Transport Phenomena in Bulk Crystal Growth Processes

C. W. Lan
Department of Chemical Engineering
National Taiwan University
Taipei, Taiwan 10617, ROC

Transport phenomena play an important role in bulk crystal growth processes. During crystal growth, the control of the growth front and the dopant concentration is crucial to crystal quality. The growth feasibility is thus determined by the heat transfer controlling the interface convexity and by the mass transfer controlling the constitutional supercooling. Through numerical modeling, a thorough understanding of the growth processes is possible, which in turn is a key to process improvement. In this paper, we will summarize some work done in my laboratory, both numerical and experimental, to illustrate the importance of understanding the transport phenomena during crystal growth processes.

1. Introduction

Large-area single crystal substrates used in electronic or optoelectronic devices are mainly grown from the melt or solution. The phase change from liquid to solid is typical of transport processes involving heat and mass transfer as well as fluid flow and growth kinetics. Several bulk crystal growth processes, such as the Czochralski (Cz), the floating-zone (FZ), and the Bridgman methods, have been widely used. During crystal growth, the transport processes play an important role in the quality of the grown crystals [1]. The most well known factors affecting the crystal quality are the interface morphology and the constitutional supercooling. Especially, for the growth in an ampoule or a crucible, a concave interface often leads to a polycrystalline growth. The interface breakdown can be induced by the constitutional supercooling leading to a cellular growth. Therefore, the control of heat and mass transfer is important to the success of crystal growth. Other factors, such as the flow stability and dopant segregation, are important as well.

Under normal gravity condition, buoyancy convection is induced by both thermal and solutal gradients, and it appears in all of the growth processes. For the growth involving a free surface, the thermocapillary force could be important. Other driving forces such as the rotation and electromagnetic forces are important as well, and they are particularly interesting to crystal growers because they can be used to further control the growth. However, the analysis of the transport phenomena due to these forces is challenging because of the strong coupling of these forces. Nevertheless, with the advance of computing power, numerical simulation has become an effective tool to understand the interplay of the transport processes [2-4]. Accordingly, the effects of these driving forces can be studied in details. Such an understanding could provide a solid foundation for process control and improvement.

In this paper, the significance of the transport processes by different driving forces will be illustrated through several case studies. To save the space, only the FZ and horizontal Bridgman (HB) methods are discussed.

2. Floating-zone crystal growth

FZ crystal growth is unique in that it is a contamination-free process. Crystals with high purity can be grown or zone-refined by this process. However, in addition to the flow induced by the buoyancy force, thermocapillary flow due to the surface tension gradients at the free surface is important. Fig. 1(a) shows the observed flow pattern and interfaces of a stationary floating molten zone of sodium nitrate ($NaNO_3$); the convex interfaces are caused by the Marangoni convection. Such convex interfaces often cause problems during growth. The outer zone length is usually too long by the time the zone being melted through causing an unstable melt zone. An effective way to control the interface shapes is through rotation. Under 200 RPM counter rotation, the thermocapillary flow can be suppressed. As a result, flat interfaces are obtained, as shown in Fig. 1(b). Although such a high-speed rotation is not commonly used, its control for a short and stable zone is effective allowing the growth of a larger crystal [5].

Other driving forces can exist using when induction heating is used. The typical one is the Lorenz force due to electromagnetic fields for an electrically conducting melt. A sample calculation for the growth of TiC using an induction coil is shown in Fig. 2. In this case, rotation is not applied. However, as shown, the thermocapillary flow is suppressed by the convection due to the Lorenz force, and the resulted interfaces being similar to the high-speed rotation are extremely concave. The flow intensity increases with the decreasing coil frequency. The control of flow through the coil design or frequency is possible. However, for high temperature applications, radiation heat loss from the melt zone is very large. Therefore, a simple way to control the zone shape is though auxiliary heaters.

Another interesting issue for FZ crystal growth is the flow instability. Unstable flow induced due to the thermocapillary convection can cause growth striations. An effective way to suppress the unstable flow is to use a magnetic field. Axial magnetic field is quite typical. However, as shown in Fig. 3, the magnetic field suppresses the flow effectively in the core region. Near the free surface, the magnetic damping is not significant. Although the flow in the core region becomes very weak, the poor mixing of the dopant due to the weak flow can result in a large segregation.

In addition to the resistance and induction heatings, optical heating is also efficient to semiconductor and oxide materials. For a mirror furnace, the lamp configuration is a key factor to adjust thermal distribution. We have designed a double ellipsoid mirror furnace for FZ crystal growth of oxide crystals such as $Sr_xBa_{1-x}TiO_3$ and rutile. During the growth, the lamp orientation is placed horizontally, which provides the most uniform heating with the steepest thermal gradients. On the other hand, the vertical lamps provide a much less uniform heating, but the thermal gradients near the growth interface are significantly lower. Defocusing can be used to control the thermal gradients as well. Some computer simulation for the mirror furnace will also be illustrated.

3. Horizontal Bridgman crystal growth

The HB technique is a widely used method in the growth of III-V compound semiconductor crystals [6]. The modeling of the HB growth is challenging in that it is a three-dimensional (3D) free-boundary problem. Because the top surface is free to the environment, the thermocapillary flow can be induced as well. Furthermore, since the thermal gradients are mainly horizontal, the induced buoyancy flow in the melt is much stronger than that in a vertical configuration. Therefore, the interface deformation due to the flow can be significant. Fig. 4 shows the effect of flow modes on the isotherms and interface shape for GaAs in a PBN ampoule. As shown, the effect of buoyancy force is significant. The effect of Marangoni flow is important only near the free surface. As show from the top view of Fig. 4(c), since the flow is diverged outwards (perpendicular to the isotherms) at the free surface, the contact angle of the interface at the crucible becomes much smaller. Such a small contact angle is usually detrimental to single crystal growth. An effective way to control the interface is to provide a local cooling from the top surface near the growth interface, while insulating the crucible. With such a modification, an inversion of the interface shape is obtained [4].

Another example for the HB growth is illustrated for $NaNO_3$, as shown in Fig. 5. Fig. 5(a) is the observed flow pattern. A shown, two flow cells are located at two ends, respectively, because the thermal gradients are restricted there. Although we have attempted to increase the heating from below, the interface is still convex due to the convective heat transfer by the buoyancy and thermocapillary flows. The calculated flow fields are illustrated in Fig. 5(b) and the isotherms in Fig. 5(c). With such a convex interface, the growth is always polycrystalline. To obtain a convex interface, a local cooling is provided at the top interface by blowing air. Such a spot cooling is effective, and the growth interface becomes convex. As a result, the growth of a single crystal becomes much easier.

References

[1] G. Muller and A. Ostrogorsky, in D.J. Hurle (Ed.), Handbook of Crystal Growth, Vol. 2b, Growth Mechanisms and Dynamics, p.709.
[2] C. W. Lan and S. Kou, J. Crystal Growth, **114** (1991) 517.
[3] C. W. Lan, J. Crystal Growth, **169** (1996) 269.
[4] M.C. Liang and C. W. Lan, 180 (1997) 587.
[5] S. Kou and C.W. Lan, US Patent, No. 5,217,565.
[6] E. Monberg, in in D.J. Hurle (Ed.), Handbook of Crystal Growth, Vol. 2a, Basic Techniques, p.52.

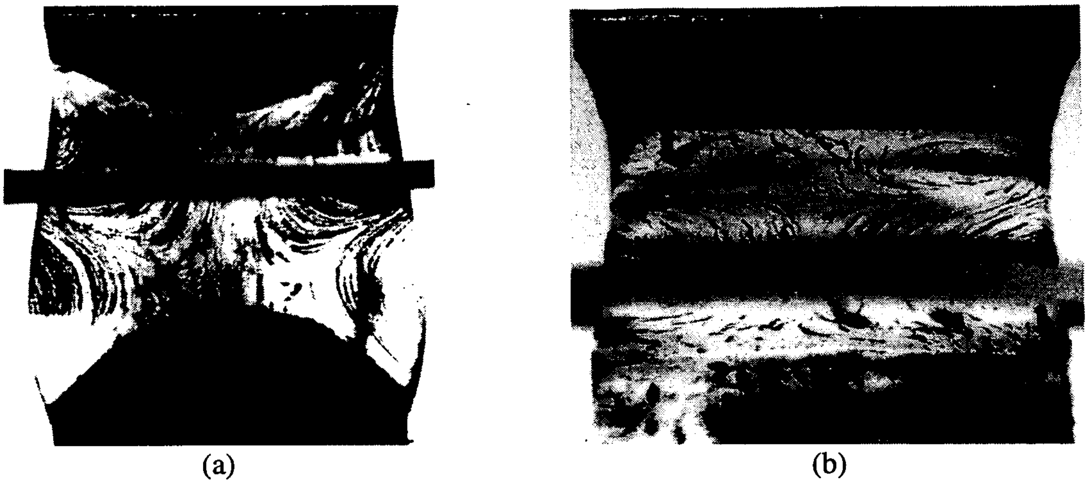
(a) (b)

Fig.1 Observed flow patterns and interface shapes for (a) stationary zone without rotation (4mm in diameter $NaNO_3$); (b) crystal growth under 200RPM counter rotation (6mm diameter).

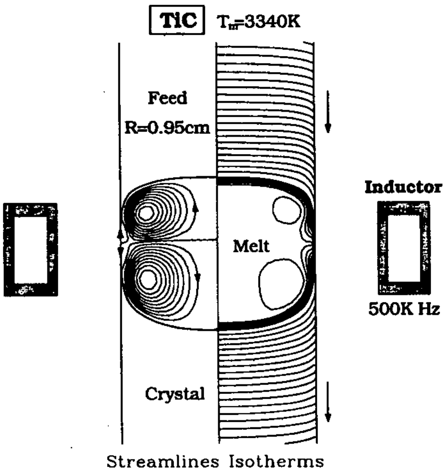

Fig.2 Flow and thermal fields and interface shapes of FZ growth TiC using induction heating.

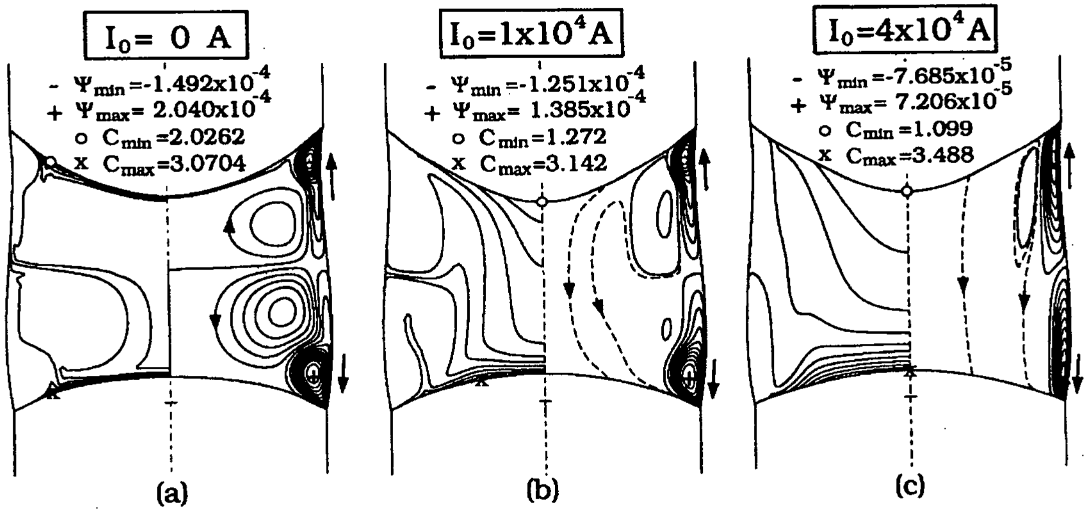

Fig.3 Dopant distribution and flow patterns in an axial magnetic field; (a) I_0=0 A; (b) 10^4A; (c) $4x10^4$ A.

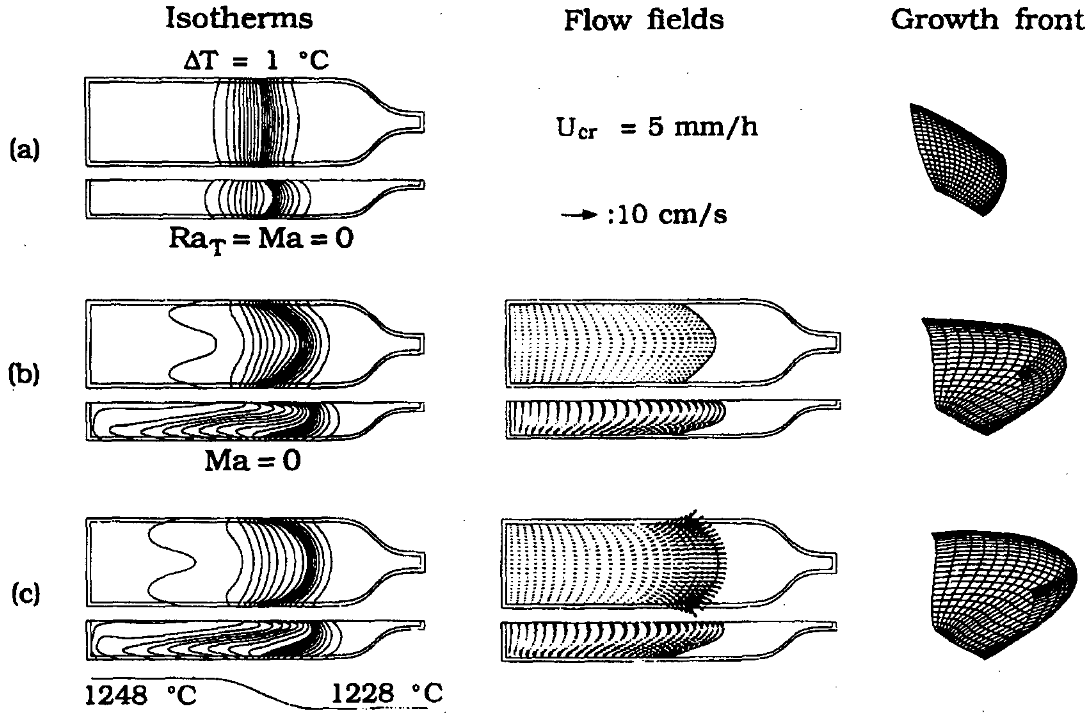

Fig.4 Effect of convection on the thermal and flow fields and interface shape: (a) conduction; (b) buoyancy convection; (c) buoyancy and thermocapillary convections.

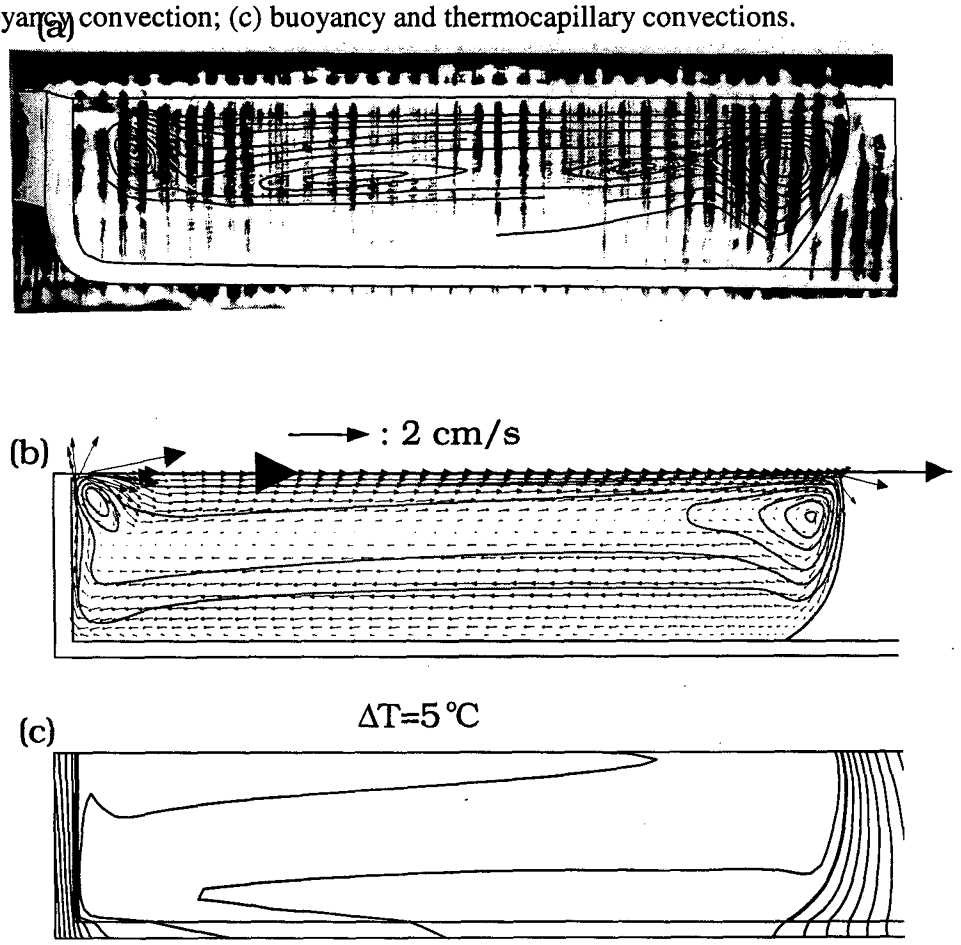

Fig.5 (a) Observed flow pattern for HB growth of sodium nitrate; (b) calculated streamlines; (c) calculated isotherms.