Growth Mechanism of Si-Faceted Dendrites

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(Received 23 January 2008; revised manuscript received 26 May 2008; published 31 July 2008)

The growth mechanism of Si-faceted dendrite was studied using an *in situ* observational technique. We directly observed the growth processes of Si-faceted dendrites from Si melts. It is found that triangular corners with an angle of 60° are formed at the dendrite tip. We present an original growth model for faceted dendrites based on the experimental evidence. The model fully explains the growth process of faceted dendrites.

DOI: 10.1103/PhysRevLett.101.055503 PACS numbers: 81.10.Aj, 64.70.dg, 68.35.bg, 81.10.Fq

Dendrite crystals grow during crystallization from a liquid or vapor phase in almost all materials containing metals, semiconductors, oxides, and organic materials. In particular, twin-related dendrites of Si or Ge, which are the so-called "faceted dendrites," have attracted much attention from both scientific and technological viewpoints due to their unique crystal structures. The surface of the dendrite is bounded by {111} habit planes, and at least two parallel twins exist at the center of the dendrite [1–12]. It is also known that the growth rate of a faceted dendrite is larger than equiaxed grains [12,13]. Such features can be applied in technologies for growing thin Si ribbon crystals [6,7] and polycrystalline Si ingots [13] for solar cells. The growth model of faceted dendrites was proposed in 1960 [3,4]. Nowadays, the model has been widely accepted [14,15] and is applicable to a variety of materials [16–24]. However, the actual growth behavior has remained a mystery because of the lack of direct evidence.

In this Letter, we show how faceted dendrites grow from Si melts. We succeeded in observing the growth processes of a faceted dendrite directly. We show that triangular corners with an angle of 60° are formed at the dendrite tip during its growth process, in contrast to the previously presented growth model. We present an original model based on our experimental evidence.

We used a newly developed *in situ* observation system based on our previous system, which consisted of a furnace and a microscope [25]. Wafer tips of high-purity Si (non-doped, better than 7N) were set in a quartz crucible inside the furnace in an ultrahigh-purity argon gas atmosphere. After melting, the sample was rapidly cooled, leading to the growth of a faceted dendrite. Images of the sample during melting and crystallization were monitored and recorded on videotapes.

Figure 1(a) shows the typical growth behavior of a Si-faceted dendrite. The crystal is growing from left to right in the images. The faceted dendrite grew faster than the rest of the crystal. The dendrite continuously propagated in both the direction of rapid growth and the direction perpendicular to the rapid growth. We performed crystallographic orientation analysis of a small area at the center of the dendrite [indicated by the small box in the right image in Fig. 1(a)] after crystallization by the electron backscattering diffraction pattern (EBSP) method and confirmed that the rapid-growth direction of the faceted dendrite was ⟨112⟩ and that the direction of the side growth was ⟨111⟩, as schematically shown in Fig. 1. We also confirmed the existence of two {111} parallel twins at the center of the dendrite [Fig. 1(b)]. Note that, although the faceted dendrite grew not only in the rapid-growth direction of ⟨112⟩ but also in the ⟨111⟩ direction perpendicular to the rapid-growth direction, in contrast with widely accepted growth models [3,4] which foresee a negligible growth in the direction of the {111} planes. In Fig. 1(a), it is in fact shown that growth occurs also in the direction parallel to the {111} planes. To obtain more information on the growth

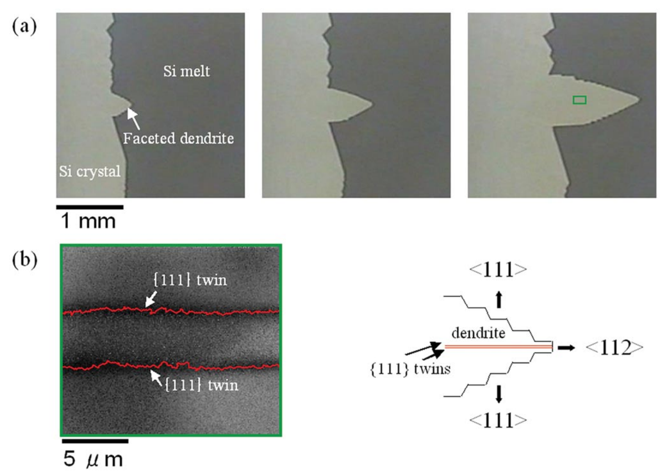

FIG. 1 (color). (a) Typical growth behavior of a Si-faceted dendrite. The dendrite grows faster than the rest of the crystal. Note that the dendrite propagates not only in the rapid-growth direction but also perpendicular to the rapid-growth direction. (b) Result of EBSP analysis at the center of the dendrite indicated by the green box in the right image in (a). Two {111} parallel twins are observed. The orientation relationship in the faceted dendrite is schematically summarized.

behavior of the faceted dendrite, we next attempted to observe the growth process perpendicular to the {111} twin planes. Figure 2(a) shows the experimental procedure. A piece of Si {111} wafer was set in a crucible, and the sample was carefully heated to melt in such a way that an unmelted part remained. Then the sample was cooled rapidly to promote dendrite growth. For comparison, another sample was cooled slowly so as not to induce dendrite growth. Crystal growth started from the unmelted "seed" wafer. In this experiment, when the dendrite appears during crystal growth, the {111} parallel twins are generated parallel to the {111} crystal surface. The direction of observation of the growing dendrite is schematically summarized in Fig. 2(a). Figure 2(b) shows the growth process of the {111} crystal during slow cooling when no twins are formed. A hexagonal crystal with 120° corners grows, which is the equilibrium shape of Si crystal

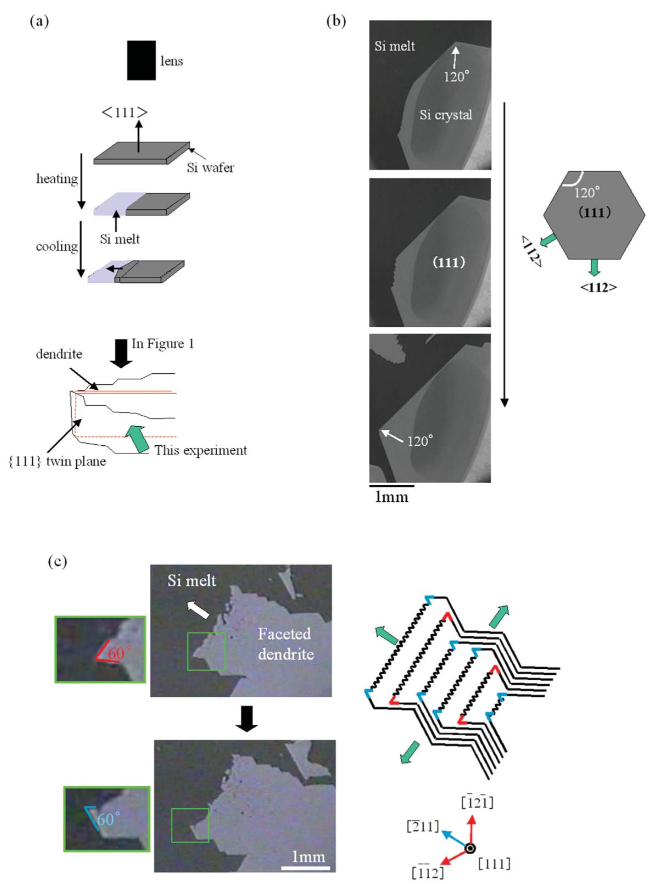

FIG. 2 (color). (a) Experimental procedure for observing the growth behavior of a faceted dendrite perpendicular to the {111} twins in the dendrite. The direction of observation of the growing dendrite is schematically shown. (b) Growth behavior of the {111} crystal with no twins. 120° corners are formed in the equilibrium shape. (c) Growth behavior of a Si-faceted dendrite observed perpendicular to the {111} twins. Note that a triangular corner of angle 60° is formed at the growth tip and that the direction of the corner changes with growth. The growth processes are schematically shown.

[3]. On the other hand, when the sample was cooled rapidly, a faceted dendrite developed [Fig. 2(c)]. We confirmed the existence of two parallel twins by analyzing a cross section cut perpendicular to the direction of rapid growth of the faceted dendrite after crystallization. The shape and growth behavior of the faceted dendrite were markedly different from those of the crystal with no twins. Note that triangular corners with an angle of 60° were formed at the tip of the dendrite and also that the direction of the corners alternately changed from outward to forward to the direction of growth, as highlighted in Fig. 2(c). Such a triangular corner is not formed in the widely accepted model of Hamilton and Seidensticker [3]. We thus obtained three important facts for the growth behavior of faceted dendrites: (1) A faceted dendrite can propagate in the ⟨111⟩ direction, which is perpendicular to the rapid-growth direction of ⟨112⟩, (2) triangular corners with an angle of 60° are formed at the tip of the faceted dendrite, and (3) the direction of the 60° corners changes during growth.

We here review the growth of the Si crystal with one and two twins according to the explanation of Hamilton and Seidensticker [3]. It is well known that {111} habit planes appear on the crystal surface during the crystallization of Si [11,14]. Figure 3(a) shows the equilibrium form of the crystal with one twin, which is bounded by {111} planes. Now we consider the situation that the crystal is growing in one direction for the sake of simplicity. One reentrant corner with an external angle of 141° (type I) appears at the growth surface. Nucleation readily occurs at the reentrant corner compared with {111} flat surfaces [3,4,11]. Therefore, the crystal rapidly grows at the reentrant corner, and a triangular crystal with a 60° corner is finally formed. Rapid growth has ceased at this time due to the disappearance of the reentrant corner. This is why the faceted dendrite does not appear when the crystal has only one twin. Next we explain the growth model of a crystal with two parallel twins presented by Hamilton and Seidensticker [3], which corresponds to the widely accepted growth model of a faceted dendrite. Figure 3(b) shows a two-twin crystal bounded by {111} habit planes. They assumed that crystal growth on the {111} flat surface hardly occurred. Rapid growth occurs at the reentrant type I corner, similar to that in the crystal with one twin. The new layer forms a new reentrant corner with an angle of 109.5° at the next twin, indicated as type II in the third figure. Hamilton and Seidensticker considered that nucleation events also occur at this type II corner. Thus, the creation of a type II corner allows the continuous propagation of the crystal in the lateral direction before the type I corner disappears, in contrast to the crystal with only one twin. Most important in their model, the reentrant type I corner does not disappear during dendrite growth, which means that no triangular corners appear at the tip of the growing dendrite. However, the model is not in agreement with our experimental results.

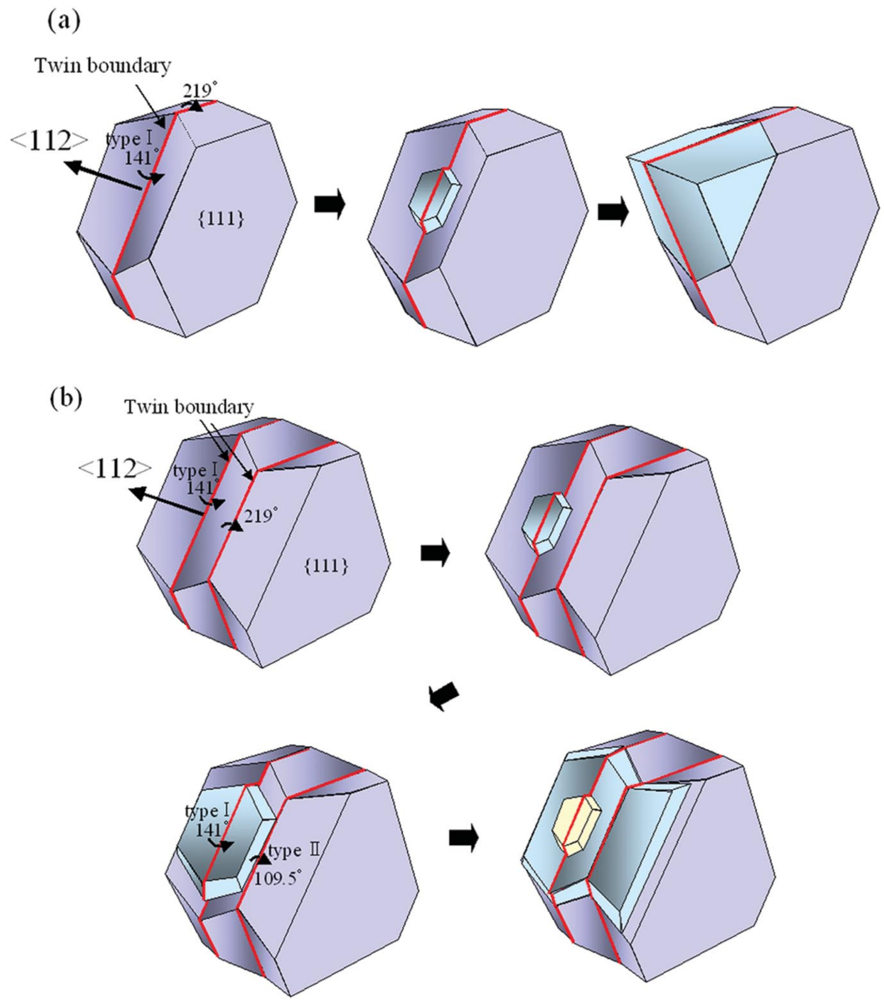

FIG. 3 (color). (a) Schematic images of growth of a crystal with one twin. The crystal is bounded by {111} habit planes. It is considered that the crystal is growing in one direction for the sake of simplicity. A reentrant corner of angle 141° (type I) appears at the growth surface. Rapid growth occurs at the corner until a triangular corner is formed. Continuous propagation was not considered to readily occur because crystal growth on the {111} flat plane did not seem to occur [3]. (b) Schematic images of the growth of a crystal with two twins, which was proposed by Hamilton and Seidensticker [3]. They assumed that nucleation events easily occurred at the reentrant type I corner and that crystal growth on the {111} flat surface was difficult. Nucleation at the type I corner leads to the formation of a new reentrant corner of angle 109.5°, marked type II (shown in the third image). They considered that nucleation also occurred at the type II corner, which permitted continuous propagation of the crystal in the lateral direction before the type I corner disappeared (right). Importantly, no triangular corner is formed during dendrite growth in their model.

Here we present an original growth model of a faceted dendrite in Fig. 4 based on our experimental evidence. In the explanation, the two twins are distinguished by labeling them twin$_1$ and twin$_2$ [Fig. 4(a)]. Rapid growth at the type I corner leads to the formation of a triangular corner with an angle of 60° at the growth tip of the faceted dendrite [Figs. 4(b) and 4(c)], which was observed in our experiment. Crystal growth can continue on the {111} flat surface although the rapid growth is inhibited due to the disappearance of the reentrant corner. In the previous model, crystal growth on the {111} flat surface seemed to hardly occur. However, we observed that significant crystal growth occurred on the {111} surface in the undercooled melt [shown in Fig. 2(a)]. After propagation of the crystal, note that two type I corners are newly formed on the growth surface at twin$_2$ [Fig. 4(d)]. Thus, rapid growth occurs there again, and triangular corners with an angle of 60° are formed in the same manner as before [Figs. 4(e) and 4(f)]. The direction of the 60° corner has been changed from Fig. 4(d) to Fig. 4(f), which is in agreement with our experimental results. Crystal growth is promoted on the {111} flat surface again, leading to the formation of a new reentrant type I corner at twin$_1$ [Fig. 4(g)]. The faceted dendrite continues to grow by repeating the same processes and forming the 60° corner at the growth tip. In the previously presented growth models [3,4], they assumed that the crystal propagated laterally owing to the formation of the type II corner at twin$_2$ and that crystal growth on the {111} flat surface was negligible. In such processes, the faceted dendrite propagates only in the rapid-growth direction. However, we observed that the faceted dendrite grew not only in the direction of rapid growth but also perpendicular to that direction, which means that crystal growth on the {111} flat surface readily occurs. The significance of the existence of two twins is not the formation of type II corners but the alternate formation of type I corners at each twin. Our model fully explains the experimental evidence of the growth behavior of the faceted dendrite. Furthermore, the twin-related growth model can be applied to not only Si but also other faceted materials.

In summary, we have investigated the growth behavior of Si-faceted dendrite using an *in situ* observation technique. Triangular corners with an angle of 60° are formed at the tip of the faceted dendrite, and the direction of the 60° corners changes during growth. We have presented an original growth model for a faceted dendrite based on the

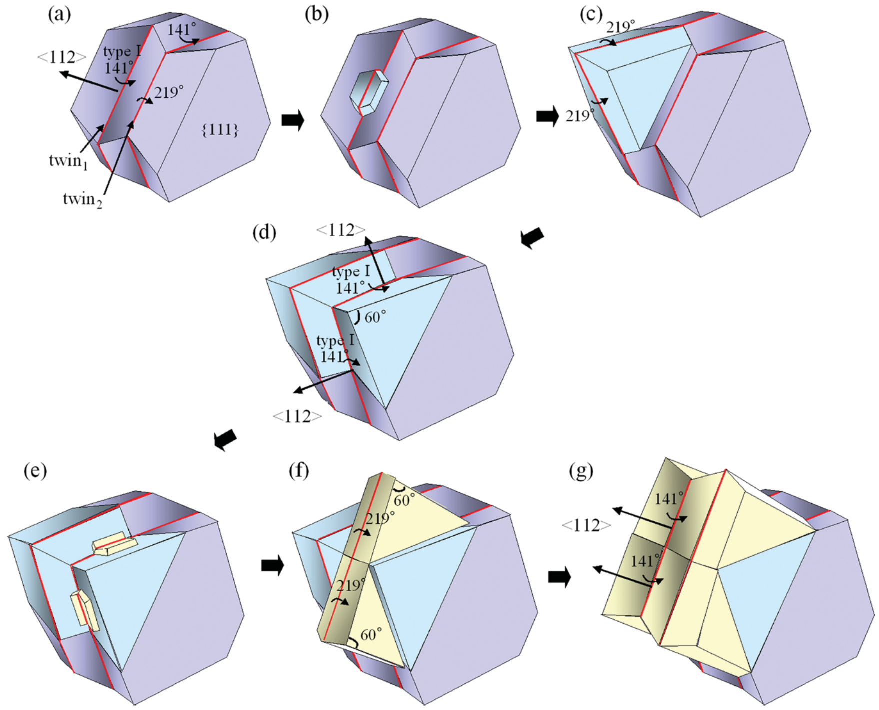

FIG. 4 (color). (a) Equilibrium form of a crystal with two twins, which is bounded by {111} habit planes, similar to that shown in Fig. 3(b). (b)–(c) A triangular corner is formed due to the rapid growth at the type I corner at twin$_1$. Crystal growth can continue on the {111} flat surface, although the rapid growth is inhibited because of the disappearance of the type I corner. Such growth on the {111} surface was noted by *in situ* observation, shown in Fig. 2(a). (d) When the triangular crystal propagates across twin$_2$, two type I corners are newly formed at twin$_2$. (e)–(f) Rapid growth occurs at the two type I corners again, and a triangular corner is formed. (g) After propagation of the crystal, a type I corner is formed at twin$_1$. The faceted dendrite continues to grow by repeating the process from (a) to (g). This model is fully consistent with the experimental evidence.

experimental evidence. The model fully explains the growth process of a faceted dendrite and also explains the role of parallel twins for the growth.

The authors thank Dr. G. Sazaki and Y. Nose for helpful discussions. This work was partially supported by the New Energy and Industrial Technology Development Organization (NEDO) and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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