the activation energy for the glide of partial dislocations in 3C-SiC. Although this energy is not clearly determined in the literature, it is fair to think that the corresponding energy is smaller than for the double cross-slip motion which implies a significant dislocation core reconfiguration [4].

Conclusions

The 3C-6H polytypic transition in SiC has been studied by diffuse X-ray scattering and transmission electron microscopy. TEM revealed that the transformation does not affect the whole crystal simultaneously. Instead, there are regions with a high density of SFs co-existing with perfect 3C regions. The SF are bounded by partial dislocations which result from the dissociation of basal plane dislocations. DXS revealed that the 3C-6H polytypic transition in SiC actually involves two different mechanisms: the first one corresponds to the nucleation of new stacking faults through the double cross-slipping of partial dislocations, and the second one corresponds to the expansion of the partial dislocations. The former is a fast process and characterized by an activation energy of $E_a = 1.5$ eV, whereas the latter is a slow process and characterized by an activation energy of $E_a = 0.54$ eV.

Acknowledgements

The authors would like to warmly thank the Region Limousin (France) for its financial support. LMGP thank the MINTEX-French ANR program (contract No. ANR-09-BLAN-0189-01) and the MANSiC-Marie Curie Research and Training Network (contract No. MRTN-CT-2006-035735) for their financial support.

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