Growth Mechanism of Pure AgX {111} and {100} Tabular Crystals Grown from the Vapour Phase

G. Bögels[a], H. Meekes[a], P. Bennema[a] and D. Bollen[b]
[a]RIM laboratory for Solid State Chemistry, University of Nijmegen,
Toernooiveld, 6525 ED, Nijmegen, The Netherlands
[b]Agfa-Gevaert N. V., Septestraat 27, B-2640, Mortsel, Belgium

Abstract

In this study the vapour growth of pure AgCl and AgBr crystals will be discussed. On copper and quartz substrates the same morphologies appear as for AgBr crystals grown form solution, namely; cubic, {100} tabular, {100} tabular with (411) twinning, cubo-octahedral, {111} tabular and needle shaped. These morphologies strongly depend on the temperature differences between the substrate and the furnace. For both AgCl and AgBr, beyond a critical temperature difference twin planes were formed resulting in {111} tabular crystals and needle shaped crystals. This made it possible to examine the twinning event. A general mechanism to explain the twinning will be presented. Twinning is not only caused by the surface supersaturation but also the size of the crystals and the charge interactions at the surface are essential. Small crystals have a higher chance of forming twin planes at a constant supersaturation owing to the crystal size effect and the surface charge effect.

I. Introduction

Different kinds of morphology of silver halide crystals are of interest in the field of photography. Particularly tabular crystals with a relatively large surface area are of high interest. In recent years many studies have been carried out to examine the growth mechanism of {111} tabular crystals[1-5] and other shapes of silver halide crystals[1]. In an earlier paper we explained the preferential lateral growth of {111} tabular AgBr crystals grown from DMSO[5]. In another study[6] we present experimental data on the different morphologies occurring in the vapour phase and focus on the similarities between the proposed growth mechanism[5] and the experimental data concerning {111} tabular crystals. In this study we will give a short overview of the latter study and focus on the twinning event of pure {111} tabular AgBr and AgCl crystals.

From the vapour phase a rich variety of morphologies appears. These morphologies depend on the temperature difference between the furnace and the substrate. For AgBr and AgCl the same morphologies were found. Relatively low temperature differences gave {100} bounded crystals, increasing the temperature difference gave cubo-octahedral crystals and at the highest temperature difference {111} tabular and needle shaped crystals were observed.

2. Experimental

Silver halide crystals were grown in an evacuated quartz tube containing about 200 mg of pure AgX (X=Cl, Br) at temperatures of 5 till 115 degrees below the melting point of AgX. The background pressure just outside the tube was around 10^{-6} mbar. The growth experiments were performed for a period of 24 to 60 hours. The crystals were grown on copper and quartz substrates. The temperature of the copper substrate had a gradient: a high temperature in the center of the furnace and a lower temperature to the outside. Due to this gradient different types of morphology appeared on different parts of the substrate. The temperature of the furnace and the copper substrate was measured to make it possible to determine the range of temperature differences for which the different morphologies were formed and the driving force at which twin planes appear.

On the copper substrate a layer of at least 2 μm of badly developed morphologies appeared. On this layer silver halide single crystals were observed. The copper substrate was placed about 25 cm in the furnace and 20 cm outside the furnace (room temperature) to obtain the temperature gradient (see figure 1). The temperature of the substrate was measured using six copper-constantan (type T) thermocouples using constantan wires welded in the substrate with a mutual separation of six centimeter. Four couples were placed inside the furnace and the other two outside. The temperature gradient over the quartz substrate was much smaller due to the relatively small thermal conductivity of quartz as compared to copper. For quartz only the actual furnace temperatures were measured. On the quartz substrate only single crystals appeared. The single crystals grown on the copper substrate had a size between 3 and 40 μm, on the quartz substrate it was between 0.5 and 10 μm. After the growth experiments the substrate was cut in parts and prepared for examination by scanning electron

microscopy (SEM). With the SEM we could find the precise position of the different morphologies and reveal the side-face structure of the {111} tabular crystals. This was done by positioning the tabular faces of the crystals perpendicular to the image and roughly measuring the angle and also by judging the shape of the side faces. The triangular (or hexagonal) shaped side faces were indexed as {111} faces and the rectangular shaped faces as {100} faces. The vacuum-pump was a Balzers TCP 1231 and the SEM used was a JEOL JSM-T300.
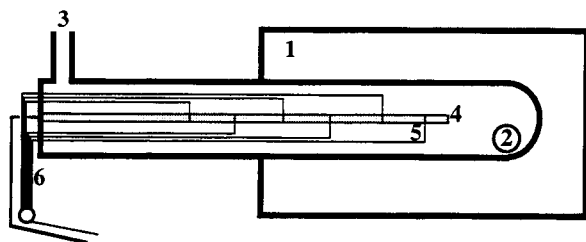

Figure 1. The vapour phase set up; 1. Furnace, 2. AgX (X=Br, Cl), 3. Vacuum pump, 4. Copper wire, 5. Thermocouple, 6. Constantan wires.

3. Results

The morphology found depends on the temperature difference between the substrate and the furnace. For low temperature differences a quartz substrate was chosen whereas for higher temperature differences a copper substrate was used. On the quartz substrate cubic crystals are found for AgBr. For AgCl at low temperature differences cubic crystals were found and for higher temperature differences cubo-octahedral crystals were found on the quartz substrate. For AgCl on the copper substrate cubo-octahedral crystals were observed and for higher temperature differences {111} tabular crystals and needle shaped crystals were found. For AgBr at increasing temperature differences cubic, cubo-octahedral and {111} tabular and needle shaped crystals appeared on the copper substrate. The furnace temperature and the precise temperature differences are listed in reference[6].

3.1 Different morphologies

The {100} area for AgCl and AgBr consists of cubic crystals, {100} tabular crystals (see figure 2), cubic crystals with (411) twinning[7] and needle shaped crystals bounded by {100} faces. The aspect ratio of the {100} tabular crystals had for AgBr a maximum around 10 whereas for AgCl tabular crystals were found with an aspect ratio around 80. The {100} needle shaped crystals can have a length of 20 times the size of the other crystals laying in that area. The {100} tabular crystals were too small to examine them in detail, but the positions where they appeared suggest that no {111} twin planes are formed in {100} tabular crystals. This will be discussed later.

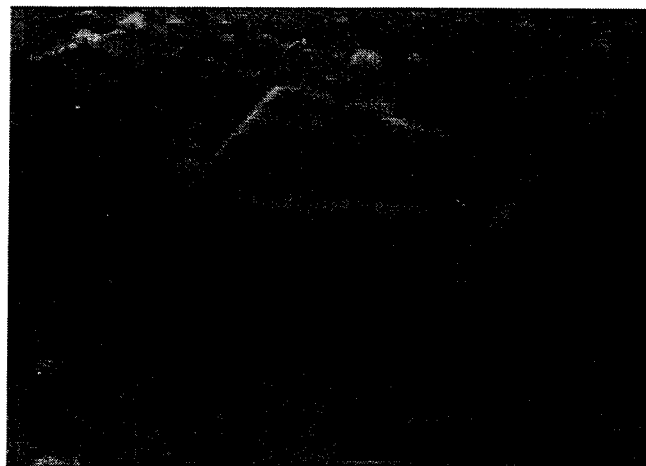*Figure 2. {100} tabular crystal of AgBr grown on a quartz substrate. The bar represents 10 µm.*

The next area, at higher temperature differences consists of cubo-octahedral crystals. In the area of the highest temperature differences {111} tabular crystals (see figure 3) and needle shaped crystals are observed. For AgCl 80% of the crystals were needle shaped and 20% were {111} tabular. For AgBr 90% of the crystals were {111} tabular and only 10% were needle shaped. The needle shaped crystals probably contain non-parallel twin planes. The growth mechanism of needle shaped crystals will be the subject of a future study[8]. The aspect ratios of the tabular crystals ranged from 3.5, at low temperature differences, to over 50 at higher temperature differences. We examined the side-face structure of tabular crystals with aspect ratios around 7 because the side-face structure was the most easily obtained for these crystals (for data see table 1).

All {111} tabular crystal sides were bounded by flat {100} and {111} faces. The side faces of the {111} AgBr and AgCl tabular crystals consist of two or three flat {111} and {100} faces forming a ridge structure, resulting in three
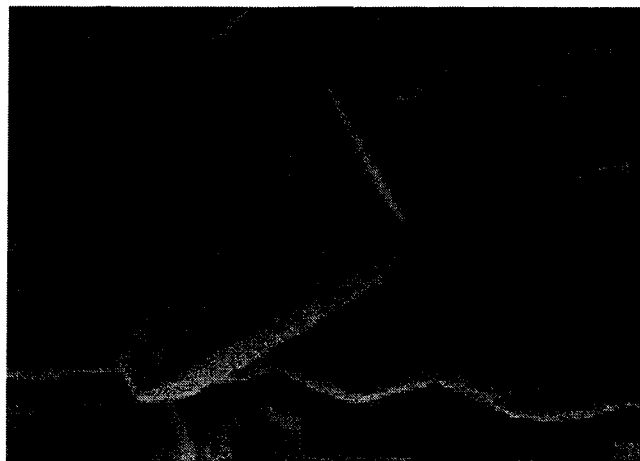

Figure 3 {111} tabular crystal of AgCl grown on a copper substrate. The bar represents 10 µm.

kinds of crystal morphology. These three kinds of morphology, or crystal groups (see table 1), were also observed for tabular AgBr crystals grown from DMSO. Note that the faces between the twin planes were too small to be observed.

From these crystal groups the number of parallel twin planes was deduced[5]. Group 1 tabular crystals contain two twin planes and group 2 and 3 contain three twin planes. It is concluded that all examined {111} tabular crystals for AgBr and AgCl could be placed in one of the three crystal groups.

TABLE 1. Aspect ratio and occurrence of the different {111} tabular crystal groups for AgBr and AgCl. Group 1 tabular crystals contain two parallel twin planes and group 2 and 3 contain three parallel twin planes. The number of twin planes is deduced from the side-face structure.

	AgBr	AgCl
Group 1		
occurrence(number)	59%(16)	29%(8)
average aspect ratio	8.4	6.0
Group 2		
occurrence(number)	11%(3)	4%(1)
average aspect ratio	4.8	7.3
Group 3		
occurrence(number)	30%(8)	67%(18)
average aspect ratio	8.5	5.4

4. Discussion

4.1 Twinning of AgCl and AgBr

The majority of the {111} tabular AgBr crystals grown from solution[5] and the vapour phase (see table 1) consists of crystals of group 1. Tabular crystals with two parallel twin planes seem, thus, to occur the most frequently for AgBr. Only a small minority of the crystals (10%) is needle shaped and probably contains non-parallel twin planes. However, for AgCl the majority (80%) was needle shaped. For the {111} tabular crystals three parallel twin planes (group 2 and 3) were in the majority, at least, from the vapour phase. For AgCl no pure {111} tabular crystals are formed in solution. It seems that twin planes are more easily formed for AgCl than for AgBr. This difference in the number of twin planes between AgCl and AgBr is hard to explain. Moreover, the temperature difference required for twinning is for AgBr and AgCl almost the same.

The observed distances between the twin planes (of group 1 and 3) were for the vapour grown crystals smaller then 0.1 µm as judged from the SEM images. Accidental twin planes[5] characteristic for group 2 crystals were for AgCl and AgBr in the minority (see table 1). Thus, most twin planes are formed during the nucleation. The chance of forming additional twin planes during growth is small. We

will explain this in the following. The temperature differences needed to form twin planes is both for AgCl and AgBr almost the same. However, the number of twin planes seems for AgCl higher (majority is needle shaped and group 3) than for AgBr (majority of the crystals is of group 1).

The {100} tabular crystals were observed in the cubic area. The temperature differences for this area were lower than the minimal temperature difference required for forming twin planes, that is for both AgBr and AgCl around 130 °C. For AgBr the cubic crystals appear until a maximum temperature difference of 125 °C and for AgCl the maximal temperate difference is even much lower[6]. Thus, the substep mechanism or the stacking fault mechanism[10] are not able of explaining the growth mechanism of {100} tabular crystals.

4.2 The twinning mechanism

In the vapour phase set up the temperature difference stays nearly constant during the experiment. This temperature difference can also be considered as the driving force for crystallization. In the industrial double-jet precipitation method the supersaturation is very high during the precipitation and decreases rapidly during the physical ripening stage. During the precipitation twin planes are formed owing to the high supersaturation. Jagannathan[9] explained the occurrence of twinning of AgBr crystals under normal precipitation conditions by a high excess of [Br-] resulting in an instability of the {111} crystal surfaces at high surface driving force. He further states that, if this concept is correct, twinning of AgBr crystals can occur at any pBr value of the reactor solution, provided that the growing {111} surface is exposed to a sufficiently high surface driving force. Jagannathan supported this by changing the ionic strength of the solution, thus, changing the stability of the {111} faces. Our experiments support the idea that an increase in (surface)supersaturation (in our experiments a higher temperature difference between vapour and substrate) leads to twinning. However, the driving force stays constant during the vapour growth experiment. So, if twinning was only caused by the bulk driving force one would expect a continuous formation of twin planes. However, we observed that the majority of the twin planes was formed in the early nucleation stage. Thus, the stability against the formation of twins on the {111} faces will be lower in the early stages of the growth process and dramatically increase during the growth process. In the following a mechanism of the formation of twin planes will be proposed that can explain the observed experimental data.

The effect of supersaturation
Fist of all we note that the chance of forming a twinned growth layer will increase with increasing supersaturation. Two dimensional nuclei that are twinned are always formed with a certain frequency. Nevertheless, the majority of the

twinned two dimensional nuclei is dissolving again because of the high formation energy of such nuclei as compared to that of regularly stacked nuclei. At higher supersaturation the critical size of a two dimensional nucleus becomes smaller. For twinned two dimensional nuclei this means that, although its critical nucleus size remains larger than that of a regular nucleus, it decreases with increasing supersaturation. Moreover, for higher supersaturation the step velocity on the faces increases and therefore the chance that a nucleus is dissolved again diminishes. Thus, at higher supersaturation twinned critical nuclei are formed relatively more frequently as compared to regular stacked ones.

The effect of crystal size

We will focus on the {111} faces of a small and a large crystal. Both crystals will be placed in an environment where twin planes can be formed (figure 4a). On both faces there is a chance of forming a 'twinned ' critical two dimensional nucleus. We assume that the chance of forming a twinned critical nucleus (shaded in the figure) is smaller than forming a correctly stacked nucleus (transparent in the figure) because the energy for the twinned nucleus is higher. If a twinned nucleus has formed on a small crystal the chance is high that it will grow out and form a new growth layer (figure 4b-d) because we assume that this growth process is relatively fast as compared to the formation of critical two dimensional nuclei. The large surface, on the other hand, has a large chance to contain more two dimensional nuclei at the same time (figure 4a). We assume that the growth rate of the normal stacked nucleus is higher than that of the twinned stacked nucleus (figure 4b). On the large crystal different 'islands' will be formed. When the islands meet (see figure 4c) the regular stacked layer is in favor owing to the lower energy. The twinned stacked layer will dissolve in favor of the regular stacked one (figure 4d). Thus, there is a size effect for the formation of twins. Small {111} facets have a larger chance of forming a complete twinned layer.
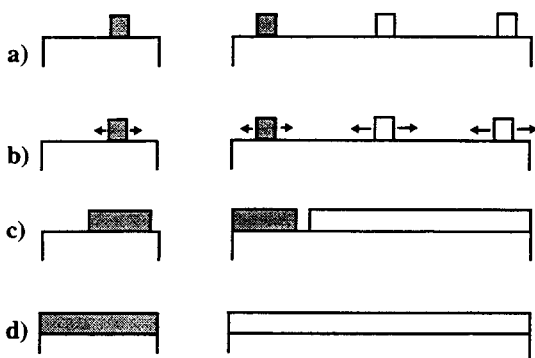

Figure 4. Different stages of growth of a small and a large {111} facet . The faces are placed in an environment where twins can be formed. The dark nuclei are twinned and the transparent ones are correctly stacked.

The effect of surface charge

If there was only a size effect on the formation of twins than the critical crystal size would decrease at higher driving forces, in other words, at higher driving force more twin planes would be formed. However, we examined {111} tabular crystals at higher driving forces and found no significant differences in the number of twin planes as judged from the shape of the crystals. Also, the ratio needle shaped/{111} tabular crystals did not significantly change at higher driving forces.

Therefore it is concluded that the critical crystal size for forming twins is not strongly dependent on the driving force. On the other hand, the driving force for which twins are formed is found to be rather critical. There seems to be a threshold driving force for which twins are formed. In our experiments this critical driving force corresponds to a temperature difference of some 128°C for AgCl and 133°C for AgBr.

A possible explanation for this could be the charge distribution for small crystals. This can give a higher surface supersaturation on the polar {111} faces and thus, increase the chance of forming twins.

A small crystal can have a net charge if both parallel {111} faces contain the same kinds of ions (silver or halide). If the size of the crystal is small enough there will be an interaction between both faces. The net charge must then be compensated and can result in a higher surface driving force. For large crystals these forces are too small to have influence on the surface driving force. Thus, smaller crystals can have more chance of forming a twin owing to the charge effect than was predicted only by the size effect.

The charge effect might also explain the differences in the number of twins formed for AgCl and AgBr. For the more ionic AgCl this charge effect would be more pronounced than for AgBr, due to the higher polarizability of Br^- as compared to Cl^-.

5. Conclusion

From the vapour both for AgCl and AgBr the same rich variety of morphologies appears as obtained for pure AgBr from precipitation. These are; cubic, {100} tabular, {100} tabular with (411) twinning, cubo-octahedral, needle shaped and {111} tabular crystals. It is concluded that {111} tabular crystals of pure AgCl can be grown without additives from the vapour phase.

The morphology classification of {111} tabular AgBr crystals grown from DMSO is also valid for the vapour phase grown ones. The examined {111} tabular crystals reveal that most twin planes were formed during the precipitation and that the chance of forming a twin plane during the growth is small. We observed a critical temperature difference, or driving force, required for forming twin planes. The minimal temperature difference required for twinning was for AgBr and AgCl almost equal. However,

the driving force had beyond this critical value no influence on the number of twin planes formed. Because the driving force was constant during the experiment the stability against the formation of twins on the {111} faces will be lower in the early stages of the growth process and dramatically increase during the growth process. This was explained by a size and charge effect.

The effect of crystal size explains that smaller crystals have a larger chance of forming twins than larger crystals. The effect of surface charge might explain the constant number of twin planes beyond the threshold driving force. The charge of the opposite {111} faces can have influence on the surface driving force of small crystals. There is also a difference in polarizability between Cl and Br and thus in the surface charge for AgCl and AgBr. This might explain the differences in number of twins formed in AgCl and AgBr.

Both for AgBr and AgCl we observed {100} tabular crystals at lower temperature differences than the critical temperature difference, or driving force, required for forming twin planes. Thus, the substep mechanism or the stacking fault mechanism are not able of explaining the growth mechanism of {100} tabular crystals grown from the vapour.

Acknowledgements

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