

Improved Imaging SIMS Applied to Banded AgBr/AgBr_{1-x}I_x Tabular Grains

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Introduction

We describe the microanalysis of model AgBr-based tabular crystals with imaging secondary ion mass spectrometry (SIMS). A goal of this work is to address practical emulsion chemistry problems associated with the design of these crystals. Accordingly, using a custom-built scanning ion microscope, we acquired two-dimensional and subsurface elemental maps of multi-shell crystals with good sensitivity at spatial resolutions often at the 0.05 μm level. We measure the structure of the AgBr and AgBr_{1-x}I_x layers and rationalize these results within the framework of precipitation science. Interdiffusions between the layers or precipitation irregularities can be measured (this is particularly interesting for megalayered crystals, those containing two or more shells). Time permitting, we also present new results concerning the role of site directing compounds on the formation of AgCl epitaxial growths on tabular crystals.

This report is a continuation and amplification of previous work reported at this series of conferences.¹⁻³ Other laboratories, notably in Belgium, have also presented studies of this kind.⁴ The current results were obtained with an upgraded microanalytical instrument, permitting the analysis of more complex crystals. Previously, we used the technique to obtain sharp (50 nm, typically, 20 nm optimum) elemental images of dispersed single crystals⁵, adsorbates on single crystals⁶, stacked emulsion layers⁷, and experimental gelatin materials⁷. The custom-designed scanning ion microprobe SIMS instrument at the University of Chicago employs a focused Ga⁺ primary ion probe and a magnetic sector mass spectrometer for SIMS analysis. Compared to previous measurements reported to this Society, obtained with a different spectrometer, the performance (detection sensitivity) of this instrument has improved by a factor better than 20. Imaging SIMS is one of the best tools for subsurface chemical measurements: the procedure is relatively quick and does not require extraordinary sample preparation. Detection sensitivity in high-spatial-resolution images, especially of halides, can be better than 0.1%.

Experimental

Silver halide microcrystals of tabular shape were precipitated according to the pAg-controlled double jet technique. The crystals presented here have an annular concentric structure. Annular regions of nominally pure AgBr alternate with iodide-containing AgBr_{1-x}I_x shells. For nucleation, 50 ml each of 1M AgNO₃ and 1M KBr were jetted into one liter of a 1.5% gelatin solution (70°C, pAg = 9.5, pH = 5.0). To enlarge the nuclei, 250 ml of 4 M AgNO₃ and 250 ml of 4M KBr solutions were double-jetted into the reaction vessel. To produce the annular shells, 750 ml of 4M AgNO₃ and a mixture of 675 ml 4M KBr and 75 ml 4M KI solutions were added via double jets (the other growth parameters were held constant). These growth phases were followed by the usual flocculation and redispersion steps. The resulting crystals are 4 to 5 μm wide with an AgBr central core and surrounding AgBr_{0.9}I_{0.1} rings. For analysis, the gelatin was removed by enzymatic degradation and the crystals spread onto gold-coated glass slides. No gold was applied over the crystals. The samples were handled in safe light conditions at all times. We present results for the three core-shell-shell samples listed in Table 1.

Sample	Core	Ring 1	Ring 2
1	AgBr 1.05 mol	AgBr _{0.9} I _{0.1} 3 mol	
2	AgBr 0.05 mol	AgBr _{0.9} I _{0.1} 1 mol	AgBr 3 mol
3	AgBr 1.05 mol	AgBr _{0.9} I _{0.1} 3 mol	AgBr 3 mol

Table 1: Core-shell-shell emulsions presented here.

The samples were analyzed with an imaging scanning ion microprobe employing SIMS. This instrument is described fully elsewhere.⁸ Briefly, a low-current (~30 pA) primary ion beam (Ga⁺) is focused to a spot approximately 50 nm wide, for this experiment. While this spot is scanned over the sample surface, secondary ions are collected and analyzed with a magnetic sector mass spectrometer. Each detected secondary ion is recorded discretely (pulse counting) for further analysis. The resulting mass-resolved "maps" can be interpreted as the two-dimensional concentration distribution of the selected element. All maps were acquired with

512×512 raster scans in times usually much less than 105s. The maps contain a wide range of signal intensities that are difficult to reproduce photographically; details are also lost during the printing of this booklet. The SIMS signal originates from the top few monolayers of the sample. The ion beam also can be used to erode into the sample, uncovering underlying material. After erosion, subsurface SIMS maps can be obtained. The ion beam eventually etches and “melts” the crystals: deep (>100 nm) images may contain artifacts. The erosion depths given here are estimates based on known ion current doses and semi-calibrated sputter rates. No cryogenic procedures were used during SIMS analysis.

Results and Discussion

The microcrystals are clearly resolved with the improved SIMS instrument. Figure 1 is a Br⁻ SIMS image of sample 1, showing the quality of the preparation procedure. Figure 2 is an I⁻ map of the same area, after eroding approximately 17 nm into the crystals. This image is part of an extended erosion sequence, an effort to determine the crystal structure at several depths. As expected, we find the AgBr tabular cores rimmed by the iodine-rich AgBr_{1-x}I_x phase. Our precipitation conditions clearly favor lateral crystal growth. On the other hand, a weak I⁻ signal also originates from the surface of the nominally pure AgBr core. This implies that in addition to lateral growth there is crystal growth normal to the [111] face, but at a much slower rate. The result is a thin layer of AgBr_{1-x}I_x covering the AgBr core. This thin shell is not completely eroded from the two rightmost crystals (as evidenced by a moderate I⁻ signal from the core areas), implying that the shell thickness is not constant among crystals. Quantitative measurements of the image

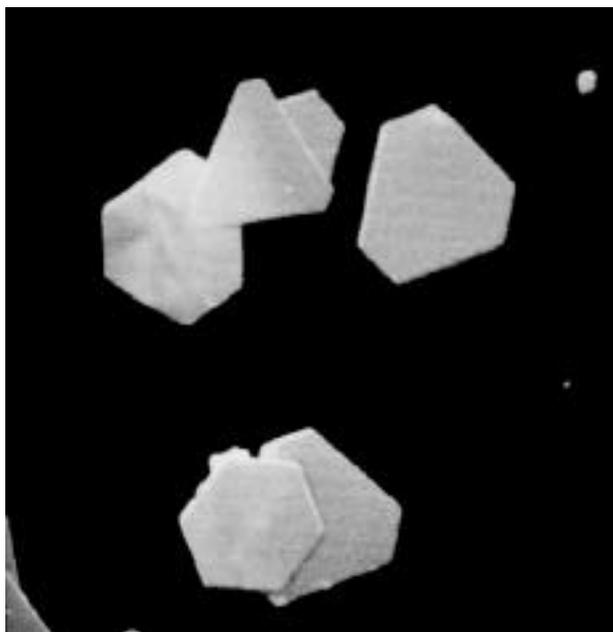


Figure 1: Br SIMS elemental distribution map of sample 1. 20 μm full scale.

data give the relative concentrations in the different structures; these results will be presented in a more extensive manuscript.

The excellent elemental/spatial resolution of the technique is exemplified by results from sample 2, figure 3. Here, the AgBr core is nominally only 1.2 mol% of the complete crystal, yet this core is still detected (the small black spot in the I⁻ map, upper right). The two crystals here have grown at very different rates: the AgBr core is very large in the lower crystal. Comparison of the two images proves that the AgBr_{0.9}I_{0.1} layer is within an enveloping AgBr shell. This can also be determined from maps obtained at a series of depths.

Sample 3 contains three phases of comparable fraction. Figure 4 is a Br⁻ map, giving the crystal morphology, and Fig. 5 is the corresponding I⁻ map. Ring 1 is rich in I, as expected. It is interesting that the outer ring 2, grown without I, actually has a significant I content (I_{ring 1}/I_{ring 2} ≈ 12).

Sample 2 furnishes additional evidence that the crystal growth normal to the main [111] face can not be neglected. Significantly, on the surface the I⁻ intensity ratio between the core and annular zones is ≈ 0.07 (I⁻_{surface}/I_{ring}; well within the detection sensitivity of the method) instead of 0.00. For sample 3, this ratio is larger, 0.16. Some signals from the core may be marred by atomic mixing that occurs during erosion and environmental contamination may affect the surface measurements.

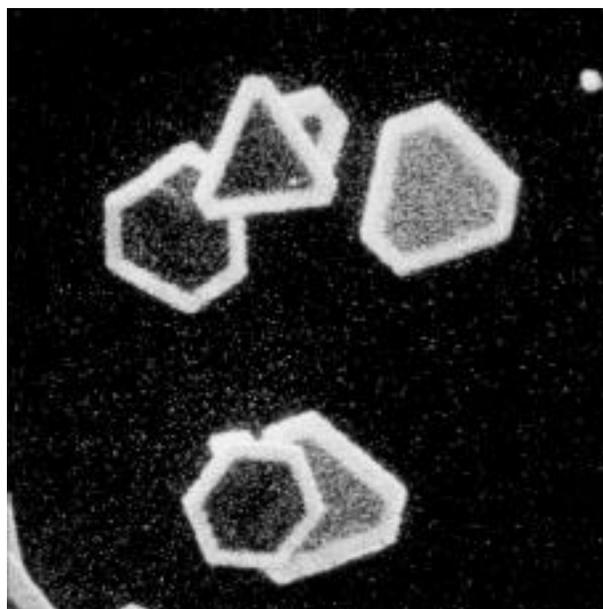


Figure 2: I SIMS image of the same area shown in Figure 1. The iodine-rich shell appears as a bright ring at the periphery of each crystal, as expected. Some I is also present on the surface in the central core area, especially on the two rightmost crystals. Approximately 17 nm prior erosion.

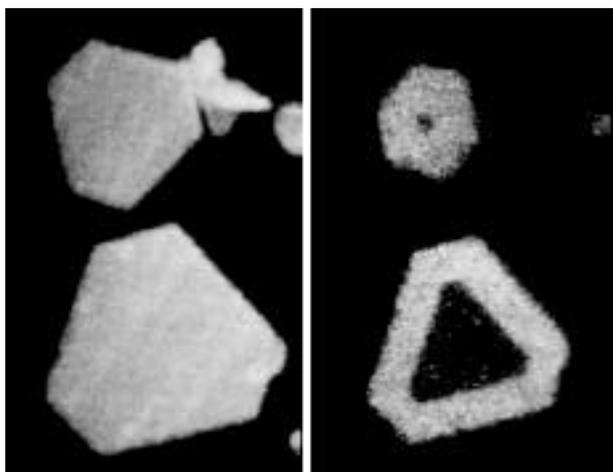


Figure 3: Br (left) and I (right) maps for one area of sample 2, after erosion to the core level. The I-containing shell is buried below the surface. A AgBr nucleus is visible in the I map, top crystal. Approximately 22 nm prior erosion, I map. Each map is 5 μm wide.

There is some variation in the structure of different crystals within the same sample. Under the precipitation conditions outlined above the crystals do not grow at constant rates. For all samples, we observe crystals that grew rapidly during the nucleation phase and others that grew much more slowly.

Imaging SIMS, in conjunction with X-ray diffraction (bulk measurements), electron microscopy (best for point measurements), and atomic force microscopy (surface measurements), is a valuable tool for gathering detailed information about the halide distribution in complex "designer" tabular grains. With SIMS, core-shell-shell

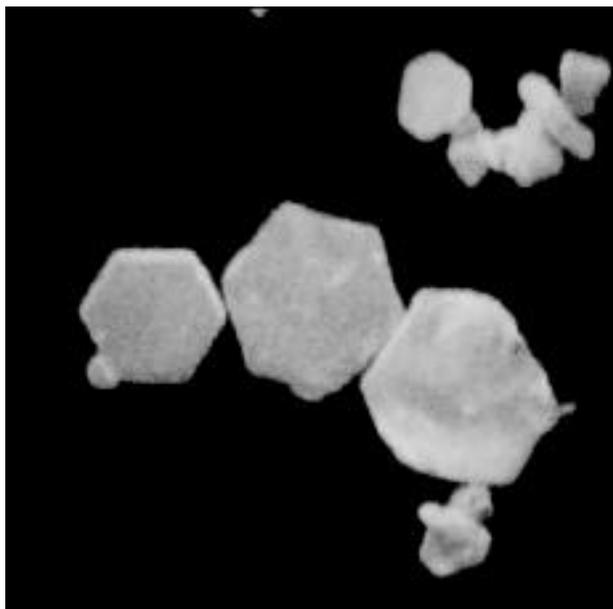


Figure 4: Br distribution in crystals, sample 3. The crystals are of varying size and form. 12 μm full scale.

precipitation protocols can be checked, and possible distribution problems, such as the presence of I in nominally pure AgBr, can be imaged. Realistically, shell structures of size about 0.1 μm can be investigated without difficulty: adequate "backup" resolution is available with the scanning ion probe technique. As a tradeoff, there is a loss in concentration sensitivity at these smallest dimensions. Studies of very complex crystals, with up to ten closely spaced shells, are in progress.⁹

References

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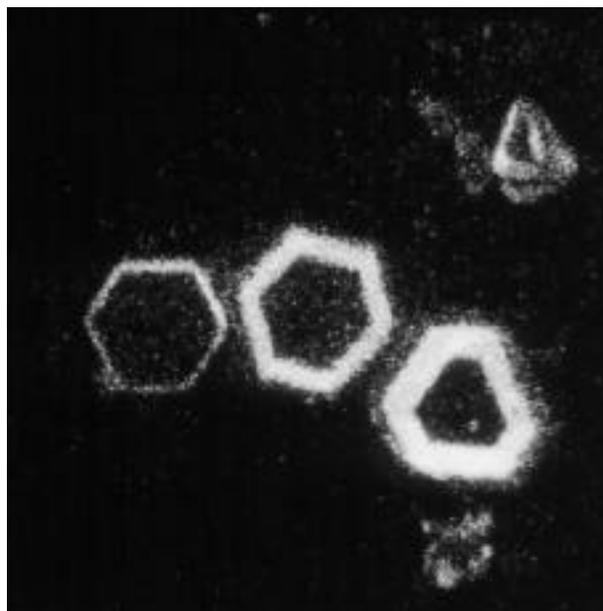


Figure 5: I map of the area presented in Figure 5, sample 3. The buried I-rich layer is clear but different in each crystal. I also originates from the core and outer shell areas. Approximately 34 nm prior erosion.