

Surface Analysis of Silver Halide Microcrystals by Imaging Time-of-Flight SIMS (TOF-SIMS)

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Introduction

The composition of the surface layer of silver halide microcrystals is essential for the final behavior of photographic materials as the latent image is formed at specific locations at the surface. During the last years, the amount of iodide (used to extend the absorption region and increase the intrinsic sensitivity of the material) in the surface layer is reduced. Instead of a homogeneous iodide distribution of several mole % throughout the entire crystal, global iodide concentrations of less than 1 mole % are used confined to a surface layer with a thickness of a few nanometers.

In this work Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is used to study the lateral and in-depth halide distributions in surface layers < 3nm. Overview images at lower magnification are used to check the homogeneity of the iodide distribution over the crystal population. With local image depth profiling, halide distributions for individual microcrystals from the same sample are calculated and compared.

Experimental

Instrumentation and Principle

The TOF-SIMS experiments were performed on a scanning ion microprobe TOF-SIMS III instrument (figure 1) developed at the University of Münster^{1,2}. This instrument is equipped with a fine focus Ga⁺ liquid metal ion source (LMIS) operating at 30 keV. The sample surface is bombarded with short primary ion pulses with a typical length of 100-200 ns. The primary ions penetrate the sample surface, losing their energy due to collisions with the sample surface (figure 2). This has two important consequences. First the primary ions will eventually be implanted at a certain depth (i.e. the penetration depth) in the sample

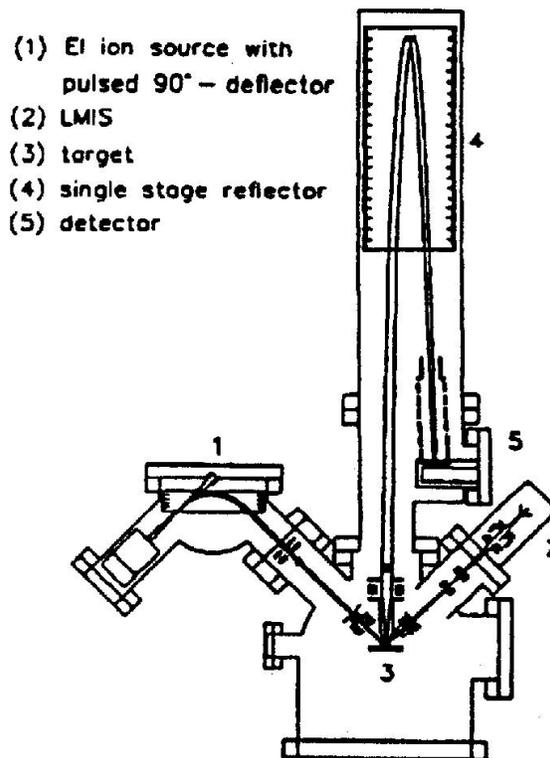


Figure 1. Schematic representation of the TOF-SIMS III SIMS instrument¹

after having lost all their energy. Consequently the sample surface will be modified³. On the other hand, there will be an energy transfer between primary ions and sample atoms, knocking these from their lattice positions and so initiating a collision cascade. The sample atoms are able to escape the solid when they have an energy higher than the surface binding energy of the sample surface and when they are close

enough to the surface (i.e. the information depth). The sputtered particles have a certain probability to become ionized during the sputtering process. The secondary ions are accelerated to 2 keV energy and are detected after an appropriate drift path through the TOF reflectron mass analyzer.

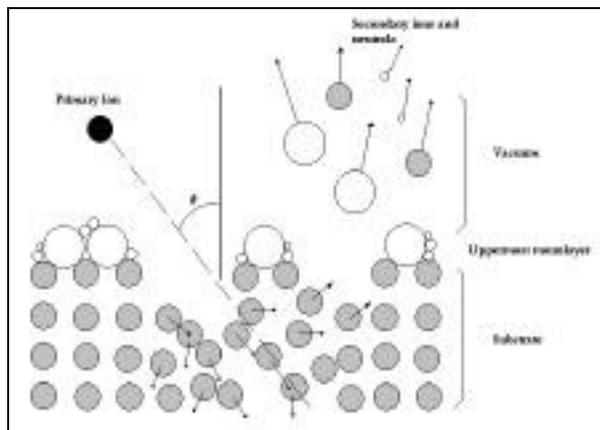


Figure 2. Particle emission from a surface after excitation with primary ions of keV energy

The information depth in TOF-SIMS is confined to a few monolayers² due to the combination of the low primary ion dose ($< 1E15$ ions/ cm^2 for one scan) delivered by the pulsed ion gun and the high transmission of the TOF reflectron mass analyzer.

Analyzed Samples

Tabular Ag(Br,I) and cubic Ag(Cl,I) crystals with iodide conversion layers at the surface were prepared with the double jet precipitation method. The global iodide concentration in each sample is < 1 mole %. The average lateral dimensions of the silver halide microcrystals is 0.8 and 0.65 μm , respectively. The studied emulsions are diluted with water and degelled. A drop of this solution is placed on a piece of polished silicon to transfer the crystals into the TOF instrument. It is evident that all manipulations and experiments were performed under the appropriate darkroom conditions.

Analysis Procedure

For each emulsion the following approach was used. First secondary ion imaging was performed at low magnification (the beam was rastered over fields ranging from $15 \times 15 \mu m^2$ to $25 \times 25 \mu m^2$) to visualize the distribution of the different halides over the crystal population. In contrast with magnetic sector or quadrupole mass spectro-meters, TOF analyzers offer the advantage of quasi simultaneous detection of all masses without further sample consumption. In this way the images of the different imaged halide distributions originate from the same "depth" and can be compared.

In a second step local image depth profiling (at higher magnification) was used to calculate and compare different

halide intensity ratios for individual microcrystals. These ratios yield at present only semi quantitative results and cannot yet be converted to concentrations because extensive studies of the differences in ionization probability of the halides under Ga^+ bombardment have not yet been performed.

Results and Discussion

Tabular Ag(Br,I)

Secondary ion images of two emulsions with different iodide conversion layers were acquired.

Overview images of the first sample (global iodide concentration of 0.6 mole %) reveal a homogenous iodide conversion layer for all microcrystals (figure 3). Then the primary ion density was increased to $1E15$ ions/ cm^2 /scan so that approximately one monolayer could be removed during one scan of the microcrystal surface. The subsequent images showed a continuous decrease in iodide intensity during the first 8 monolayers. This decrease in iodide intensity is compensated by an increase in bromide intensity. With local area image depth profiling the different $I/(I+Br)$ ratios for the different images were calculated.

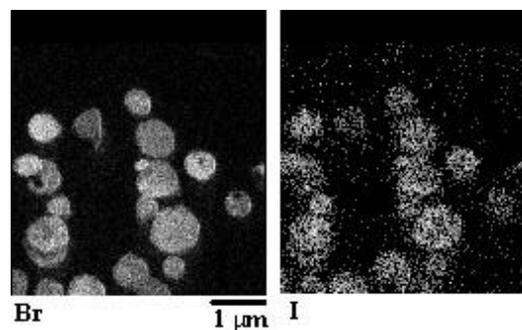


Figure 3. High resolution secondary Br and I TOF ion images. Imaged field = $5 \times 5 \mu m$. Measured lateral resolution is ca. 70 nm

In the overview images of the second sample (global iodide concentration of 1.8 %) a different distribution is visible (not shown). Within the crystal population, some microcrystals with highly enriched (but not pure, as also bromide was detected) iodide surface layers are present. In combination with local image area depth profiling (figure 4) two different types of microcrystals in this sample could be identified.

Type 1 in figure 4 represents the microcrystals with the highly enriched iodide surface layer, type 2 represents the majority of the crystal population with a lower iodide content in the surface layer. Apart from the difference in concentration, also a difference in thickness of the surface layer was observed (not shown).

The lateral resolution of all the secondary ion images was measured with computer generated line profiles in the images in different directions and is about 70 nm.

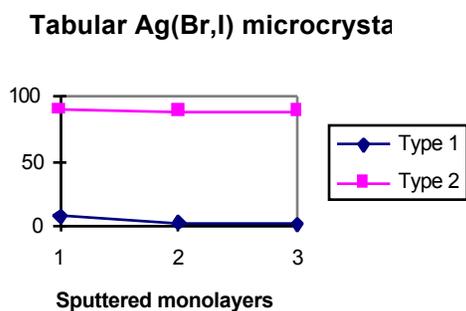


Figure 4. Local image depth profiling of the two different types of microcrystals found in the second sample

Cubic Ag(Cl,I) Microcrystals

Figure 5 shows high resolution secondary chloride and iodide images of cubic Ag(Cl,I) microcrystals (global iodide concentration of 0.4 %, lateral dimension 0.65 μm). The non equivalent angles of incidence of the primary ions on the different sides of the crystal result in a different secondary ion yield for different sides of the cube. This creates a three dimensional effect that makes the cubic morphology clearly visible in the image.

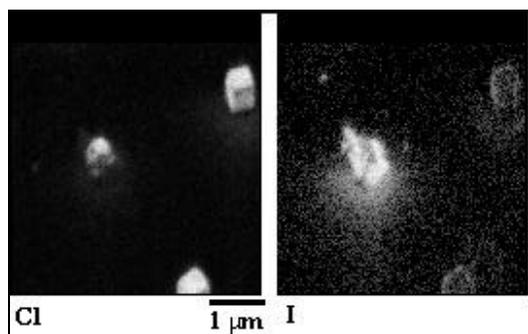


Figure 5. Scanning ion images of Cl and I of cubic Ag(Cl,I) microcrystals. Clear differences between the iodide enrichment of the different crystals can be distinguished

One cubic crystal shows again a clear difference in iodide enrichment at the surface (cfr. tabular Ag(Br,I)). The

enriched surface layer is very irregularly shaped. For the other cubic crystals complementarity between chloride and iodide images can be observed. Higher iodide contents are detected at the edges and corners of the cubic crystals.

Again the lateral resolution of these images was determined with line profiling and appeared to be 70 nm.

Conclusion

Feasibility studies on tabular and cubic silver halide microcrystals demonstrate the power of TOF-SIMS for the determination of the different halide distributions in the surface layer. High resolution scanning ion images with lateral resolutions of 70 nm were used to characterize surface layers with a thickness < 3nm of crystals with global iodide concentrations of ca. 1 mole %. For these thin layers, the results are clearly superior than the ones obtained with dynamic SIMS analysis.^{4,5,6} With the developed analysis procedure, individual microcrystals in one sample can be studied and compared.

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