Full-length paper

Different void shapes in Si at the SiC thin film / Si (111) substrate interface

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Running title: Void shapes at the SiC / Si(111) interface

Keywords: transmission electron microscopy; SiC film; Si substrate; interface; voids; equilibrium void shape

Abstract

The shape of interfacial voids formed in the epitaxial SiC/Si(111) heterosystem just underneath the SiC film has been investigated using optical microscopy and transmission electron microscopy (TEM). SiC films are grown on Si(111) substrates at two different substrate temperatures (specimen type 1 at 850°C, specimen type 2 at 1050°C) using solid-source molecular-beam epitaxy (MBE). At 850°C substrate temperature the well-known triangular void shape with primary {111} facets is formed in the Si substrate confirming the results already reported by Learn and Khan in 1970. When growing at 1050°C substrate temperature a new void shape showing a hexagonal appearance in the plan-view direction is found. By indexing the hexagonal void planes, other facets with higher surface energies than the usual {111} type facets have been observed leading to a void shape near the equilibrium void shape in a cubic crystal. As in the case of the triangular shaped voids, the formation process of the hexagonal shaped voids should start from the {111} planes, however, due to the higher substrate temperature, planes with higher surface energies are formed in addition.

Introduction

Silicon carbide (SiC) is an excellent semiconductor material for high power, high temperature and high frequency devices because of its thermal, electronical and physical properties. The deposition on silicon (Si) allows to integrate the silicon carbide technology into the mature silicon technology. The growth of 3C-SiC thin films on Si is a challenging task for heteroepitaxy due to the large mismatches in lattice constants (~20%) and thermal expansion coefficient (~8%).

Already in 1983 Nishino et al. [1] reported about the large area growth of 3C-SiC on silicon by chemical vapour deposition (CVD). There is a trend nowadays to the use the molecular-beam-epitaxy (MBE) [2-7] over the CVD [1, 8, 9] for SiC deposition. Compared to the CVD, the MBE method has the potential to produce SiC layers at lower temperature and with higher purity [5].

One of the problems associated with heteroepitaxial growth of SiC on Si is the formation of voids at the SiC/Si interface just beneath the film. This poses a problem in SiC/Si device applications because one of the most promising applications of SiC, the wide bandgap emitter SiC/Si heterobipolar transistor (HBT), requires an excellent interface [2, 8]. Therefore in the first step the void creation has to be understood before in a second step it can be avoided.

It is already known [3, 10-13] that the voids directly underneath the SiC layer in the Si substrate are formed by coalescence of Si vacancies which result from the Si outdiffusion through the SiC film. The shape of these voids in a Si(111) substrate are always described as triangulars, formed by {111} facets [10, 12] and no other shapes have been reported so far.

In this paper we show by transmission electron microscopy (TEM) and optical microscopy studies that the void shape at the SiC/Si interface in the Si substrate is influenced by the growth temperature of MBE grown SiC layers. We discuss, to the best of our knowledge for the first time, the appearance of hexagonal shaped voids in the light of the creation of the equilibrium void shape in a cubic substrate.

Experimental

The SiC films were grown in a two-source solid-state molecular-beam-epitaxial (MBE) deposition equipment (RIBER MBE System).

We compare the investigation of SiC thin film / Si(111) specimens grown at different substrate temperatures. The SiC film in specimen type 1 was grown on the Si(111) substrate without carbonization at 850°C with a growth rate of 4 nm/min. The final film thickness was about 150nm (for more details see [4, 14]). At specimen type 2 the SiC film was deposited on a Si(111) at higher growth temperature without carbonization of the substrate surface and a growth rate of about 2 nm/min. The substrate temperature was increased at the beginning of the growth process up to 1050°C and was stable during the entire deposition time. The SiC film thickness was about 150 nm (for more details see [6, 7]).

The TEM foils were prepared for examination both in plan-view and in cross-sectional view using standard techniques and investigated by optical microscopy and TEM using a JEOL JEM1200 and JEM4000EX.

Results and discussion

Typical void at the SiC/Si heterosystem

Fig. 1 shows a low-magnification TEM bright-field image in $[1\bar{1}0]$Si zone axis orientation where a typical void in the Si substrate just underneath the SiC layer is easy to see. The facets as indicated in the figure are of {111} type. As will be seen below, from the low-magnification cross-sectional view only the shape of the void is not possible to determine.

Void shape at 850°C substrate temperature, specimen type 1

Fig. 2 shows the plan-view optical micrograph of a thin SiC film grown on a Si(111) substrate at 850°C substrate temperature. The bright triangular shaped features are the voids in the substrate. They are visible because of the lower thickness of the specimen at this areas. In Fig. 3a which shows a plan-view TEM image (see [14]) of the same specimen the shape of the void is seen as an exact triangle. (The slightly deviation from an equilateral triangle is due to the high tilting in TEM observation.) These void facets are the energetically favourable {111}-planes showing the angle of 70.53° between {111} planes. The (111) facet parallel to the interface (see Fig. 1) limits the bottom of the void and leads to the appearance of the void shape as a reverse truncated trigonal pyramid. On the base of the existing models [10, 12, 13, 15] we summarise the void creation in the following way:

As mentioned in [10-12], the reason for their creation is the Si deficit in the growing film. At a SiC surface the Si adatoms have a higher desorption rate than the C adatoms (energy of adsorption [eV/atom]: Si on β-SiC(111)=3.81, C on β-SiC(111)=8.82 [16]). As was found by [3, 10-12] the loss of Si atoms at the surface is compensated by the migration of Si atoms from the Si substrate. The chemical bonding of the Si atoms is weaker in the substrate than in the SiC film (Si-Si=2.8eV and Si-C=3.9eV) [16]. In contrast, the diffusion of the excess C atoms is improbable [3] because the chemical C-C bonding is very strong (5.4eV) [16].

Inhomogenities at the substrate surface are the starting point of the Si-outdiffusion. It is very likely that in the growing SiC layer defects like dislocations, grain boundaries or stacking faults are the energetically favourable paths of the Si diffusion. The migration of the Si atoms to the surface of the growing layer can be performed as vacancy diffusion along these defects [15, 17]. It is then possible that the vacancies coalesce and form a small void beneath the SiC film at the layer/substrate interface (Kirkendall effect [19]). As long as Si atoms are then needed to form the SiC layer, the Si-outdiffusion should take place from the voids already developed. As in the cubic closed-packed Si-crystal, the {111}-planes are the faces with the lowest surface energy ($\gamma(111)=1.23\ \mathrm{Jm}^{-2}$ [18]). It is understandable that these planes form the facets of the void.

The cross-sectional HRTEM-image obtained at the $[1\bar{1}0]$ zone of Si (Fig. 3b) shows that there is a facet in addition between inclined {111} planes. As the angle between this facets and the (111) facet was measured to be 35°, these are {110} facets. (The angle between {110} and related {111}-planes is 35.26° [19].) Although {110} surfaces have a higher surface energy ($\gamma(110)=1.16\gamma(111)$ [18]) and are not as stable as {111} planes, their occurrence is energetically possible because it reduces the surface area and the entire surface energy of the void as a cavity. One could propose that this faceting is a kinetical effect [20].

Void shape at 1050°C substrate temperature, specimen type 2

Fig. 4 shows the plan-view optical micrograph of a SiC film grown on a Si(111) substrate at a growth temperature of 1050°C. The modification to a hexagonal appearance of the void shape is obviously seen in the plan-view TEM image as well (Fig. 5a). The truncation of the corners of the regular hexagon is possible to see. Fig. 5b is a cross-sectional HRTEM image obtained at $[1\bar{1}0]$ zone of Si of a hexagonal void. In addition to facets already appearent in triangular voids ((111), (110), $(11\bar{1})$), other facets are observed in the $[1\bar{1}0]$ zone. These were found to be (001), (113), (112), (331), (551), and ($33\bar{1}$) facets. Compared to the {111} planes, these crystal lattice planes are energetically unfavorable (for instance: $\gamma(001)/\gamma(111)$=1.10..1.15, $\gamma(113)/\gamma(111)$=1.12 [18]). We suppose that they appear because more energy was inserted into the crystal system during the deposition at higher temperatures, and facets with higher surface energy can be developed.

Process of the formation of hexagonal voids (specimen type 2)

The higher substrate temperature seems to lead to the formation of void facets with high surface energy. It is mentioned in [18], that a crystal system anneals at a temperature, high enough that the diffusion around the internal surfaces of the void is sufficient, then all voids should attain the equilibrium shape. The internal void shape in this case is identical to the external crystal equilibrium shape. For a cubic crystal like Si this is to a good approximation a tetrakaidecahedron, simplistically it can be named a truncated octahedron. (It is obtained by cutting off a solid with eight faces. In the new solid the corners are transformed into squares and the triangular faces of the octahedron turn into regular hexagons.) We expect that the observed hexagonal shape is close to the equilibrium void shape in a cubic crystal. On the base of the above observation, we suggest the following model for the formation of the hexagonal shaped voids:

As can be seen from the plan-view optical micrograph of specimen type 2 in Fig. 6a, small triangular voids and larger voids showing the hexagonal appearance (see also Fig. 4) exist in one specimen simultaneously. Therefore it can be assumed that a two step formation process does take place. We suppose that in the first step the Si vacancies, coalesced at the SiC/Si interface, form a small void with the shape of a reverse trigonal pyramid limited by the energetic favourable {111} planes. In the scheme in Fig. 6b, the traces (cuts) of these {111} planes are drawn as a regular triangle, which should represent the situation how the small trigonal voids (see Fig. 6a) are formed. In the second step the size of the void becomes larger.

The development of a void in the substrate is crystallographically comparable with the solution of a crystal. This process is very sensible against the temperature [19] and will not take place at low surface mobility of the atoms. At the beginning, lattice planes with the lowest rate of movement and the highest density of atoms are developed ({111} planes) followed by facets with higher rate of movement, lower density of atoms in the plane, and higher surface energy (in the $F\,m\bar{3}m$: (100), (110), (112), (113) [19]). The {112}-planes are the main reason for the hexagonal appearance of these voids in plan-view (see Fig. 6b). Six {112} planes (angle of 60° between them) exist in the <111> zone. Starting from the trace of two {112} lattice planes, as a kinetical effect, the respective {110} facet begins to grow with an angle of 30° to the {112} plane.

Conclusions

In the present study we found a drastical influence of the growth temperatures (850°C and 1050°C) on the shape of the voids formed in the Si(111) substrate underneath the SiC film. Two different void shapes were observed; the well-known reverse trigonal pyramid formed during layer growth at 850°C substrate temperature and a new hexagonal shape created at 1050°C substrate temperature only. In the latter case we demonstrate that the lattice planes forming the void shape are not only the low surface energy facets already observed in triangular voids, but facets with higher surface energy are formed in addition. Their mechanism of creation can be understood due to the higher mobility of the Si adatoms on these facets. Therefore a void shape approaching the tetrakaidecahedron (the equilibrium void shape of a Si crystal) could be reached.

Acknowledgement

The authors would like to thank Dr. Andreas Fissel for providing the SiC specimen and Dr. P.D. Brown from the University of Cambridge (UK) for his help with the HRTEM. The work was supported by the Deutsche Forschungsgemeinschaft.

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Figures:

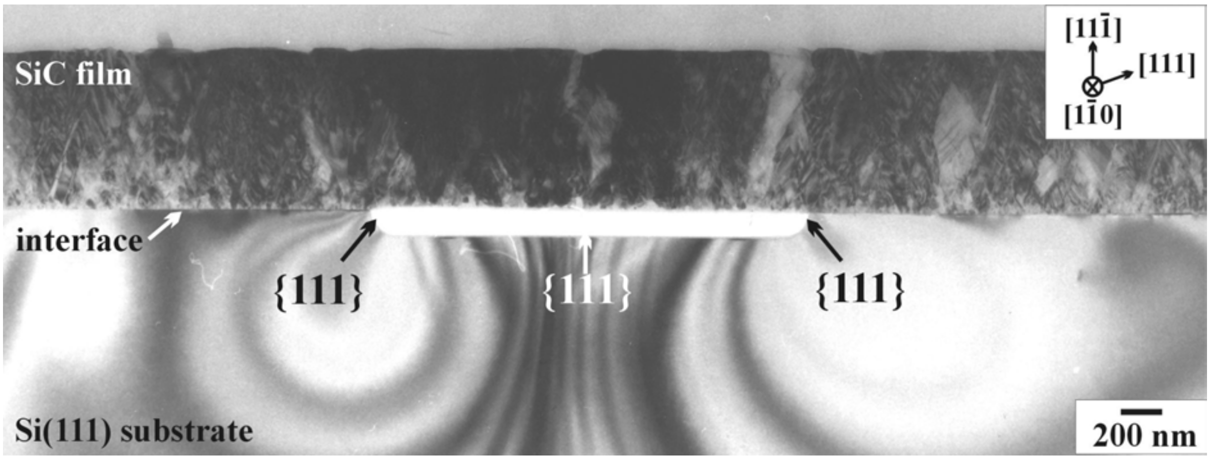

Fig. 1. Low-magnification cross-sectional bright-field TEM image of a SiC film on a Si(111) substrate, obtained in the $[1\bar{1}0]$ zone of Si, showing a typical void (bright feature in the middle of the image) at the film/substrate interface (marked by arrow at the left image side) just underneath the film in the substrate. The primary faceting of the voids are the {111} type planes as indicated by the marks.

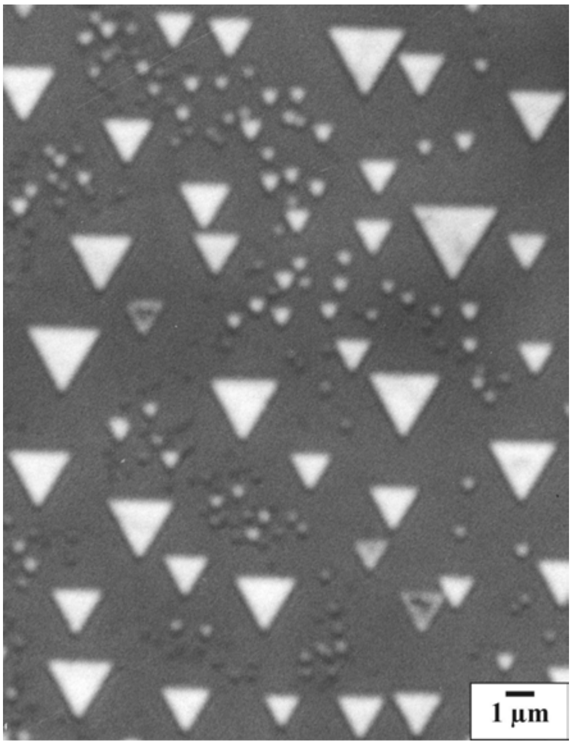

Fig. 2. Low-magnification optical micrograph in plan-view direction of the SiC layer on Si(111) substrate grown at 850°C substrate temperature (specimen type 1) showing the perfect triangular void shape (bright features) originated from the {111} lattice planes of the cubic Si substrate.

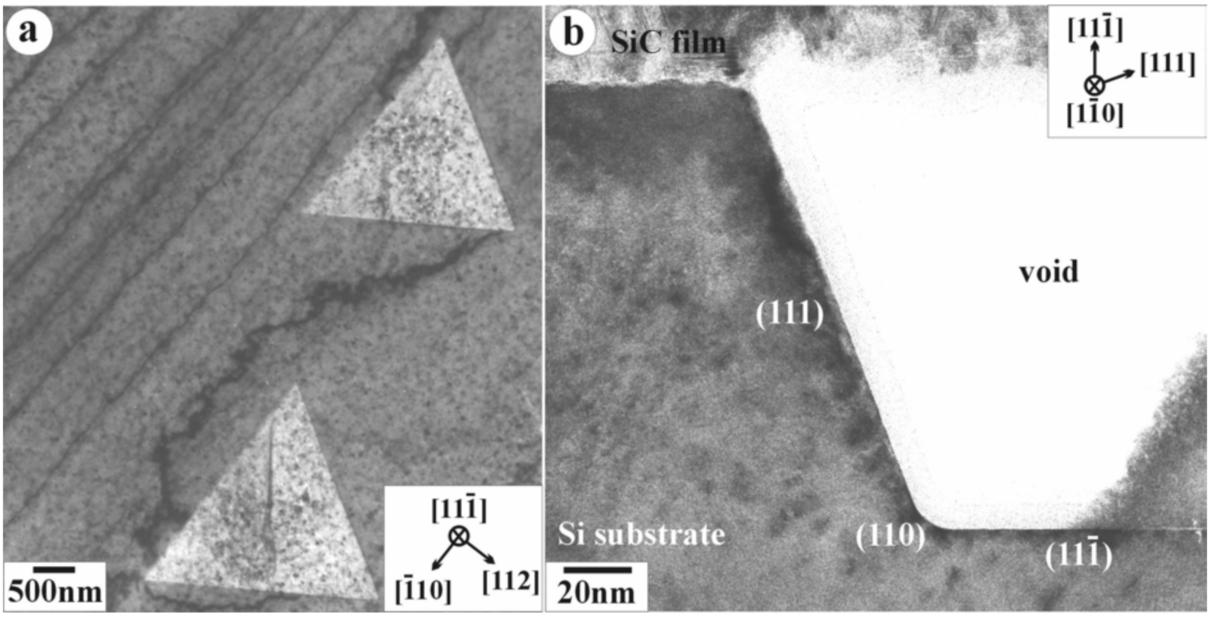

Fig. 3. (a) Plan-view bright-field TEM image, obtained in the [111] zone of Si, and (b) high-resolution cross-sectional bright field TEM image, viewing along the [1$\bar{1}$0] zone axis of Si, showing the shape of a interfacial triangular void beneath the SiC film in the SiC/Si(111) specimen grown at 850°C substrate temperature (specimen type 1). In the plan-view direction (a) the perfect triangular void shape (bright features) is obviously seen. In the cross-sectional view (b) the primary {111} faceting (showing the angle of 70.53°) of the triangular void and the (110) truncation into the void (angle of 35.26° to the related {111} plane} is indexed.

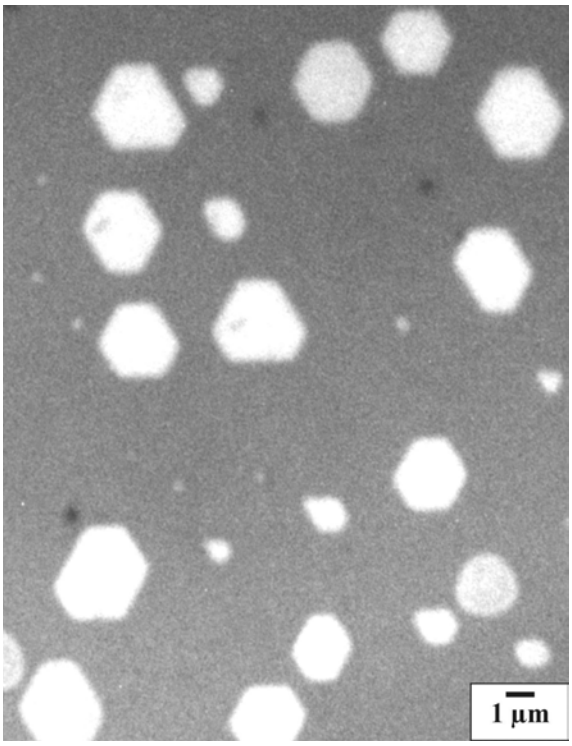

Fig. 4. Low-magnification optical micrograph in plan-view direction of the SiC layer on Si(111) substrate grown at 1050°C substrate temperature (specimen type 2) showing the new hexagonal void shape (bright features).

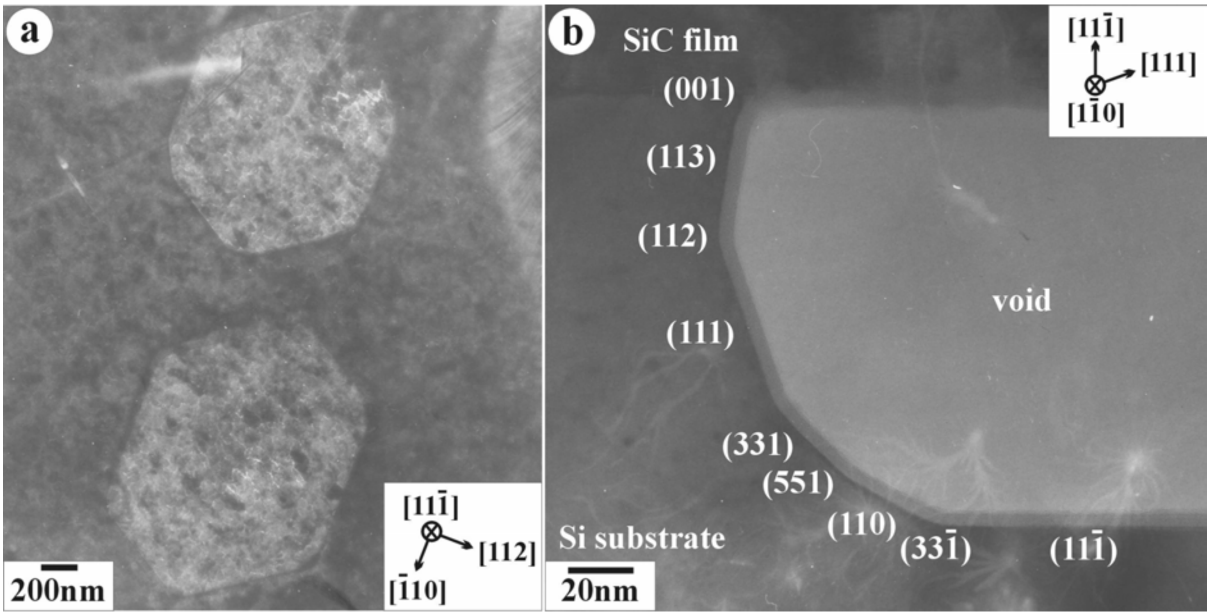

Fig. 5. (a) Plan-view bright-field TEM image, obtained in the [111] zone of Si, and (b) high-resolution cross-sectional bright field TEM image (zone axis close to $[1\bar{1}0]$ of Si) showing the shape of a interfacial hexagonal void underneath the SiC film on Si(111) at 1050°C substrate temperature (specimen type 2). In the plan-view direction (a) the hexagonal appearance of the void shape with truncations of the corners of the regular hexagon (bright features) is seen. In the cross-sectional TEM image (b) the facets of the hexagonal void in the $[1\bar{1}0]$ zone are indexed. In addition to the facets of the triangular voids, {111} and {110} (see Figure 3b), lattice planes with higher surface energy are formed.

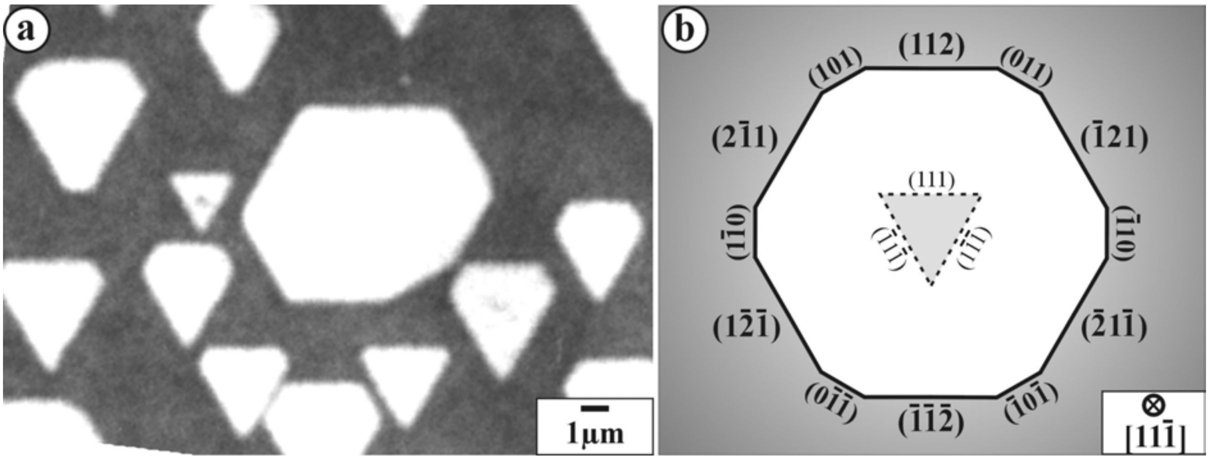

Fig. 6. (a) Low-magnification optical micrograph in plan-view direction of the SiC layer on Si(111) substrate grown at 1050°C substrate temperature (specimen type 2, see also Fig. 4) showing bright small triangular voids (originated from the {111} lattice planes) which get more and more truncations with increasing void size up to the appearance of the large hexagonal shaped voids. (b) Schematic drawing (in a $\langle 111 \rangle$ zone of Si) of a hexagonal shaped void (black solid line) as a regular hexagon primary limited by the {112} facets (angle of 60° between them) and truncated by {110} facets (angle of 30° to the respective {112}). In the middle of the hexagon is a small triangular void with the primary {111} facets (doted lines as the traces to the (111) plane) as the first step of the creation of a hexagonal void by increasing the void size and truncating by facets with higher surface energy.