Direct Observation of Stacking Fault Structure in (111) Tabular Silver Halide Grains by High-Resolution Electron Microscopy

Samuel Chen, S. Jagannathan, R. V. Mehta, R. Jagannathan, and A. E. Taddei

Eastman Kodak Company, Imaging Research and Advanced Development, and Manufacturing Research & Engineering, Rochester, New York 14650-2151

Cross sections of (111) AgBrI platelets have been examined by low- and high-resolution transmission electron microscopy. They provide direct microstructural evidence for stacking fault arrangement between the internal twin boundary and the external grain surface. Their orientation relationship also provides insight into how (111) and (100) surfaces can coexist at the tabular-grain surface.

Journal of Imaging Science and Technology 42: 399–401 (1998)

Introduction

Silver halide (111) platelet crystals are the basic photonic detectors in photographic materials. The photographic properties of these materials can be widely varied by changes in the microcrystal preparation processes. The introduction of iodide into the AgBr lattice may enhance its photoresponse, but accompanying its incorporation into the fcc AgBr lattice, structural defects can form. It is now known that stacking faults[1,2] as well as dislocation networks[3] are possible structural defects found in (111) AgBrI, and transmission electron microscopy (TEM) is one technique well suited to probe the details of their internal microstructure.

Because (111) AgBrI platelets have the natural tendency to lie flat on their major tabular face, various plan-view TEM (and many other imaging-based) techniques have used this characteristic to probe for tabular surface features and internal defect microstructures with the probing electron beam approximately along the [111] direction. While this type of analysis is useful, it is limited to the observation of crystallographic defects that induce diffraction contrast to this viewing direction. Viewing in the orthogonal direction can provide complementary information, but at the cost of more elaborate sample preparation procedures. However, an in-depth understanding of most crystallographic defects requires such cross-section analysis, especially in this multiply-twinned material.[4,5]

The occurrence of stacking faults in AgBrI platelets has been a recent topic of interest. These are believed to be inclined planes extending throughout all the twinned variants,[1] and their removal is believed to be useful for certain photographic applications.[2] In this article we show both plan-view and microtomed cross-section data to reveal new insights into stacking fault occurrences. In addition, secondary microtwin segments have been found and high-resolution lattice images are able to provide evidence for the coexistence of (111) to nominally (100) surfaces on the tabular face.

Original manuscript received March 16, 1998

Experimental

AgBrI Platelet Preparation. High-aspect-ratio AgBr/AgBrI (core/shell) platelets were precipitated in aqueous gelatin solution according to the following procedure: nucleation of a pure AgBr core was carried out at 35°C by adding an aqueous solution of silver nitrate to approximately 0.086-M solution of sodium bromide containing ca. 0.2% bone gelatin. Subsequently, an $AgBr_{0.88}I_{0.12}$ shell was precipitated onto the pure AgBr core in the following manner. The gelatin concentrated in the suspension obtained from the nucleation step was increased to about To 0.6% and the temperature to 75°C. Additionally, silver nitrate, sodium bromide, and potassium iodide solutions were added to the suspension during which the pAg, i.e., –log[Ag^+], of the suspension was maintained at about 8.78. At the end of the growth step, the suspension was cooled to 40°C and the residual dissolved electrolytes were removed by a phthalated gelatin coagulation technique.[6] The final pH was adjusted to about 5.5 and pAg to about 8.30 at 40°C. The resultant platelets were found to have an equivalent circular diameter of ca. 2.94-µm. A representative plan-view TEM image of platelets obtained from this procedure is shown in Fig. 1.

TEM Analysis. For plan-view analysis, the diluted crystal suspension is directly deposited onto carbon-coated TEM Cu grids. For cross-section analysis, the above suspension was spin-coated onto an acetate support with additional gelatin and the resultant film was trimmed to a small size for cross sectioning. Using cryoultramicrotome, with cooling to about –110°C, thin sections (about 50-nm thick) were cut and floated off onto holey carbon films supported on molybdenum TEM grids. All TEM observations were carried out using a liquid-nitrogen-cooled holder, and high-resolution lattice images were taken at 200-kV using an instrument with a 0.28-nm point-to-point resolution. The combination of {111} and {002} lattice fringes in the image was sufficient to elucidate the orientation relationship of specific planes across the various defect boundaries in the AgBrI platelets.

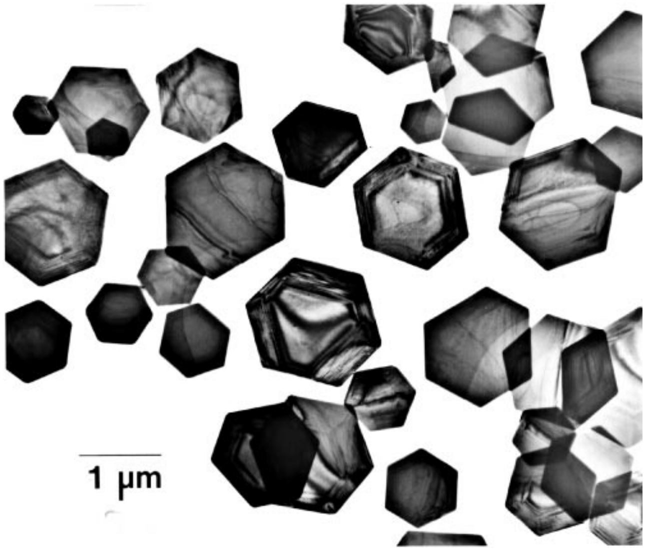

Figure 1. Plan-view TEM image of AgBr/AgBrI (core–shell) platelets used in cross sections.

Figure 2. Cross-section image of AgBrI platelet showing the existence of internal (111) twin boundaries. Secondary twin boundaries occasionally found in the upper (or lower) primary twin regions. They have now been detected in the middle twin region.

Results and Discussion

In plan-view TEM images, the outer shell region of all the $AgBr_{0.88}I_{0.12}$ platelets can exhibit three sets of black/white striation-like contrast fringes, which are irregularly spaced and run parallel to the platelet edges (Fig. 1). The intensity of these lines changes with sample tilt, and opposing pair sets exhibit zero contrast under two-beam $(\bar{2}20)$ dark field conditions. From these images, the Burgers vector of the stacking faults are calculated to be $[11\bar{2}]$ identical to that first determined by Goessen et al.[1]

Stacking fault microstructures were further analyzed from microtomed cross sections. Figure 2 is a representative TEM image of the cross section of a platelet showing two internal twin boundaries, running parallel to the major {111} tabular surfaces. In approximately 10% of the platelets obtained by this growth procedure, one or more secondary twin bands (inclined at an angle of 70° 32' to the primary twin plane) were detected and analyzed (Fig. 3). Detailed examination of the cryosections by TEM in conjunction with sample tilting revealed the presence of secondary twin bands only in the top or the bottom segments of the doubly twinned platelets, i.e., no secondary twins were observed in the middle segment. Also, there was no correlation between the position of the secondary twin bands in the top with those in the bottom segments.

The determination that these bands are microtwins was based on high-resolution lattice fringe patterns. Figure 4 shows a low-temperature high-resolution lattice image of a secondary twin band obtained with the incident electron beam aligned parallel to the $[1\bar{1}0]$ direction. The

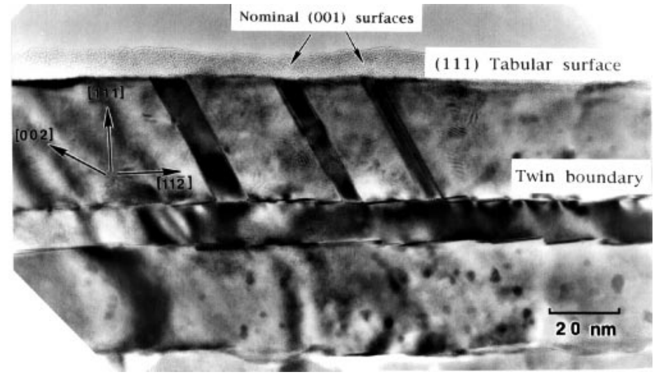

Figure 3. Cross-section image showing three secondary twin bands. Their external surfaces appear to be nominally (001) surfaces.

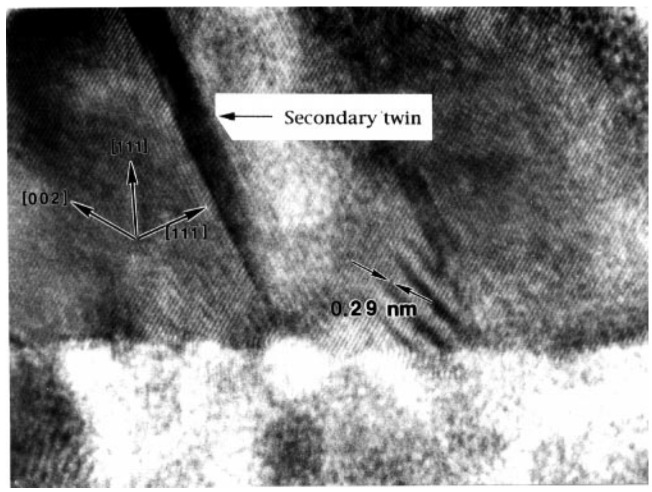

Figure 4. Low-temperature high-resolution lattice image of a secondary twin band. The secondary twinning occurs across the (111) plane inclined at 70° 32′ to the primary (111) twin boundary. The (002) spacing, as indicated, is 0.29-nm.

imaged lattice lines revealed secondary twin boundaries across the $(1\bar{1}1)$ planes. They also provide the geometrical orientation for the (002) planes in the primary twin relative to the (002)′ plane of the secondary twin. This relationship, when applied to the secondary twins, such as those in Fig. 3 suggests that the external surfaces of some of the secondary twin bands (see arrows in Fig. 3) can terminate with the low-index (001)′ planes. This tabular surface morphological evidence, supported by lattice plane orientation data, indicates that {111} and {100} planes can coexist at a growth front in AgX material.[7]

While such an inclined plane/twin boundary is one form of stacking fault to, their density (both within a given section and from section to section) is much too low compared to the density of black/white contrast fringes seen in all the AgBrI shell of plan-view images. Therefore, the stacking faults in plan-view images cannot correspond to only the inclined planes that fully traverse a given twin variant.

Instead, the cross-section experimental data suggest an alternative explanation. The major twin planes (parallel to the major {111} surfaces) appear to be segmented by a high density of kinks, producing a multiply-stepped twin boundary morphology (Fig. 3). Such kinks are dislocations and may have structural characteristics similar to those first described by Hamilton[8] and Sprackling.[9] These short twinning dislocation segments can exhibit stacking fault contrast fringes because the vertical displacement to the twin boundaries is accompanied by a Burgers vector shift of $\frac{a}{6}[11\bar{2}]$ in the (111) plane boundary. The presence of a high density of localized stacking faults on the twin boundaries in cross-section views would be consistent with the observed high density of black/white contrast fringes seen in plan-view images. It is of interest to note also that this alternative explanation may correlate with the experimental observation that Ag^{o} may preferentially localize on the twin boundaries (Hamilton[10]) or that such defects may preferentially trap Ag^{o} interstitials (Ohzeki, Urabe and Tani[11]).

We also point out that it is unlikely very thin secondary twin bands would go undetected due to any resolution limitation of the TEM. An atom packing analysis of the thickness of such secondary twin bands, confined within a major twin variant, indicates that once the twin is initiated, it must revert back to the major twin variant. This is necessary for the latter structure to continue in its lateral growth, in order to propagate the overall tabular grain morphology. Thus, the minimum thickness of the secondary twin band is three AgX layers, i.e., $3 \times (111)$ d-spacing, or ~1 nm. A structural defect of this size would be easily observed in most modern TEMs. Finally, note that microtwin bands can form within a twinned segment, but such a micro-twinned region can be locally confined and not force the tabular grain to grow into a different particle morphology, such as a two nonparallel twinned tetrahedral particles.[12,13]

Summary

Stacking faults in (111) AgBrI platelet crystals were examined by both plan-view and cross-section transmission electron microscopy. These defects are unlikely to be due to inclined planes fully traversing all the twin variants. Instead they appear related to the kinks in the internal twin boundaries. Furthermore, secondary twin bands can form within a major twin variant. From high-resolution lattice images, these bands can terminate at the (111) tabular surface with a nominal-(100) orientation.

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