A Study of Rate and Mechanism of Growth of Twinned Tabular Grains of Silver Bromide^{*}

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Experiments were made on the anisotropic growth mechanism of tabular grains, according to which the predominance of their lateral growth rate over the vertical was ascribed by Jagannathan et al. to rapid growth of the self-generating {100} faces on their side surfaces at low pBr. This mechanism was supported by analyses of the preferential adsorption of a dye to {100} faces on the side surfaces. The lateral and vertical growth rates of tabular silver bromide grains at critical supersaturation were measured in reaction solutions with varied pBr values as functions of their equivalent circular diameter (D_c) and thickness (h). The lateral growth rate at low pBr was larger than the growth rate of cubic grains and increased with increasing D_c and decreasing h, whereas the vertical growth rate at low pBr was smaller than the growth rate of octahedral grains. This result indicates that the diffusion of solute ions through the solution from the vicinity of the main surfaces to that of the side surfaces enhanced the anisotropic growth of the grains at low pBr. At high pBr, the lateral and vertical growth rates were small, nearly equal to each other, and decreased with increasing D_c , obeying the diffusion-controlled scheme. At some intermediate pBr, the lateral growth rate decreased with increasing D_c and was still much larger than the vertical growth rate, providing the opportunity for the precipitation of monodisperse tabular grains.

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Introduction

Twinned tabular grains of silver halides are of great importance for highly sensitive photographic emulsions.¹ One of the most important properties of tabular grains is their large specific surface area, which is favorable for the preparation of spectrally sensitized emulsions with high sensitivity for the following reasons: (1) The sensitivity of spectrally sensitized emulsions is, in principle, proportional to the average surface area of the emulsion grains, because sensitizing dyes that absorb incident light are adsorbed on the grain surface in monomolecular layers.¹⁴ (2) The orientation of sensitizing dye molecules on the main surfaces of tabular grains is more suitable for absorbing incident light than that of the dye molecules on other grains when the main surfaces are parallel to the surfaces of the layer.⁵

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To realize the merits of tabular silver halide grains in photographic materials, it is highly desirable to precipitate monodisperse tabular silver halide grains.^{4,6} Extensive studies on the mechanism of regular grains have established that monodisperse regular grains can be precipitated through diffusion-controlled grain growth, according to which the growth rate decreases with increasing grain size.⁷⁻¹² It is not certain if this guiding principle is also applicable to the precipitation of monodisperse tabular grains, because the mechanism of growth of tabular grains is different from that of regular ones in that tabular grains grow anisotropically, whereas regular grains grow isotropically. It is therefore important and interesting to study the rate and mechanism of the growth of tabular grains.

The anisotropic growth of tabular grains, according to which the lateral growth rate is larger than the vertical growth rate,^{7,13} was at first ascribed to the presence of reentrant grooves on side surfaces composed of {111} faces.¹⁴⁻¹⁵ In the last decade, that proposal has been examined, and it has been proposed anew that the unique crystallographic planes present at the corners of the sidefaces¹⁶ or on the contour of the acute lip¹⁷ are the preferred sites for the nucleation of new growth. A model with the application of the spherical diffusion field and the rapid interfacial transport of solutes to the diffusion-controlled growth of a tabular grain was proposed as a detailed process of its anisotropic growth and was used to explain the following empirical characteristics known for the growth of twinned tabular grains of silver bromide in a solution with relatively high bromide ion concentration: (1) They grow exclusively in the lateral direction and (2) the size distribution becomes wider as they grow.¹⁶

All of the above models rely on the self-generating {111} faceted side face structure, which has been questioned on the basis of ball-model simulation. Instead, a concept of cubo-octahedral side faces has been proposed to explain the anisotropic growth of tabular grains.^{18,19} Namely, it is assumed that the side faces of tabular grains are bounded by {100} as well as {111} planes, self-generating and stabilizing the {100} faces, and that the predominance of the growth rate of {100} faces over that of {111} faces at low pBr is the cause of the anisotropic growth of tabular grains.

It is therefore expected that the lateral and vertical growth rates of tabular grains in comparison with the growth rates of octahedral and cubic grains provide instructive knowledge for the examination of the growth mechanism of tabular grains. The growth rates and mechanisms of cubic and octahedral grain growth have been extensively studied by many groups of investigators.^{7–12,20–22} In particular, it has been found that grain growth under a high supersaturation condition is important for the precipitation of monodisperse regular silver halide emulsion grains. Measurements of the growth

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rate of various regular silver halide grains at the critical supersaturation point have provided very important information for the study of the growth mechanism and design of emulsion grains.

However, it is rather difficult to measure the growth rate of tabular grains, because they grow anisotropically. Sugimoto²³ and Karpinski and Wey²⁴ reported their analyses on the growth mechanism of tabular silver bromide grains under the condition that only the side surfaces of the grains grew according to a physical ripening process in the presence of many fine silver bromide grains. Sugimoto proposed that the side surfaces of a tabular grain grew by receiving solute ions diffused directly toward its side surfaces and also solute ions that diffused toward the main surfaces and were interfacially transported to the grain's side surfaces.²³ This interfacial transport of solute ions has been criticized on the basis of the ball-model simulation.^{18,19}

On the other hand, Karpinski and Wey proposed that a tabular grain grew by receiving solute ions, which diffused toward the side surfaces of the grain.²⁴ By use of the luminescence property of silver iodobromide, Maskasky has made tracks for the growth of tabular grains by adding iodide ions in increments during the growth of tabular silver bromide grains and observing optical micrographs made of the luminescence to determine the position of the iodide ions in the grains.²⁵

The growth rate of tabular grains studied by Sugimoto and later by Karpinski and Wey was measured at low supersaturation. Maskasky did not measure the growth rate of tabular grains. The growth mechanism of tabular grains has not yet been studied on the basis of their growth rate at the critical supersaturation condition in contrast to the study of the growth mechanism of regular grains. No guiding principle is available for the preparation of monodisperse tabular grains. Sugimoto has pointed out that the size distribution of tabular grains becomes wider as they grow.¹⁶

The work reported here was undertaken to study the growth mechanism of tabular grains with cubo-octahedral side surfaces and to seek a guiding principle for preparing monodisperse tabular silver halide grains by measuring the growth rates of a series of tabular silver bromide grains at the critical supersaturation condition with various pBr values of reaction solutions and by comparing them with the growth rates of octahedral and cubic grains. In addition, the adsorption by the grains of a dye with strong preference for $\{100\}$ faces was analyzed to obtain evidence for the mechanism.

Experiments

The electron micrographs and dimensions of the tabular and octahedral AgBr grains used are shown in Table I and Fig. 1, respectively. Included are a series of tabular grains with nearly the same average thickness and different average area of main surfaces (Emulsions A, B, C, and D), and a series of tabular grains with nearly the same average area of main surfaces and different average thickness (Emulsions B, E, and F). The dimensions of these grains were determined from electron micrographs of their carbon replicas. The average thicknesses of tabular grains were calculated from the lengths of their shadows, which were formed by sputtering of gold and palladium onto the grains from a fixed angle before the preparation of their carbon replicas. The uncertainty of the measured values of the average thickness of tabular grains was 6.4%.

The growth rates of a series of tabular grains at the critical supersaturation point were given by the maximum

rate of addition of an aqueous solution of $AgNO_3$ that could be provided for the growth of the grains without forming any new grains when aqueous solutions of $AgNO_3$ and KBr were simultaneously added, keeping the pAg of the reaction solution at a fixed value. Measurements of the growth rate were made under these conditions: temperature 75°C; pBr 2.49, 2.78, 3.07, and 3.65; and initial gelatin concentration 2.3%.

According to the illustrations in Fig. 2, the growth rate of the volume of a tabular grain is given as,

$$dV/dt = S_t(dr/dt) + S_r(dh/dt),$$
(1)

where V is the volume of a grain; S_t and S_r are the areas of the side and main surfaces of the grain, respectively; r and h are the equivalent circular radius of the main surface and the thickness of the grain, respectively; and (dr/dt) and (dh/dt) are the lateral and vertical growth rates of the grain, respectively. Then

$$a = (dh/dt)/(dr/dt) = dh/dr,$$
(2)

$$\frac{dr}{dt} = \frac{dV}{dt} \frac{S_r}{S_r}, \qquad (3)$$

$$dh/dt = (dV/dt)/(S_t/a + S_r).$$
 (4)

The values of S_t and S_r were those shown in Table I, and dV/dt could be measured according to the above procedure. The values of dr/dt and dh/dt were thus calculated. The ratio of dr/dt to dh/dt, which was designated as a, was given by the tangent at the beginning of grain growth in the curve showing the change in equivalent circular radius of the main surface as a function of the change in the thickness of tabular grains. Because the change in the radius of the main surface was actually in a linear relationship with the change in the thickness of tabular grains, a was given by the slope of the straight line.

The presence of $\{100\}$ faces on the side surfaces of tabular silver bromide grains was examined by analyzing the adsorption of 3,3'-bis(4-sulfobutyl)-9-methyl-thiacarbocyanine (Dye 1) to the grains in emulsions on the basis of their diffuse reflectance spectra and the Kubelka–Munk equation,^{26,27} expressed as

$$K/S = (1-R)^2/2R = c\varepsilon/S,$$
(5)

where *R* is the diffuse reflectance of a thick emulsion layer at the wavelength of light absorbed by the dye molecules under specific conditions; *K* and *S* are absorption and scattering coefficients, respectively; *c* is the concentration of the dye molecules under the specific condition; and ε is the extinction coefficient of the dye molecules. It is well established that Dye 1 molecules are preferentially adsorbed to the {100} faces of silver halide grains to give a double band peaking at 520 and 600 nm, then adsorbed to

TABLE 1. Dimensions of Emulsion Grains Used

2*r*-equivalent circular diameter, *h*-thickness







Figure 2. Illustration of lateral and vertical growth rates of tabular grains (dr/dt and dh/dt, respectively), where r and h are the equivalent circular radius and thickness of a tabular grain, respectively.

the {111} faces to give a J-band peaked at 625 nm after the saturation of the {100} face by the dye molecules.²⁶

The growth rate of tabular silver bromide grains was measured in the presence of small amounts of Dye 1 and 3,3'-bis(sulfopropyl)-5,5'-dichloro-9-methyl-thiacarbocyanine (Dye 2), which adsorbs preferentially to {111} faces,²⁶ in order to examine the proposal that the anisotropic growth of tabular AgBr grains is caused by the rapid growth of the {100} faces on the side surfaces, as compared with the growth of the {111} faces on the main surfaces at relatively low pBr values.^{18,19}

Results and Discussion

Figure 3 shows the growth rates of cubic and octahedral AgBr grains at critical supersaturation and the solubility of AgBr as functions of pBr. In the range of pBr \approx 3.65, where the solubility of AgBr is small, the growth rates of cubic and octahedral AgBr grains were very small and



Figure 3. Solubility and critical growth rates of cubic silver bromide grains with edge length of 0.68 μ m (\Box) and octahedral silver bromide grains with edge length of 0.72 μ m (\bigcirc) as functions of pBr.

nearly equal to each other. With decreasing pBr, the solubility of AgBr increased, and the growth rates of those grains increased. The increase in the growth rate of cubic grains with decreasing pBr was larger than the increase in the growth rate of octahedral grains.

Figure 4 shows the growth rates of the volumes of tabular grains with an average thickness of 0.1 μ m and octahedral grains at critical supersaturation as functions of their surface areas at various pBr values. The increases in the grain volume of tabular grains and octahedral grains could be compared as functions of surface area, because the amount of solutes provided by diffusion is considered to be nearly the same for a tabular grain and an octahedral one when their surface areas are nearly equal. The volume growth rates of tabular and octahedral grains decreased with increasing pBr of the reaction solution dur



Figure 4. Volume growth rate of tabular (\Box) and octahedral (\bigcirc) silver bromide emulsion grains as functions of their surface area and pBr of reaction solutions.



Figure 5. Changes in the thickness (*h*) and equivalent circular diameter (D_c) of tabular silver bromide grains during their growth under critical supersaturation in solutions with various pBr values. The values of $\Delta h/\Delta D_c$ were 0.950, 0.054, and 0.034 for pBr of 3.65, 3.07, and 2.49, respectively.

ing their growth. The volume growth rate of tabular grains was larger than that of octahedral ones in a reaction solution with small pBr values during their growth; the discrepancy between them decreased with increasing pBr value and disappeared at pBr 3.65. The large volume growth rate of tabular grains with respect to that of octahedral ones at low pBr could be attributed to high lateral growth rate of a tabular grain with respect to that of the usual {111} faces.

Figure 5 shows the ratio of the increase in the equivalent circular diameter of the main surface to the increase in the thickness of tabular grains when grown at critical supersaturation in the reaction solutions with pBr values as indicated in the figure. The experiments started with the smallest grains in Fig. 5, which grew at critical supersaturation according to the procedure described in the Experimental section to give the second smallest grains. Similar experiments were repeated for the second smallest grains to grow to the second largest ones, and for the second largest grains to the largest ones. At low pBr values, the diameter of the main surface increased more rapidly than did the thickness of tabular grains. At pBr 3.65, the increases in the diameter of the main surfaces and the thickness of a tabular grain were nearly equal to each other, indicating that the tabular grains grew isotropically. Because the increase in the diameter of the main surface was in a nearly linear relationship with the increase in the thickness of a tabular grain, the tangent at the origin of the relation of the increase in the thickness with the increase in the diameter of the main surface of a grain was given by $\Delta h / \Delta r$.

The lateral and vertical growth rates of tabular grains were then given by their volume growth rate and $\Delta h/\Delta r$ at the critical supersaturation in light of Eqs. 1 through 4. Figure 6 shows the lateral and vertical growth rates of tabular AgBr grains with an average thickness of 0.1 μ m as functions of the average equivalent circular diameter of their main surfaces at critical supersaturation in the reaction solutions with pBr values of 2.49, 3.07, and 3.65.



Figure 6. Lateral (\bigcirc) and vertical (\Box) growth rates of tabular AgBr grains as functions of their equivalent circular diameters (D_c) .



Figure 7. Fluxes of solute ions as indicated by arrows for the growth of a tabular grain at low pBr. The rectangle indicates the side view of a tabular grain.

At pBr 3.65, the lateral and vertical growth rates were small, equal to each other, and they decreased with increasing diameter of the main surfaces of tabular grains. This result indicates the disappearance of the anisotropic growth of tabular grains at pBr 3.65, and could be attributed to the condition of the diffusion-controlled growth of tabular grains owing to the low solubility of AgBr at pBr 3.65, as was observed for the growth of octahedral and cubic AgBr grains at that pBr value.

At pBr 2.49, the lateral growth rate was overwhelmingly larger than the vertical growth rate of tabular grains. The concentration of solute ions in the vicinity of the main surfaces is therefore considered to be larger than that in the vicinity of the side surface, and the diffusion of solute ions from the vicinity of the main surfaces to that of the side surfaces took place, as illustrated in Fig. 7. This idea could be supported by the fact that the lateral growth rate of a tabular grain increased with increasing diameter of



Figure 8. Lateral growth rate of tabular silver bromide grains as a function of their thickness at pBr 2.35.



Figure 9. Growth rate of octahedral grains (\Box) and main surfaces of tabular grains (\bigcirc) together with solubility of silver bromide as a function of pBr.

its main surfaces, because the ratio of the area of side surfaces to that of the total surface decreased with increasing diameter of the main surfaces and fixed thickness of a tabular grain.

Figure 8 shows the lateral growth rate as a function of average thickness of a series of tabular silver bromide grains with nearly the same average diameter and with variation of thickness. As seen in this figure, the lateral growth rate decreased with increasing average thickness of the grains. The amount of solute that diffused from the vicinity of the main surfaces to that of the side surfaces should be nearly the same for those grains, and the amount of the solute per unit area of the side surfaces should decrease with increasing thickness of the grains. This would account for the fact that the lateral growth rate decreased with increasing average thickness of the tabular grains with nearly the same average diameter of the main surfaces.

Figure 9 shows the growth rates of {111} surfaces of octahedral silver bromide grains and the main surfaces of tabular grains and the solubility of AgBr as a function of pBr values of the reaction solutions. Although the growth rate of octahedral grains increased with decreasing pBr values, in accordance with the increase in the solubility with decreasing pBr values, the growth rate of the main surfaces (i.e., vertical growth rate) of tabular grains decreased with decreasing pBr values. This result could also support the diffusion of solute ions from the vicinity of the main surfaces to that of the side surfaces during the anisotropic growth of a tabular grain, as described in the discussion of Fig. 8.

As seen in Fig. 6, at pBr 3.07, the lateral growth rate was still considerably larger than the vertical growth rate of the tabular grains. However, the lateral growth rate decreased with increasing diameter for the tabular grains with relatively small diameter. As seen in Fig. 9, the solubility of silver bromide was lower and therefore the amount of solute ions provided by their diffusion in solution was less at pBr 3.07 than at pBr 2.49. We therefore conclude that the amount of solute ions that diffused from the vi-



Figure 10. Diffuse reflection spectra of thick emulsion layers composed of tabular silver bromide grains with an equivalent circular diameter of $1.14 \ \mu m$ and thickness of $0.1 \ \mu m$ and Dye 1 in increasing amounts. The volumes of a methanol solution of Dye 1 $(1.1 \times 10^{-2} \text{ mol/L})$ added to emulsion layers, each of which contained $5.45 \times 10^{-2} \text{ mol of AgBr}$, were 0.2, 0.4, 0.6, 0.8, 1.2, 1.6, 2.0, 3.0, 4.0, 5.0, and 6.0 cm³. The diffuse reflectance decreased with an increasing amount of dye.

cinity of the main surfaces to that of the side surfaces was also smaller at pBr 3.07 than at pBr 2.49. The lateral growth rate could therefore obey a diffusion-controlled scheme, according to which the lateral growth rate should decrease with increasing diameter of the main surfaces. For larger grains, however, the lateral growth rate increased with increasing diameter of the main surfaces of tabular grains, as was observed for the growth of the grains at pBr 2.49.

Figure 10 shows the diffuse reflectance spectra of thick emulsion layers composed of tabular silver bromide grains with an average equivalent circular diameter of 1.14 μ m and an average thickness of 0.1 μ m and Dye 1 in increasing amounts. The absorption spectra of the dye adsorbed on the surfaces of the tabular grains in small amounts show a double band with absorption peaks at 600 and 520 nm, attributed to the dye on the {100} faces of the silver halide grains. With increasing amounts of dye, the spectra show a J-band peaking around 625 nm, attributed to the dye on the {111} surfaces of silver halides. Thus, there were certainly {100} faces on the surfaces of the grains; with increasing amounts of dye, the dye molecules first adsorbed to the {100} faces and then to the {111} faces of the grains after the {100} faces had been saturated by the dye.

The value of $(1 - R)^2/2R$ at the absorption peak of the J-band, which was proportional to the amount of the dye on the {111} faces, was plotted in Fig. 11 against the amount of the dye. With increasing amounts of dye, the experimental values were plotted on three straight lines. The dye molecules on the first straight line were adsorbed to the {100} faces on the surfaces of the grains, those on the second straight line were adsorbed to the {111} faces after the {100} faces had been saturated by the dye, and those on the third



Figure 11. The values of $(1 - R)^2/2R$ at 620 nm of the diffuse reflectance of the emulsion layers indicated in Fig. 10 as a function of the volumes (in cm³) of a methanol solution of Dye 1 (1.1 × 10⁻² mol/L) added to emulsion layers containing 5.45×10^{-2} mol of silver bromide.

line were in the gelatin phase of the emulsion. The amounts of dye that created the crossing point between the first and second lines and that between the second and third lines give 10.0% as the ratio of the area of the {100} faces to the total surface area of the tabular grains.²⁶

Figure 12 shows the influence of Dyes 1 and 2 on the lateral growth rate of tabular grains in a solution at low pBr. As seen in the figure, Dye 1 depressed the lateral growth of the grains, whereas Dye 2 did not. It is known that Dye 1 is adsorbed preferentially to {100} faces, rather than to {111} faces, whereas Dye 2 is adsorbed preferentially to {111} faces rather than to {100} faces.²⁶ The growth of surfaces is considered to be depressed by dye molecules adsorbed to the surfaces. Therefore, the result shown in Fig. 12 could support the idea that {100} faces were present on the side surfaces of the tabular grains and grew more rapidly than the main surfaces, bringing about their anisotropic growth.



Figure 12. The increase in equivalent circular diameter of tabular grains during their growth in the presence of Dyes 1 and 2 (ΔD_{Dye}) with respect to that in the absence of any dye (ΔD_{type}) as functions of the surface coverage of the grains by the dyes. The results with Dyes 1 and 2 are shown by \bigcirc and \square , respectively. The areas occupied by a Dye 1 molecule and by a Dye 2 molecule were 62 Å² and 81 Å², respectively.

Discussion of the Mechanism of Tabular Grain Growth

According to the proposed concept of cubo-octahedral sidefaces, $^{18,\overline{19}}$ the predominance of the growth rate of $\{100\}$ faces on the side surfaces of tabular grains over that of {111} faces on the main surfaces at low pBr is the cause for the anisotropic growth of tabular grains. This concept could be supported by the results obtained in this investigation. The existence of {100} faces on the side surfaces of tabular silver bromide grains was confirmed by use of the preferential adsorption of Dye 1 to {100} faces on the surface of silver bromide grains. The concept was further evidenced by the observation that the lateral growth of tabular silver bromide grains was depressed, not by Dye 2 with preferential adsorption to {111} faces, but by Dye 1 with preferential adsorption to {100} faces on the surfaces of silver bromide grains.

Note that 10% surface coverage by Dye 1, which in Fig. 11 resulted in total coverage of the $\{100\}$ faces, caused the lateral growth rate to be reduced only to 90% of its normal value and that substantial reduction in lateral growth rate appeared to occur only after Dye 1 was also adsorbed to around 20% of the {111} faces of the grains. The result shown in Fig. 11 is believed to have been obtained under equilibrium condition, which was achieved by agitating the emulsions for a long time. On the other hand, the results shown in Fig. 12 were obtained under dynamic conditions with competition between the grain growth and dye adsorption. This condition could be the reason that an amount of Dye 1 more than that required for the total coverage of the {100} faces was needed for substantial reduction in the lateral growth rate.

The lateral and vertical critical growth rates of tabular silver bromide grains, which were measured and compared with the critical growth rates of cubic and octahedral silver bromide grains, could also support the proposed concept of cubo-octahedral side faces and clarify the characteristics of the growth of tabular grains. Although growth rates of grains were dependent on their sizes,⁷⁻¹² the comparison between the results shown in Figs. 3 and 6 indicates that the growth rate of the side surfaces of tabular grains was larger than that of cubic grains at low pBr. The result shown in Fig. 9 also indicates that the growth rate of the main surfaces of tabular grains was smaller than that of octahedral grains at low pBr.

The above results indicate that the diffusion of solute ions through the solution from the vicinity of the main surfaces to that of the side surfaces enhances the anisotropic growth of tabular grains. This concept was supported by the observation that the lateral growth rate of tabular silver bromide grains was increased by Dye 2 with its preferential adsorption to {111} faces, as shown in Fig. 12, because it is considered that the preferential adsorption of Dye 2 to the main surfaces composed of {111} faces depressed their growth and enhanced the diffusion of solute ions from their vicinity to that of the side surfaces of the grains. Therefore, we point out that the diffusion of solute ions, together with the predominance of the growth rate of the {100} faces over that of the {111} faces at low pBr, is important for understanding quantitatively the anisotropic growth of tabular grains.

The guiding principle for the preparation of monodisperse grains through diffusion-controlled grain growth, which is quite useful for regular grains,⁷⁻¹² is also available for the preparation of monodisperse tabular grains,

although it is diminished by the diffusion of solute ions from the vicinity of the main surfaces of a tabular grain to that of its side surfaces. The anisotropic growth rate, which decreases with increasing diameter of the main surfaces, can be readily observed at relatively low pBr values for relatively small tabular grains and thus provides the opportunity for the preparation of monodisperse tabular grains.

Conclusion

- 1. A method was provided to measure the lateral and vertical growth rates of tabular silver halide grains at the critical supersaturation and was applied to the study of the mechanism of their anisotropic growth.
- 2. The measured values of lateral and vertical growth rates of tabular AgBr grains in comparison with those of octahedral and cubic grains indicated that the anisotropic growth of the tabular grains resulted both from the rapid growth of self-generating {100} faces on their side surfaces at low pBr, as proposed by Jagannathan et al., and from the diffusion of solute ions through reaction solutions from the vicinity of the main surfaces to that of the side surfaces.
- 3. The above mechanism of the anisotropic growth of tabular grains was evidenced by the analysis of the effects of dyes with preferential adsorptivity to {100} and {111} faces on the anisotropic growth.

References

- (a) Anonymous, Res. Discl. (Item 22534) 225: 20 (January 1983); (b) J. T. Kofron and R. E. Booms, J. Soc. Photogr. Sci. Technol. Jpn. 49: 15 (1986); (c) A. F. Sowinski and P. J. Wightman, J. Imaging Sci. 31: 162 (1987); (d) R. E. Jacobson, N. R. Axford, and A. Ford, J. Imaging Sci. 38: 140 (1990).
- H. Zwicky, Z. Wiss. Photogr. 53: 68 (1959).
- 3. (a) T. Tani, J. Imaging Sci. 29: 93 (1985); (b) T. Tani, J. Imaging Sci. Technol. 39: 31 (1995).
- T. Tani, Photographic Sensitivity: Theory and Mechanisms, Oxford 4. University Press, New York, 1995, Chapter 8.
- S. Watanabe and T. Tani, J. Imaging Sci. Technol. 39: 81 (1995).
- G. R. Bird, Optimizing the Entire Photographic System for Informa-6. tion Capture, in Preprint for Tokyo Symposium, sponsored by Soc. Photogr. Sci. Technol. Japan, July 1980, Tokyo.
- T. Tani, in Ref. 4, Chapter 2.
- 8. J. S. Wey and R. W. Strong, Photogr. Sci. Eng. 21: 14 (1977).
- J. S. Wey and R. W. Strong, Photogr. Sci. Eng. 21: 248 (1977). 9.
- R. W. Strong and J. S. Wey, Photogr. Sci. Eng. 23: 344 (1979). 10.
- J. D. Lewis, J. Photogr. Sci. 27: 24 (1979). 11.
- 12 M. Saito, Rate equation for growth of silver halide grains under fixed degree of supersaturation, Annual Conference of Soc. Photogr. Sci. Technol. Jpn., May 1980, Tokyo.
- 13. (a) R. W. Berriman and R. H. Herz, Nature (London), 180, 293 (1957); (b) J. F. Hamilton and L. E. Brady, J. Appl. Phys. 29: 994 (1958)
- D. R. Hamilton and R. G. Seldensticker, J. Appl. Phys. 31: 1165 (1960). 14
- J. F. Hamllton and L. E. Brady, J. Appl. Phys. 35: 414 (1964). 15.
- T. Sugimoto, *Photogr. Sci. Eng.* **28**: 137 (1984). J. E. Maskasky, *J. Imaging Sci.* **31**, 15 (1987). 16.
- 17
- R. Jagannathan, R. V. Mehta, J. A. Timmons, and D. L. Black, Phys. 18 Rev. B. 48: 13261 (1993).
- 19 R. V. Mehta, R. Jagannathan, and J. A. Timmons, J. Imaging Sci. Technol. 37: 107 (1993).
- A. Hirata and S. Honishi, Bull. Soc. Sci. Photogr. Japan, 16: 1 (1966). 20.
- T. Sugimoto, J. Colloid Interface Sci. 93: 461 (1983). 21
- 22 R. Jagannathan, J. Imaging Sci. 32: 100 (1988).
- 23. T. Sugimoto, Photogr. Sci. Eng. 28: 137 (1984)
- 24. P. H. Karpinski and J. S. Wey, J. Imaging Sci. 32: 34 (1987).
- 25. J. E. Maskasky, J. Imaging Sci. 31: 15 (1987).
- T. Tani, J. Imaging Sci., 29 165 (1985). 26.
- 27 A. H. Herz, R. Danner, and G. Janusonis, in Adsorption from Aqueous Solution, American Chemical Society, Washington, D.C., 1968, p. 173.