Homogeneous Nucleation of Fine Cd and Zn Crystals Grown by VLS (Vapor-Liquid-Solid) Mechanism*

By Hisami Yumoto**, Yoshihiko Gotoh** and Naohiro Igata**

Cd or Zn fine crystals having the shape of whiskers or polyhedrons were grown by a physical vapor deposition method. Their growth mechanism was VLS (Vapor-Liquid-Solid) growth. The nucleation of the crystal growth occurred in the eutectic alloy droplet (homogeneous nucleation) and not at the interface between the droplet and a glass substrate (heterogeneous nucleation). The purpose of the present study is to explain this reason.

In order to decide the nucleation type (homogeneous or heterogeneous), we introduced the parameter Y defined as $Y = \gamma_{SG} - (\gamma_{LG} + \gamma_{SL})$, where γ_{SG} , γ_{LG} and γ_{SL} are the interfacial tension between the crystal and the glass, between the liquid and the glass, and between the crystal and the liquid, respectively. When $Y > 0$, the nucleation type is homogeneous, and when $Y < 0$, it is heterogeneous.

In the case of VLS-grown Cd or Zn crystals, it was found from the data on the surface tension that the parameter Y was positive. Therefore, it was concluded that the nucleation type of the Cd or Zn crystals was homogeneous.

(Received June 1, 1989)

Keywords: cadmium, zinc, whisker, crystal nucleation, homogeneous nucleation, surface tension, crystal growth, vapor-liquid-solid growth, physical vapor deposition

I. Introduction

The applications of whiskers to composite materials have been considered. The growth mechanisms of the whiskers, however, have not been clarified enough. Only the VLS (vapor-liquid-solid) growth mechanism has been proved experimentally. Wagner and Ellis first found this mechanism, using Si semiconductor⁽¹⁾. This mechanism proceeds essentially as follows. When a Au particle is placed on a Si substrate, a Si-Au liquid alloy droplet is formed at a lower temperature than the melting points of Si and Au, because the Si-Au system is eutectic. In general, a liquid surface is regarded atomistically to be extremely rough, compared to a solid surface. A liquid surface is, therefore, a preferred site for deposition. When Si vapor is supplied to the Si substrate with the Si-Au liquid droplet, the

droplet takes in more Si vapor than the Si solid substrate does. The droplet becomes super-saturated with Si. The excess Si is precipitated at the interface between the substrate and the droplet, and the liquid droplet rises over the original substrate. Finally a whisker grows having the droplet on the tip. As Si is transported from vapor phase through liquid to solid and contributes to the crystal growth, this growth mechanism is called the VLS mechanism. The authors have studied the VLS mechanism of metals such as Cd and Zn⁽²⁾⁽³⁾. It was found from the results that nucleations occurred inside of eutectic droplets and did not appear at the interface between the substrate and the liquid droplet.

It is said, however, that the formation energy of the nucleation at the interface (heterogeneous nucleation) is lower than that of the nucleation in the liquid (homogeneous nucleation), therefore, heterogeneous nucleation prevails over homogeneous nucleation. In fact, there are many reports in favor of the occurrence of heterogeneous nucleation⁽⁴⁾. The latent heat of crystallization is released mostly through the glass substrate so that this is also favorable to heterogeneous nucleation.

* This paper was originally published in Japanese in J. Japan Inst. Metals, 53 (1989), 367.

** Department of Materials Science and Technology, Faculty of Industrial Science and Technology, The Science University of Tokyo, Noda, Chiba 278, Japan.

The above statements, however, contradict the authors' experimental results. The purpose of this study is to investigate of eutectic droplets and spherical crystals of Cd or Zn in the early stage of VLS growth, and to confirm that homogeneous nucleation dominates heterogeneous nucleation in the VLS growth of these crystals, and to prove that there exists the case in which homogeneous nucleation energetically prevails over heterogeneous nucleation.

II. Experimental

The middle part of Pyrex glass of 9 mm in outer diameter and about 100 mm in length was narrowed to 2–3 mm in outer diameter, so that the growth chamber consisted of the high and the low temperature zones as shown in Fig. 1. A Cd metal rod of 99.9999% purity was placed in the high temperature zone. Powder of an element (Bi or Sn) as an additional impurity, which forms a eutectic alloy droplet with Cd, was sprinkled inside the wall of the glass tube in the low temperature zone. The growth chamber was sealed in the vacuum of 10^{-3} Pa.

The high temperature zone was maintained at a constant temperature between 603 and 753 K, and the low temperature zone was kept at a constant temperature between 473 and 573 K. This made the temperature gradient as shown in Fig. 1. The Cd vapor was supplied by this temperature gradient from the high temperature zone to the low temperature zone, where the Cd vapor reacted with powdered Bi or Sn decreasing the melting point. When the supply of Cd vapor to the droplet continued, the concentration of Cd in the droplet was super-

saturated and the extra Cd precipitated. This is the VLS growth mechanism of Cd crystals.

The experimental procedure for Zn crystals was similar to that of Cd crystals. The growth conditions, however, were: $T_v=703\text{--}753\text{ K}$, $T_s=573\text{--}683\text{ K}$. The purity of a Zn rod was 99.999%, and the additional impurity was Bi or Sn.

Scanning electron microscopy (SEM) and X-ray microprobe analysis (XMA) were used for morphological observations and chemical analysis, respectively.

III. Results

When additional impurity powder of Bi was sprinkled on the inside wall of the low temperature zone and the Cd vapor was supplied there from the high temperature zone, the Cd–Bi liquid droplets were formed in the early stage of VLS growth.

Figure 2 shows SEM and X-ray images of Bi in a cross-section of Cd–Bi liquid droplets after quenching. White parts indicate the existence of Bi. The growth time of the droplets of Fig. 2(a) and (c) was 1.8 and 3.6 ks, respectively. We can see that a Cd ratio increased with increasing growth time. This means the Cd vapor from the high temperature zone was gradually taken in a droplet. The partial flat face of the lower hemispherical end was due to the contact with the glass wall during crystal growth.

Figure 3(a) and (b) show SEM image and X-ray image of Bi, respectively, of a Cd spherical crystal. This crystal started to grow by the VLS mechanism. It should be noticed that the Cd–Bi liquid film covered also the interface with the glass.

Figure 4 shows SEM and X-ray images of Bi on the bottom parts of three Cd spherical crystals at the early stage of VLS growth. We can see from Fig. 4(a) and (b) that the bottom part of a crystal was covered with the Cd–Bi liquid within a short growth time of 1.8–3.6 ks. When a Cd crystal is grown via its homogeneous nucleation in a Cd–Bi droplet, Bi impurity atoms are always excluded to the surroundings of the crystal. Hence, Bi exists on the surface of the Cd crystal. If a Cd crystal

Fig. 1 Schematic drawing of an experimental apparatus for VLS growth.

Fig. 2 Cross-section of two Cd-Bi quenched liquid droplets at the early stage of VLS growth. (a) SEM image, (b) X-ray image of Bi; growth condition is T_v (temperature of the sublimation zone)=644 K, T_s (temperature of the condensation zone)=553 K, t (growth time)=1.8 ks. (c) SEM image, (d) X-ray image of Bi; T_v =635 K, T_s =547 K, t =3.6 ks.

Fig. 3 Cross-section of a spherical Cd crystal grown by VLS mechanism from a Cd-Bi droplet; T_v =635 K, T_s =547 K, t =3.6 ks. (a) SEM image and (b) X-ray image of Bi.

Fig. 4 Bottom surfaces of three spherical Cd crystals grown by VLS mechanism from each Cd-Bi droplet. (a) SEM image, (b) X-ray image of Bi; $T_v=634$ K, $T_s=545$ K, $t=3.6$ ks. (c) composition image, (d) X-ray image of Bi; $T_v=634$ K, $T_s=545$ K, $t=3.6$ ks. (e) SEM image, (f) X-ray image of Bi; $T_v=637$ K, $T_s=494$ K, $t=14.4$ ks.

Fig. 5 (a) a hexagonal prismatic Cd crystal grown from a Cd-Bi droplet, having $\{0001\}$ basal planes and $\{10\bar{1}0\}$ prismatic planes; $T_v=649$ K, $T_s=459$ K, $t=18$ ks. (b) a Cd whisker grown from a Cd-Sn droplet, having a Cd-Sn eutectic alloy droplet on the tip; $T_v=643$ K, $T_s=523$ K, $t=18$ ks.

is grown by heterogeneous nucleation, Bi atoms cannot enter the interface between the glass and the crystal. Figure 4(a) and (b) show the existence of Bi around a Cd crystal during VLS growth. We can see the homogeneous nucleation occurred in the VLS growth. Therefore, it was reconfirmed that a Cd crystal was not grown by the heterogeneous nucleation which generated at the interface with the glass substrate, but it was grown by the homogeneous nucleation which occurred in a Cd-Bi droplet. This was confirmed also in other systems: Cd-Sn, Zn-Bi and Zn-Sn.

The amount of a Cd-Bi liquid was decreased during VLS growth, because the additional impurity of Bi was incorporated into a growing Cd crystal⁽²⁾. Figure 4(c)–(f) indicate that as the amount of the liquid was decreased by the incorporation of Bi atoms into a crystal, the liquid phase was not able to cover the bottom part after a long growth time of 3.6–14.4 ks. As a result, the solid surface of the bottom appeared.

Figure 5(a) shows a hexagonal prismatic Cd crystal grown from a Cd spherical crystal after the long growth time of 18ks. There was no liquid on any surfaces of the crystal nor at the interface with the glass substrate. When the additional impurity powder was changed from Bi to Sn and then the Cd vapor was supplied, a Cd whisker was grown as shown in Fig. 5(b). A Cd-Sn eutectic liquid existed on the tip of the whisker⁽³⁾.

Judging from the final morphology mentioned above, It seemed as if a Cd crystal had

grown directly from the interface with the glass substrate. The crystal at the early growth stage, however, was not grown from the interface with the substrate. It was concluded that nucleation of VLS growth was homogeneous in these eutectic systems.

IV. Discussion

If we neglect the anisotropy of crystal planes, the free energy change ΔG_{hom} of homogeneous nucleation with a spherical shape of radius r is given by

$$\Delta G_{\text{hom}} = -4/3\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{\text{SL}}, \quad (1)$$

where ΔG_v is volume free energy, γ_{SL} is the solid-liquid interfacial free energy (interfacial tension between solid and liquid)⁽⁵⁾.

Next we consider the occurrence of heterogeneous nucleation from a liquid. When θ is defined as the contact angle between the nucleus and the glass substrate, it is well known that Young's equation holds

$$\gamma_{\text{LG}} = \gamma_{\text{SG}} + \gamma_{\text{SL}} \cos \theta, \quad (2)$$

where γ_{LG} , γ_{SG} , and γ_{SL} are the liquid-glass, solid-glass and solid-liquid interfacial tensions, respectively. The volume of the heterogeneous nucleation is $\pi r^3(1 - \cos \theta)^2(2 + \cos \theta)/3$. The surface area of the nucleus contacting with the glass is $\pi(r \sin \theta)^2$ and the surface area contacting with the liquid is $2\pi r^2(1 - \cos \theta)$. The free energy change of the heterogeneous nucleation ΔG_{het} is given from these results as,

$$\begin{aligned} \Delta G_{\text{het}} = & -\pi r^3(1 - \cos \theta)^2(2 + \cos \theta)\Delta G_v/3 \\ & + \pi(r \sin \theta)^2(\gamma_{\text{SG}} - \gamma_{\text{LG}}) \\ & + 2\pi r^2(1 - \cos \theta)\gamma_{\text{SL}}. \end{aligned} \quad (3)$$

Substituting eqs. (1) and (2) into eq. (3), ΔG_{het} is rewritten⁽⁵⁾ as,

$$\Delta G_{\text{het}} = \Delta G_{\text{hom}}(2 + \cos \theta)(1 - \cos \theta)^2/4. \quad (3')$$

If Young's equation holds, then $|\cos \theta| \leq 1$ and $\Delta G_{\text{het}} \leq \Delta G_{\text{hom}}$. This shows that in general, heterogeneous nucleation occurs more easily than homogeneous nucleation. When $\cos \theta = -1$, ΔG_{het} is equal to ΔG_{hom} . This condition

is satisfied at the point contact ($\theta=180^\circ$) after the decrease in contact area between the crystal and the substrate. In this case, we find from eq. (2) that $\gamma_{SG}=\gamma_{LG}-\gamma_{SL}\cos\theta=\gamma_{LG}+\gamma_{SL}$. However, when $\gamma_{SG}>(\gamma_{LG}+\gamma_{SL})$, the crystal nucleus does not touch the substrate and homogeneous nucleation appears. Here Young's equation does not hold, so that eq. (3') derived from Young's equation also does not hold. Hence, we cannot always say that $\Delta G_{het}\leq\Delta G_{hom}$. It is concluded that when $Y=\gamma_{SG}-(\gamma_{LG}+\gamma_{SL})<0$, heterogeneous nucleation occurs preferentially and that when $Y>0$, homogeneous nucleation prevails⁽⁶⁾.

We will prove the condition that $Y>0$ holds in the eutectic systems investigated in this paper. When nucleation takes place in a vacuum, the crystal-glass interfacial tension γ_{SG} is written using Young's equation.

$$\gamma_{SG}=\gamma_G-\gamma_S\cos\omega, \quad (4)$$

where γ_G and γ_S are the surface tensions of the glass and the crystal, respectively, in a vacuum. ω is the contact angle of the embryo. Considering that the spherical cap of the liquid is mounted on a glass in a vacuum, we get, in the same way, the interfacial tension γ_{LG} between the liquid and the glass by the equation

$$\gamma_{LG}=\gamma_G-\gamma_L\cos\phi, \quad (5)$$

where γ_L is the surface tension of the liquid droplet in a vacuum, and ϕ is the contact angle of the droplet. Y is obtained from eqs. (4) and (5) as

$$\begin{aligned} Y &= \gamma_{SG} - (\gamma_{LG} + \gamma_{SL}) \\ &= \gamma_L\cos\phi - \gamma_S\cos\omega - \gamma_{SL}. \end{aligned} \quad (6)$$

Thus we do not need to know the value of the surface tension γ_G of the glass.

The surface tension γ_S of (0001) faces of Cd and Zn crystals is 0.561 N/m (483 K) and 0.809 N/m (623 K), respectively⁽⁷⁾⁽⁸⁾. However, γ_S required for Young's equation is not the surface tension of a (0001) face, but is the surface tension of a curved face, because the shape of nucleus on a glass substrate is hemispherical (or polyhedral). The surface tension of a curved face is regarded as the average of the surface tension of many high-index surfaces. When the axial ratio deviates from the ideal, the

anisotropy of the surface tension of hcp metal such as Cd or Zn becomes large⁽⁹⁾. In the cases of Cd and Zn, the ratio of the surface tensions of various faces to that of (0001) face is above two times⁽⁹⁾. The authors estimated from this result the surface tension γ_S of a curved face of Cd and Zn crystals was 1.22 N/m (483 K) and 1.618 N/m (623 K), respectively⁽⁸⁾.

The values of γ_L has rarely been obtained experimentally. Okajima *et al.*⁽¹⁰⁾ and Kucharski⁽¹¹⁾, however, obtained the values of γ_L in Cd-Sn and Zn-Bi systems, respectively, changing both temperature and concentration. Substituting their data into Young's equation, the authors have already calculated the interfacial tension γ_{SL} ⁽⁸⁾. These results are summarized in Table 1.

Finally we estimated from our experimental results that $\phi=130^\circ$, $\omega=140^\circ$ and calculated the values of Y from these data. These results are also added in Table 1. It is found from Table 1 that $Y>0$ holds both in the Cd-Sn and the Zn-Bi systems. Therefore, it is said that homogeneous nucleation occurred in these systems.

In general, the condition of $\gamma_{SG}<\gamma_{LG}+\gamma_{SL}$ holds in vapor growth, and nucleation takes place on some material (heterogeneous nucleation). However, the interfacial energy γ_{SL} between the liquid and the growing crystal is considered to be low in a solution-rich system such as eutectic, because the interfacial energy is decreased by the bonding of crystal atoms with solution atoms of the same element, compared to the bonding of crystal atoms with solvent atoms. If the crystal-glass interfacial energy γ_{SG} is large enough in this system, homogeneous nucleation occurs. On the other hand,

Table 1 Summary of the values of the surface tension, the interfacial tension and the parameter Y in the Cd-Sn and Zn-Bi systems.

System	Temperature (K)	γ_S (N/m)	γ_L (N/m)	γ_{SL} (N/m)	Y (N/m)
Cd-Sn	483	1.122	0.569	0.354	0.163
	553	1.104	0.599	0.354	0.126
Zn-Bi	623	1.618	0.480	0.950	0.036
	673	1.600	0.410	0.504	0.516

as the temperature of the growing part is kept constant during VLS growth, the latent heat of the crystallization is not released to any particular place, and is released towards all directions. This is also one factor to make ready the occurrence of homogeneous nucleation. For example, in the Bridgeman method heterogeneous nucleation appears at the low temperature zone of the Tammann tube during crystal growth. However, in VLS growth supersaturation is a rate determining factor, but the release of the latent heat does not determine the growth rate. Hence, it is regarded as crystal growth at a constant temperature without temperature gradient between the crystal and substrate. It seems from these reasons that nucleation at the early growth stage did not take place on the substrate, it occurred in a liquid.

V. Conclusion

It was shown theoretically that when $Y < 0$, heterogeneous nucleation is occurring on a substrate, and when $Y > 0$, homogeneous nucleation is taking place in a liquid. It was

confirmed that nucleation was homogeneous in the case of VLS grown Cd or Zn crystals from each eutectic droplet, because it satisfies the condition of $Y > 0$.

REFERENCES

- (1) R. S. Wagner and W. C. Ellis: *Trans. Met. Soc. AIME*, **233** (1965), 1053.
- (2) R. R. Hasiguti, H. Yumoto and Y. Kuriyama: *J. Cryst. Growth*, **52** (1981), 135.
- (3) H. Yumoto, R. R. Hasiguti and Y. Kuriyama: *J. Cryst. Growth*, **67** (1984), 383.
- (4) Edit. Comm. of Techn. Hand Book of Cryst.: *Technical Hand Book of Crystal*, Kyoritu Pub, Tokyo (1971), p. 227.
- (5) D. A. Porter and K. E. Easterling: *Phase Transforms in Metals and Alloys*, Van Nostrand Reinhold (UK), England, (1981), p. 186.
- (6) B. Chalmers: *Principles of Solidification*, John Wiley and Sons, New York, (1964).
- (7) R. Kern, G. Le Lay and J. J. Metois: *Current Topics in Materials Science*, Vol. 3, North-Holland, Amsterdam, (1980), p. 155.
- (8) H. Yumoto, R. R. Hasiguti, T. Watanabe and N. Igata: *J. Cryst. Growth*, **87** (1988), 1.
- (9) W. A. Miller, G. J. C. Carpenter and G. A. Chadwick: *Phil. Mag.*, **19** (1969), 305.
- (10) K. Okajima and H. Sakao: *Trans. JIM*, **23** (1982), 111.
- (11) M. Kucharski: *Arch. Hunt.*, **22** (1977), 181.