

Relative Quantification of a Transition Metal Dopant in a Polycrystalline Matrix by TOF-SIMS

Overview: TOF-SIMS is not typically viewed as a quantitative analysis technique due, in part, to the fact that the secondary ion yield changes as a function of matrix composition. However, it is desirable to use time-of-flight secondary ion mass spectrometry (TOF-SIMS) for quantitative analysis applications due to its inherently high abundance sensitivity and trace-level detection limits. Quantitative analysis is possible and is routinely achievable in any of the following concentration ranges with appropriate reference materials: < 1 ppm – 0.5 at.%, 0.5 – 5.0 at.%, and > 5.0 at.%. A difficulty is sometimes encountered when analyzing polycrystalline solids because the ion yield changes with the crystallographic orientation of each grain. In this Note we use the PHI *nanoTOF* to illustrate the ability to perform quantitative analysis across multiple grains of an In-doped, polycrystalline CuS specimen. The In dopant is present throughout the polycrystalline CuS matrix having a nominally uniform concentration profile. The ability of TOF-SIMS to visualize chemical information in a spatially resolved manner will be utilized for the purposes of demonstrating quantitative equivalence across multiple grain orientations. The In concentration is not specified here because the intention is only to demonstrate that signal variation across multiple grains and twinning boundaries is easily accommodated in the effort to produce quantitative results.

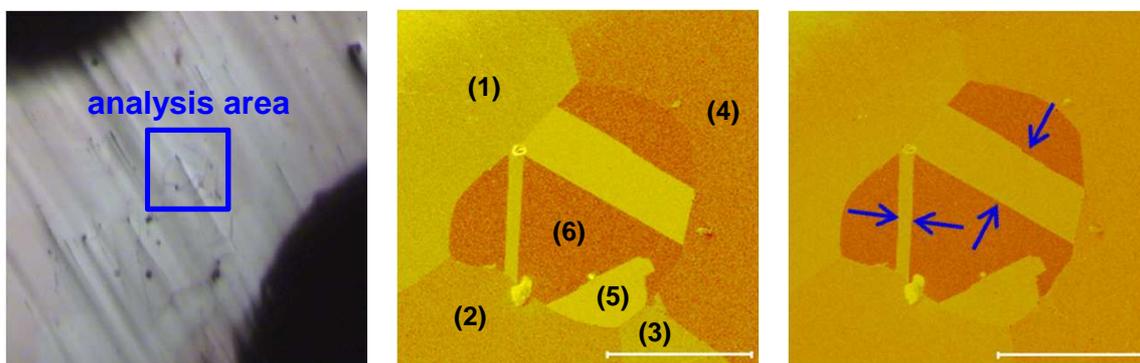


Figure 1. Images of the In-doped CuS metal surface after surface cleaning by Ar⁺ sputtering at 5 keV. (LEFT) Optical image at the analysis position. The approximate analysis area is identified. (CENTER) Total ion image (+SIMS) of the CuS grains within a 250 μm x 250 μm field-of-view (the marker is 100 μm). Six individual grains are identified. (RIGHT) Total ion image (-SIMS) of the CuS grains within a 250 μm x 250 μm field-of-view (the marker is 100 μm). Two sets of twinning boundaries within the central grain are identified by blue arrows.

Experimental: The In-doped CuS sample was introduced for analysis in the as-received state and an area of the surface was sputter-cleaned prior to analysis using 5 keV Ar⁺ ions. All TOF-SIMS measurements were made on a PHI TRIFT V *nanoTOF*. A 30 keV Au⁺ primary ion beam, operating at a DC current of 100 pA, was used to acquire chemical images of the surface in both the positive and the negative secondary ion polarities. Analysis was performed with a 150 μm x 150 μm field-of-view or a 250 μm x 250 μm field-of-view, in each case having a 256 pixel x 256 pixel digital raster. The primary ion dose was maintained well within the static limit, i.e. ≤ 2.9x10¹¹ Au⁺/cm², for each analysis. A raw data stream file was collected to allow full post-acquisition evaluation (i.e. retrospective analysis) of the data.

Results: An optical image of the metallographically polished and sputter-cleaned CuS sample, and the corresponding TOF-SIMS total ion images at 250 μm x 250 μm fields-of-view, are shown in Figure 1. The total ion images reveal several grains of the polycrystalline CuS sample. Additionally, the central grain encompasses two twinning boundaries. The twinning boundaries join at a common point where a particle is observed. This particle is likely a residue of mechanical polishing, and it is a reasonable assumption that the twinning boundaries were produced during mechanical polishing.

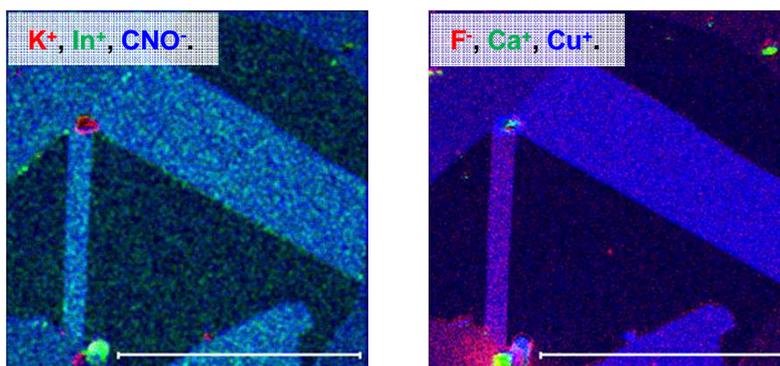
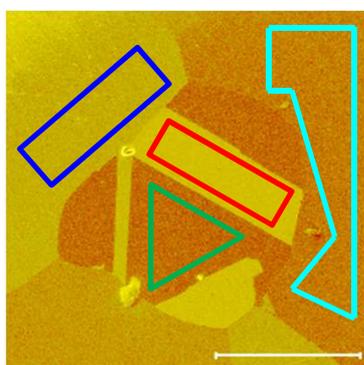


Figure 2. (LEFT) False-color overlay of K^+ (39 m/z; red) from the polishing compound residue, the In^+ dopant (115 m/z; green), and the CNO^- fragment (42 m/z; blue) from the polishing compound residue. (RIGHT) False-color overlay of F^- (19 m/z; red) and Ca^+ (40 m/z; green) from the polishing compound residue, and Cu^+ (63 m/z; blue) from the CuS matrix. The field-of-view is $150 \mu m \times 150 \mu m$, and the marker is $100 \mu m$. Note that the overlay images are composed of ion images from each secondary ion polarity and are in perfect registry.



ROI	color	Cu/In ratio
1	red	288
2	green	271
3	lt. bl.	295
4	dk. bl.	285
	Average	285
	RSD	9 (3.2%)

Figure 3. (LEFT) Total ion image (+SIMS) of a $150 \mu m \times 150 \mu m$ field-of-view from the CuS specimen with several grains identified for semiquantitative comparison. The grains identified for comparison have greatly differing total ion signals, and a set of twinning grains is also selected for comparison. (RIGHT) The tabulated Cu^+/In^+ ratios from each of the identified regions-of-interest (ROIs). Independent of the orientation-related ion signals, the ratio of the integrated counts of Cu^+ to In^+ have a statistically small deviation and reveal that quantitative analysis is feasible.

Several elemental and fragment ion images are overlaid in false color and presented in Figure 2. The F^- , K^+ , Ca^+ and CNO^- components arise from polishing compound residue. The Cu^+ matrix and In^+ dopant components are also shown. The instrument was calibrated prior to analysis, so the ion images from each secondary ion polarity are in perfect registry. The dual polarity imaging provides a useful tool when evaluating the spatial correlation or anticorrelation of chemical components. Notice that the particle at the junction of the twinning boundaries is comprised of K^+ and Ca^+ ; this observation confirms that the twinning was induced during mechanical polishing.

The main objective is to determine whether or not the relative In concentration is equivalent across different grains. The Cu^+ and the In^+ signals appear to vary with the total ion signal, and these signals appear to vary with each crystallographic orientation of the Cu matrix. It is important to recognize that the differences in ion signal across the various grain orientations is a well known ion channeling effect (i.e. a "SIMS effect") that can be corrected with normalization. In TOF-SIMS, the simplest way to achieve normalization is by a ratio to a common ion signal. Since it is known that the Cu composition is constant, a ratio of In^+ and Cu^+ will provide a reliable normalization of the In composition across the various grain orientations.

Several regions-of-interest (ROIs) are identified in the total ion image shown in Figure 3. There are four grains selected, including two grains across a twinning boundary, having large differences in signal intensity. The tabulated data is also given in Figure 3. The relative standard deviation (RSD) of the measurements is 3.2% which is well within the attainable repeatability limits for typical TOF-SIMS measurements [1].

Conclusion: Relative quantification was demonstrated with the PHI TRIFT V *nanoTOF* on an In-doped CuS polycrystal by comparing the Cu⁺/In⁺ ratio. It was demonstrated that, while the total ion yield changes across different crystallographic orientations of the polycrystalline matrix, the relative concentration of each grain may be ascertained with high confidence. It was also demonstrated that normalization of secondary ions signals may be used to eliminate the ion yield variations. With an appropriate concentration standard the abundance of indium in each copper grain may be determined; however, as stated in the Overview, the intention here was only to demonstrate that signal variation across multiple grains and twinning boundaries may be accommodated in the effort to produce quantitative results.

The high sensitivity of TOF-SIMS enables detection of species having a low abundance, and the parallel detection capability allows full molecular and isotopic characterization of the matrix chemistry. A particular strength of the PHI *nanoTOF* as it relates to trace abundance sensitivity for quantitative analysis is the TRIFT mass spectrometer which is designed for maximum secondary ion transmission and the lowest spectral background. Superior transmission is achieved by spatial focusing of the secondary ions in the mass spectrometer to minimize the ion losses, and superior signal-to-background is achieved by the automatic filtering of metastable decay species that give rise to spectral background noise.

Acknowledgements and References:

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