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Morphological instabilities of CBr_4 crystals during growth from vapors

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We have studied the surface morphological instabilities of CBr_4 crystals during growth from vapors. We have found that the crystal-growth morphologies depend not only on temperature and supersaturation, but also sensitively on the total pressure of inert gas in the vapor. With increasing inert gas pressure, at otherwise the same growth conditions, crystals with initially smooth surfaces first develop cellular patterns and then evolve into dendritic structures. Although these cellulars and dendrites bear morphological similarity with those found in melt and solution-growth experiments (i.e., the product $W^2R=\text{const}$, with W being either the width of a cellular or the radius of a dendritic tip, and R the growth rate at the corresponding solid front) the destabilizing mechanism appears to be more complex than that from bulk nutrient diffusion. We have found that the surface diffusion on the substrate also plays an important role in surface morphological instabilities in vapor crystal growth.

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When a crystal grows by diffusion-limited transport, its morphology may lose the stability of a smooth or faceted form and evolve into a cellular or dendritic structure. The morphological instability occurs most commonly in melt and solution growth (for reviews, see Refs. [1,2]). They also appear in vapor growth [3–5] and sometimes in thin-film expitaxial growth [6]. Recently, we have found that morphological instabilities can even occur during solid-solid (polymorphic) phase transitions [7].

For crystals that grow from liquid (melt or solution) the theory of morphological instability is well established [8,9]. In this situation, the surface stability depends mainly on the transport of heat and solute in the contacting liquid phase. In a vapor-growth system, however, the theory for morphological instability is not well understood. In comparison to the melt and solution growth, the diffusivity of growth species in the vapor is closely dependent on the total pressure and usually is several orders of magnitude larger than that in the melt and solution growth. Hence the diffusion-limited condition is less satisfied and anisotropic surface kinetics is more important in the vapor growth. This was clearly demonstrated by our recent results from computer simulations [10,11]. Moreover, in most vapor-growth systems, a substrate is used. This, of course, will influence the crystal-growth morphology.

Recently, in a series of experiments, we have systematically studied the growth morphologies of CBr_4 (monoclinic) crystals at temperatures that are slightly below the polymorphic transition (from monoclinic to face-centered cubic) point (~47 °C) [12]. We have found that crystals are mostly faceted and their morphologies are quite stable. By varying temperature and supersaturation, we have studied both thermal and kinetic surface roughening as precursor to the polymorphic transition. In this paper we report a quantitative study of the morphological instabilities of CBr_4 fcc crystals growing from vapors.

The experiment was conducted in a vapor-growth cell which was specially designed for *in situ* observation of the crystal morphology under well-defined conditions of temperature, supersaturation, and total pressure (for details, see Ref. [12]). The source temperature T_s and the crystal temperature T_c, and thus the supersaturation [12]$\sigma \sim \Delta T = T_s - T_c$, were controlled within a resolution of $\pm 0.01\,^\circ\text{C}$ (in the text, we use ΔT interchangeably for the σ). After introduction of the purified material, the growth cell was evacuated and backfilled to a desired inert gas pressure. Nucleation on the glass substrate was initiated via a sudden decrease of the T_c (increase of supersaturation). The growth crystals were monitored live with a Leitz optical microscope equipped with various long-working-distance objectives. The observed image was either directly recorded with an automatic camera or stored in high-resolution video and digital recorders with 1024×1024 pixels/screen and 256 gray levels. Stored images were selectively processed and quantified with a lateral resolution of $0.3\ \mu\text{m}$. The final images were photographed directly from the screen of a high-resolution monitor.

In comparison to the earlier experiments conducted in the monoclinic phase [12], the CBr_4 crystals at the high-temperature fcc phase are all round and no facets have been observed throughout our current experiments (although some faceted negative crystals had been claimed before [13]). Hence the stabilizing effect of anisotropic surface kinetics is relatively weak and diffusion-limited transport condition is more pronounced.

Results in Fig. 1 show crystal morphological evolution with increasing total pressure. Since the vapor pressure of CBr_4 at the current experiment temperature range is (only a few torrs [14]) much less than that of the inert gas pressure, the total pressure is actually the pressure of the inert gas. At a total pressure of $P=12$ torr, a smooth and round crystal surface is observed [Fig. 1(a)]. (Note that the white flat area at the center of the crystal is not a facet, it results from setting the microscope out of focus.) However, as the total pressure increases to $P=80$ torr [Fig. 1(b)] cellular patterns develop from the earlier

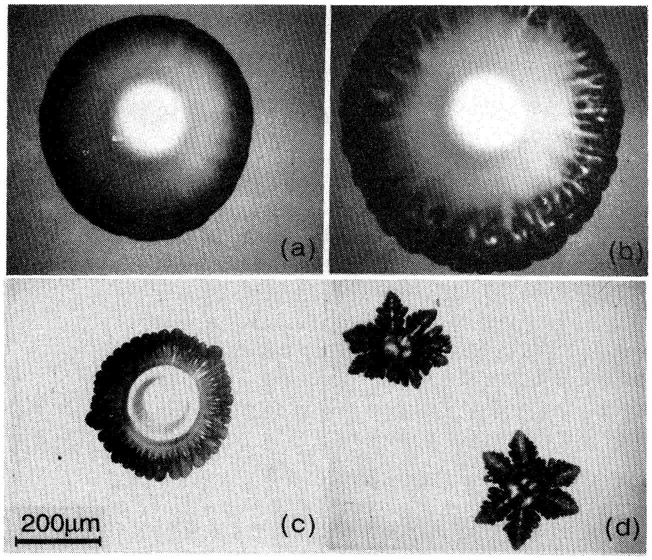

FIG. 1. Growth morphologies of CBr_4 crystals as a function of total (inert gas) pressure at $T_c = 50\,^\circ C$, $\Delta T = 0.21\,^\circ C$. (a) $P = 12.7$ torr; (b) $P = 80$ torr; (c) $P = 350$ torr; (d) $P = 1$ atm.

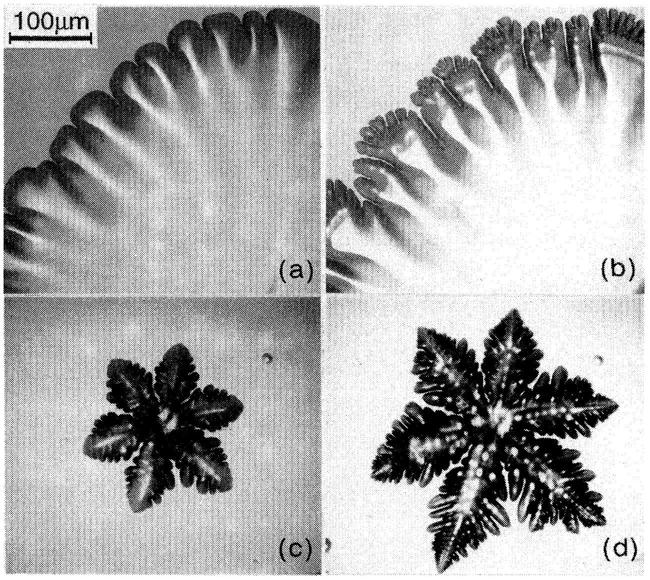

FIG. 2. Growth morphologies of CBr_4 crystals as a function of supersaturation at $T_c = 49.9\,^\circ C$. (a) $P = 284$ torr, $\Delta T = 0.02\,^\circ C$; (b) $P = 284$ torr, $\Delta T = 1.73\,^\circ C$; (c) $P = 700$ torr, $\Delta T = 0.20\,^\circ C$; (d) $P = 700$ torr, $\Delta T = 0.70\,^\circ C$.

smooth surface. With a further increase of total pressure to $P = 350$ torr [Fig. 1(c)], the crystal's smoothness starts to break at an even earlier stage with many finer cellular tips. Finally, when the total pressure increases to one atmosphere, dendritic crystals take place [Fig. 1(d)].

The evolution of crystal morphologies from smooth to cellular and to dendritic structure with increasing total pressure is due to a decrease of diffusivity of CBr_4 molecules in the vapor phase. From the theory of gas kinetics, one knows that the mass diffusivity is inversely proportional to the total pressure [15]. With increasing total pressure, CBr_4 molecules undergo more collisions with vapor particles (mainly inert gas), and diffusion-limited conditions become more pronounced, and hence, the crystal becomes more unstable. Such changes of crystal morphology with increasing total pressure are in good agreement with our earlier results of computer simulation [11]. By employing a modified diffusion-limited Monte Carlo model, we have found that crystal surfaces change from completely flat to center depressed and finally become dendritic with increasing mean free path (or decreasing total pressure) in the vapor phase.

In addition to the total pressure, supersaturation is also an important factor in controlling crystal-growth morphology. This is clearly shown in Fig. 2 for two different total pressures [$P = 284$ torr in Figs. 2(a) and 2(b), and $P = 700$ torr in Figs. 2(c) and 2(d)]. At $P = 284$ torr, when supersaturation is very low ($\Delta T = 0.02\,^\circ C$) the crystal grows at a very low rate and its morphology shows cellular forms with large widths [Fig. 2(a)]. When the supersaturation suddenly increases to $\Delta T = 1.73\,^\circ C$, the earlier wide cellulars immediately break into many finer fingers growing at a much higher growth rate [Fig. 2(b)]. At $P = 700$ torr, similar morphological change is observed [Figs. 2(c) and 2(d)] except in this case the crystal has become dendritic with sixfold symmetry. When the supersaturation is very low [$\Delta T = 0.2\,^\circ C$, Fig. 2(c)] these dendrites grow slowly with large tip radius. As supersaturation increases to $\Delta T = 0.70\,^\circ C$ [Fig. 2(d)], the earlier large dendrites immediately adjust their tips to smaller radii.

We have quantitatively measured the growth rates of these dendritic tips and cellular fronts at different supersaturations and total pressures. The result is plotted in Fig. 3. As one can see from this figure, at the same supersaturation the growth rate is always larger when the total pressure is lower. Another interesting point shown in Fig. 3 is that when the total pressure is at 700 torr the growth rate increases monotonically with supersaturation, but when the total pressure is at 100 torr the growth rate increases first and then becomes roughly constant (~2 μm/sec) when the supersaturation approaches about 1.5 °C. To understand the physical causes of this leveling

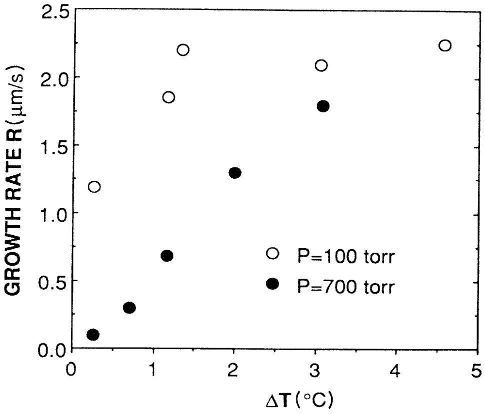

FIG. 3. Lateral growth rate R as a function of supersaturation.

in growth rate with increasing supersaturation at $P=100$ torr, we have calculated the heat balance between heat creation during crystallization and heat dispersion via the glass substrate. From the thermodynamic data of CBr_4, and the heat conduction data of the glass, we have found that when the crystal (lateral) growth rate reaches about 2 μm/sec, the heat released during crystallization can no longer be conducted away in time through the glass substrate. The accumulated heat at the growth front reduces the interfacial supersaturation and hence limits the growth rate from increasing further.

We have also measured the tip radius of dendrites and the width W of the cellulars at various growth conditions by image enlargement. Then, from the obtained value of the W and the corresponding growth rate R we have calculated the product W^2R, which is shown in Fig. 4. As one can see from this figure, the W^2R is a constant with respect to the supersaturation at a total pressure of $P=700$ torr. The constant product of W^2R is one of the most important results in the theoretical development of morphological stability for melt and solution growths [16,17]. It reveals a universal relationship between the growth rate and tip radius of a dendrite (or width of a cellular) in a diffusion-limited growth condition. The result in Fig. 4 has clearly demonstrated that such a relation may still hold in vapor growth when the total pressure is close to 1 atm. However, at lower total pressure as shown in Fig. 4, the product W^2R is no longer a constant. This is because, in this situation, the growth is more or less limited by surface kinetics and heat balance rather than by the mass diffusion.

According to the theoretical result of Langer and Müller-Krumbhaar [17] the product W^2R should scale linearly with the diffusivity D (i.e., $W^2R \sim \bar{d}_0 D/\alpha^*$, where α^* is a dimensionless stability constant, $\bar{d}_0$ the capillary length) and hence inversely proportional to the total pressure in our vapor-growth experiment. However, the result in Fig. 4 only shows an increase of about 3–4 times when the total pressure decreases from 700 to 100 torr (even at low supersaturations where heat balance is not a problem). Therefore the growth species may not be totally transported through the vapor diffusion. We think that materials diffusion on the substrate also plays an important role in our vapor crystal-growth experiment. This can be clearly seen from Fig. 5, in which two dendrites are found to grow toward each other. When they are far away, the two tips grow independently at a constant rate [Fig. 5(a)]. However, as they grow close within a critical distance of about 15 μm their growth rates start to slow down, and in the mean time the tip radii becomes larger (fatter). We have found that the closer they are the slower they grow and the fatter they become [Figs. 5(b) and 5(c)]. It seems that these two dendritic tips refuse to be in contact [it takes almost 20 min for these two tips to finally meet, Fig. 5(d)]. We explain such a phenomenon as follows: The source materials first impinge on the substrate from vapor, and then they diffuse toward the growth front via surface diffusion. When these two dendritic tips grow close within a certain distance, their diffusion fields overlap and the material supply becomes depleted due to growth species competition, and hence, their growth rates decrease. The closer the dendritic tips are, the more severe is the materials depletion and the more difficult it is for the tips to grow. From the distance in which the two dendritic tips begin to slow down, we can estimate the width of the surface diffusion boundary layer, which is about 15 μm in this case.

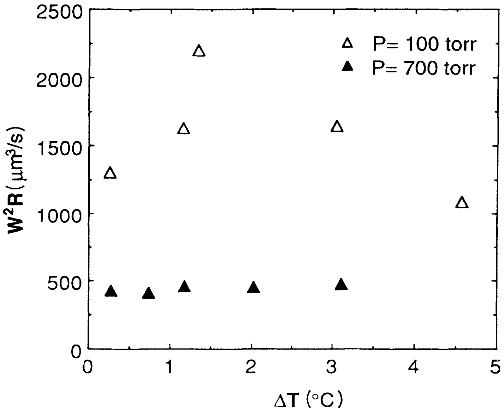

FIG. 4. Product of W^2R as a function of supersaturation.

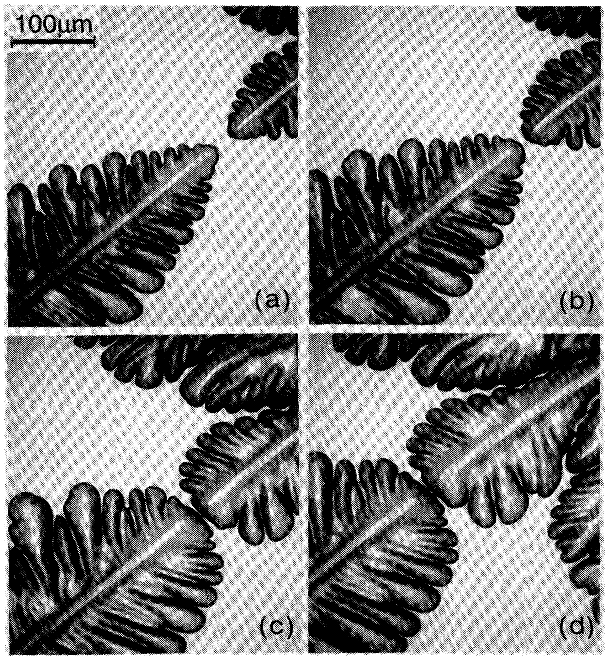

FIG. 5. Dendritic tip fattening and growth-rate slow down due to materials depletion at the growth front. (a) Time to count; (b) 40 sec later; (c) 10 min later; (d) 20 min later.

In conclusion, we have found that crystal-growth morphologies depend not only on temperature and supersaturation, but also sensitively on the total pressure of inert gas in the vapor. With increasing inert gas pressure, crystals with initially smooth surface first exhibit a cellular pattern and then evolve into dendritic structures. We have found, in the vapor growth, that the product of the square of dendritic tip radius (or width of cellular) and the corresponding growth rate remains a constant with changing supersaturation at a total pressure close to 1 atm, similar to the result found in melt and solution growth. However, the destabilizing mechanism appears to be more complex than that from bulk nutrient diffusion, although these dendrites (and cellulars) bear morphological similarity with those found in melt and solution-growth experiments. We have found that the surface diffusion on the substrate also plays an important role in crystal morphological instabilities in vapor growth.

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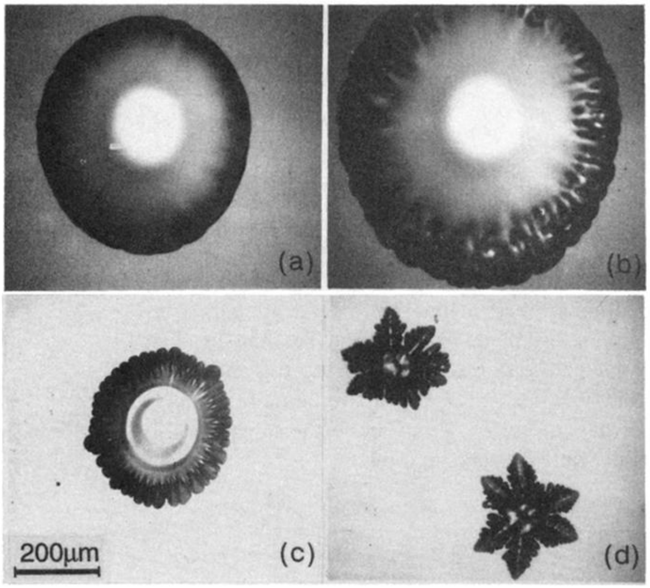

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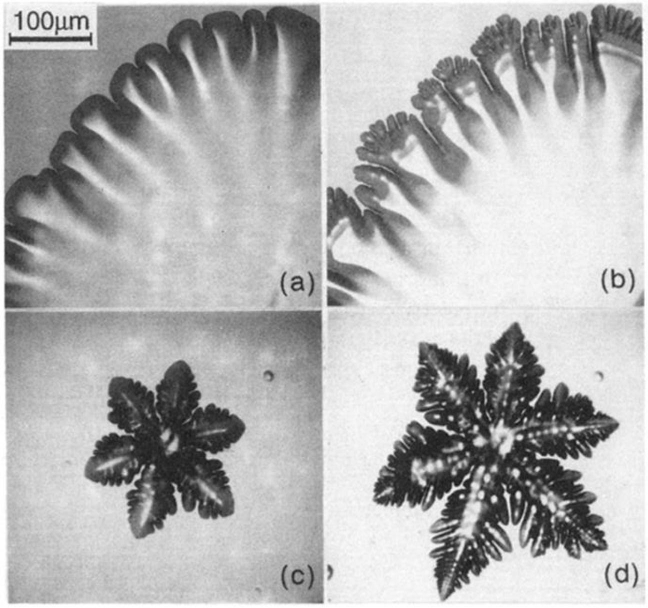

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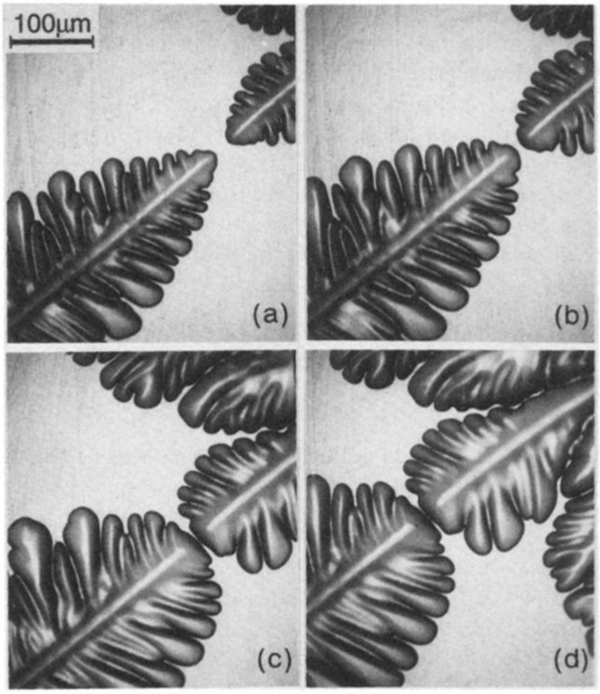

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