Morphologies of solid-liquid interface and surface steps during rapid growth of BaB_2O_4 single crystals

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The evolution of solid-liquid interface during BBO single crystal growth was studied by the differential interference microscopy. And the step morphology on (0001) surface of the as-grown crystal was observed by the atomic force microscopy as well. It was found that the transition from a flat solid-liquid interface to a skeletal shape will occur in case of rapid growth. However, AFM images of surface steps revealed morphology differences correlated with crystallographic directions. The steps advancing along $\langle 10\bar{1}0 \rangle$ direction form the step flow, whereas those steps propagating along $\langle 01\bar{1}0 \rangle$ direction shape into step segments. Measurements of step heights by AFM indicated that it is the high anisotropy of the dimension of growth unit and step bunching due to the enlargement of concentration difference along the surface that results in the anisotropy of step morphologies.

crystal growth, morphological instability, growth step, AFM observation

1 Introduction

Generally single crystals are obtained with very low growth rates, which inevitably increases the cost. Recently scientists are endeavoring to promote the growth rate to reduce the cost of growth for commercial demand. However, the physical properties of the as-grown crystal will become deteriorated if the growth rate is high^[1]. So the improvement of rapid growth technique is very important for the wide use of single crystals, and nowadays, much effort has been made. For example, the growth habit of crystal, diffusion and convection effect in the melt, and the phenomenon of heat and mass transfer during rapid crystal growth have been the focuses of many researches^[2–6]. Unfortunately, up to now, in nearly no case the properties will not be greatly deteriorated by rapid growth^[7,8].

The main difficulty that hinders the improvement of rapid growth technique is the incompre-

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hension about the growth mechanism with very fast growing rate. The enhancement of diffusion and decrease of convection in heat and mass transfer for rapid growth will result in the variation of crystal growth mechanisms and the consequent variation of microstructure^[9]. Then the deep understanding of crystal mechanism as well as the evolution of microstructure is important for the improvement of rapid growth technique, which, however, has been seldom reported. Furthermore, the decrease of supercooling due to the decrease of convection^[10] can lead to the formation of defects, such as inclusions and twinned crystals. This is also correlated with the variation of crystal growth mechanisms.

In recent years, atomic force microscopy (AFM) has been proved an effective technique for investigation of the growth mechanism and surface morphologies of single crystals with a spatial resolution of nanometer scale^[11]. The aim of this paper is to deeply investigate the surface morphology of BBO single crystal by AFM, based on the optical observation of growing processes. The focus is concentrated on the instability of step morphology on the surface, which is an attempt of deeply understanding the crystal growth mechanism of rapid growth.

2 Experiments

The growth device was a loop-shaped heater with a diameter of 1.6 mm, which was made of Pt wire ($\phi 0.2$ mm). The heater was placed horizontally, and its temperature was controlled by a combination of a stabilized DC power supply (YJ-69) and a thyristor voltage regulator (ZK-50). A Pt-10%Rh thermocouple ($\phi 0.08$ mm) was applied to measuring the temperature. Temperature fluctuations of less than $\pm 2^\circ\text{C}$ at 1100°C were guaranteed by this arrangement.

The mixture of $\text{Li}_2\text{B}_4\text{O}_7$ and BaB_2O_4 (70wt%) was melted and suspended on the Pt loop with the temperature of 855°C . At first, a tinny crystal seed was formed in the center of the melt by adjusting the amount of the liquid and the temperature. Then the temperature was decreased and a supercooling was given, which allowed the crystal to grow in two dimensions. The growth rate was controlled by the supercooling of the melt. The interfacial morphology and the crystal shape were observed in real time during the growth by a differential interference microscope (BH-2, Olympus)^[12]. Finally, the surface morphology of the as-grown crystal was *ex-situ* observed by an atomic force microscopy system (SPI3800V&SPA300HV, Seiko II) when it was cooled to room temperature.

3 Results and discussion

3.1 Effect of growth rate on crystal shape

The crystal morphologies observed by differential interference microscopy are shown in Figure 1. The growth rate V in Figure 1(a) is $10\ \mu\text{m/s}$ and in Figure 1(b) is $80\ \mu\text{m/s}$. It can be clearly seen that the solid-liquid interface is flat when the growth rate is low, where a hexagonal shape can be obviously observed (Figure 1(a)). However, morphological instability occurs in the process of rapid growth. As seen from Figure 1(b), the interface is deformed and the crystal presents a shape of snowflake. In general, this kind of interface with the center region depressed is called skeletal shape^[13]. Usually, morphological instability of growing interface may introduce growth imperfections such as inclusions, twins, grain boundaries and dislocations, which must be a strong attraction to the researchers. In the following, our focus will be the investigation of surface mor-

Figure 1 Morphologies of BBO single crystal observed by differential interference microscopy. (a) Growth rate is 10 $\mu\text{m/s}$; (b) growth rate is 80 $\mu\text{m/s}$.

phologies obtained by rapid growth.

Figure 2 schematically illustrates how the skeletal shape is formed. At the initial stage of the growth, the shape of growing crystal is hexagonal, as shown in Figure 2(a). However, the $\{10\bar{1}0\}$ faces will disappear with the crystal size increasing due to its faster moving rate. Thus the $\{\bar{1}010\}$ faces distinctly show, which leads to the shape of quasi hexagon (Figure 2(b)). When the crystal grows even larger, the central region of the growing face is depressed and the skeletal shape is formed, as can be seen in Figure 2(c). The variation of growth units' incorporation into the crystal is responsible for the habit difference of the faces with differing indexes^[14], whereas the skeletal shape is possibly caused by the extremely non-uniform supersaturation in front of the interface owing to the rapid growth rate. This can be interpreted when the transport phenomenon is taken into account. Generally, the melt convection can enhance the heat and mass transfer. So, the reduction of convection during rapid growth will result in the non-uniformity of the supersaturation.

Figure 2 Schematic of the shape evolution during rapid growth of BBO single crystal.

By optical microscopy only the exterior shape of the crystal can be observed. And the micro-structure of the surface on the scale of sub-micron is difficult to be identified by this method, which, however, can be realized by AFM. In the following, the surface morphology of the as-grown BBO crystal will be analyzed in detail by AFM, the aim of which is to investigate the physical mechanism of rapid growth.

3.2 AFM observation of BBO (0001) surface morphology

The (0001) surface was divided into several regions as shown in Figure 2 according to the sym-

metry of the crystal structure. Here, region *A* refers to the area whose exterior boundary is $\{\bar{1}0\bar{1}0\}$ faces, while region *B* is bounded by $\{10\bar{1}0\}$ faces. The AFM images of (0001) surface are shown in Figure 3.

Figure 3 AFM images of BBO (0001) surface for different regions as indicated by Figure 2. (a)–(c) are the morphologies of region *A*, *B* and their boundary regions, respectively.

Figure 3(a) shows the AFM morphology of region *A*, where the step flow is discerned. The steps propagate along the $\langle 10\bar{1}0 \rangle$ crystallographic direction, and the orientation of the step flow is in $\langle 12\bar{3}0 \rangle$ direction. In present experiment, steps usually originate from the edge of the growing interface (namely the boundary of region *A* and *B*) and propagate to the face center. This is driven by the higher solute concentration at the face edges, where more growing species are supplied^[15]. It means that the edges of the face are the sources of steps. In addition, steps in region *A* become rough when approaching the face center, which is illustrated in the bottom-right part of Figure 3(a). The roughening of steps is mainly caused by step bunching which has great effect on the interracial morphologies.

In contrast to the morphology of step flow in region *A*, some instable step segments are found in region *B*, as shown in Figure 3(b). Here, the direction of moving interface is along $\langle 21\bar{3}0 \rangle$. The length of step segment and the area of the terrace become smaller with the distance along the growth orientation. Similarly, step segments are also the result of step bunching.

One more interesting phenomenon is that some straight steps are found by AFM at the boundary of region *A* and *B*, as shown in Figure 3(c), which is not visible in the optical method. These straight steps move in the plane of $\{2\bar{1}10\}$ faces, and they are the originally generated steps. In other words, they are steps of the sources. Here, we call the boundary of region *A* and *B* region *C* in order to conveniently describe it. The AFM images of region *A*, *B* and *C* are illustrated simultaneously in Figure 4 in a perspective view. Because the faces $\{2\bar{1}10\}$ move fastest, the straight steps on them will disappear with growth continuously proceeding. Since the steps in regions *A* and *B* both develop from the steps in region *C*, one can conclude that the morphological difference of region *A* and *B* is not related to the difference of step sources. Furthermore, there are no screw dislocations or any two-dimensional nucleation of islands observed on (0001) surface, so it can be doubtlessly concluded that BBO crystals grow through a step flow mechanism for the present case.

3.3 Measurements of step height on (0001) surface of BBO single crystal

The measurement of surface height *z* normal to the face allows us to quantitatively characterize the

Figure 4 A perspective view of BBO (0001) face morphology by AFM. *A* and *B* refer to the regions signed in Figure 2, and *C* is the boundary region of *A* and *B*.

surface profile, $z(x)$, along the coordinate x parallel to the orientation of the step flow. Figure 5 shows the variation of z versus x . It demonstrates that the surface morphology is unsteady with a staircase structure observed. This hints that the surface is a vicinal face very close to (0001). The ratio of step height to step spacing indicates only a slight misorientation from the adjacent singular face. However, the slopes of the vicinal surface are different for the three regions. The misorientated angles for the three regions are $\varphi_A = 2.20^\circ$, $\varphi_B = 0.64^\circ$ and $\varphi_C = 0.11^\circ$, respectively. In region *C*, the height of steps is the smallest, which is only 5 nm on average. This is about the height of four crystal cells. The average spacing of the step flow is about $2.8 \mu\text{m}$. The step height in region *A* is the largest, which is up to 36 nm on average, nearly equal to the height of 28 cells. The step spacing is also the largest, which is about $6 \mu\text{m}$. In region *B*, the step height is 12 nm or so, and it is about the height of ten cells. The spacing is also the moderate, which is $4 \mu\text{m}$. It is noted that the height and spacing of the steps in region *B* are irregular due to the discontinuous step segments.

In general, the crystal growth is the process that the growth units are incorporated into the solid-liquid interface. In the melt of BBO, the basic growth unit is anionic coordination polyhedron growth units or their clusters^[14]. The dimension of the clusters is related to the melt/solution station

Figure 5 Cross-sectional profiles of the surface heights z along the direction of step flow (i.e. the direction of solid-liquid interface movement) by AFM. The subscripts in z mean the three regions *A*, *B* and *C*, respectively. x is the displacement along the direction of the step flow.

as well as the growth conditions^[16]. In effect, the step height is close to the dimension b of growth unit. So it can be clearly seen that the dimension of BBO growth unit is on the scale of nanometers. In the condition of rapid growth, the value of b differs in different directions. In the moving direction of the high-index interface, b is small; whereas in that of the low-index interface, it is large. This mainly results from the inhomogeneous surface supersaturation field due to rapid growth. It is the high anisotropy of the dimension of growth unit and step bunching due to the enlargement of concentration difference along the surface that results in the anisotropy of step morphologies.

The changes of growth rates have great influence on the entry of growth units to the crystal lattice, which can be exhibited by the step bunching. The step bunching is generally considered to be induced by the impurities in the melt/solution; however, the effect of impurities on step movement is selective. Steps are easily formed on $\{2\bar{1}10\}$ surface due to the abundance of supplied species. The area of such interface is comparatively small, so the steps are straight since the effect of impurities can be ignored. The supersaturation field varies slowly for $\{10\bar{1}0\}$ interface due to the low moving rate, and then a little coarseness is found on the steps. Step bunching is significant for $\{10\bar{1}0\}$ interface for its fast growth rate and large area. Consequently, step segments are the most observable morphologies. The effect of impurities on crystal growth is realized by influencing the characteristic of absorbed layers^[17,18].

Sangwal^[16] has pointed out that the bunching phenomenon and the dimension of growth units (i.e. step height) are highly anisotropic. This has been verified by our present observation result. Furthermore, step morphologies on the exposed surface are found also anisotropic.

4 Conclusions

Growth rate has significant effect on the shape of interface and surface morphologies as BBO single crystal grows from a high temperature solution. If the rate is low, the solid-liquid interface is flat and stable. Nevertheless, the morphology instability occurs and a skeletal shape is formed with a high rate. Investigation on surface morphology by AFM demonstrates that BBO single crystal grows by the mechanism of step flow. The average height of the steps is on the scale of nanometers. On the exposed (0001) surface, the step morphologies are different along different orientations. This is caused by the anisotropic of growth unit dimension and the step bunching induced by the inhomogeneous surface supersaturation field during rapid growth.

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