Determination of Trace Element Distribution in Cr Sputter Targets by 3-d SIMS

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Secondary ion mass spectrometry (SIMS) is a powerful and effective approach for the characterization of the lateral and three dimensional distribution of trace elements in solids. The investigation of the trace element distribution in two chromium samples which were produced by sintering process and hot isostatic pressing is reported. By applying two-dimensional (2-d) SIMS, it is shown that in both samples the gaseous impurities O and N diffuse to the grain boundaries. Three-dimensional (3-d) SIMS measurements illustrate that there are major differences in the spatial distribution of trace elements.

1. Introduction

The microelectronics industry with its permanent search for miniaturizing and higher speed is the driving force for the development of high purity materials. Refractory metals are frequently used for metallization of electronic devices. This is due to their physical characteristics like low resistivity and high temperature stability. They derive their qualities not only from the concentration but also from the three-dimensional distribution of bulk impurities [1]. Chromium sputter targets can be produced by sintering process or hot isostatic pressing (HIP). During the hot isostatic pressing process, the raw material is encapsulated in steel containers and by applying high pressure and high temperature a homogeneous and compact material is formed. In the sintering process the chromium powder is first compressed at room temperature and then heated to 2/3 of the melting temperature. In an additional step the material is rolled for compressing and shaping into its final form.

In the flat panel display manufacturing process those two kinds of sputter targets are competition products used for the metallization of the black matrix and color filters. That is the reason why the characterization by means of GDMS and SIMS is of technological interest. Glow discharge mass spectrometry (GDMS) has emerged as a standard technique used for the quantitative bulk analysis of contaminants in the µg/g range. To achieve two- and three-dimensional elemental distribution information SIMS is a common technique supporting microelectronics technology. SIMS has analytical characteristics such as high detection power (ppm range) and the possibility of detecting all elements including hydrogen. To obtain lateral images a primary ion beam homogeneously illuminates the sample by scanning at about 100 frames per second over an area of typically 500 x 500µm. A point to point representation without loss of lateral position information is achieved by a set of ion lenses. Each pixel on the sample is imaged directly on a fluorescent screen and recorded by a CCD camera. The typical lateral resolution is 1µm. The spatial elemental distribution is achieve by creating layer by layer images as the primary ion beam sputters into the sample. 3d-SIMS can be seen as combination of imaging mode and depth profile analysis. The depth resolution is about 20 nm.

2. Results and Discussion

Figures 1 and 2 illustrate the grain boundary enrichment of the highly diffusable impurities O and N in both chromium samples. Chromium was recorded in order to detect the grain structure. This is possible because the different orientation of the grains influences the sputter coefficient and therefore the intensity of the secondary ion signal. Nitrogen is represented by CN because of the higher sensitivity of this mass compared to N. It was confirmed that no spectral interferences occurred. As result of this experiment we can see in both samples the same tendency of oxygen and nitrogen to enrich at the grain boundaries.

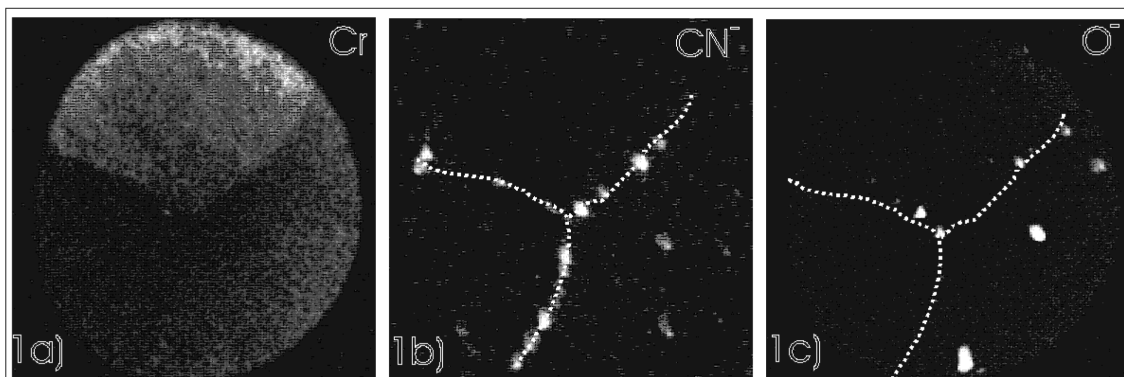

Fig. 1: SIMS images (150 x150µm) of the HIPped chromium sample (100nA Cs^+ primary ions).

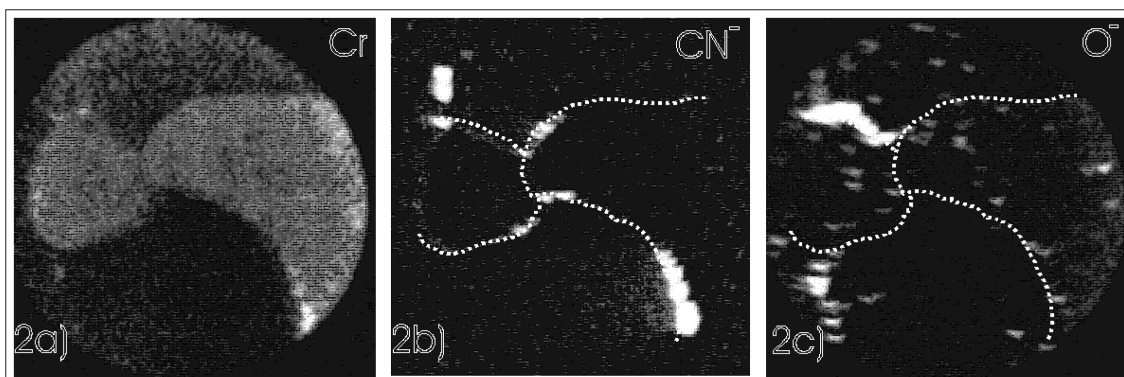

Fig. 2: SIMS images (150 x150µm) of the sintered chromium sample (100nA Cs^+ primary ions).

Fig. 3 to 6 represent the three-dimensional distribution of the elements Na, Ca, O and Cl. Two kinds of primary ions were used, O_2^+ to record the distribution of the metallic impurities and Cs^+ to investigate electronegative trace elements (O, F, Cl, S, CN^- for N).

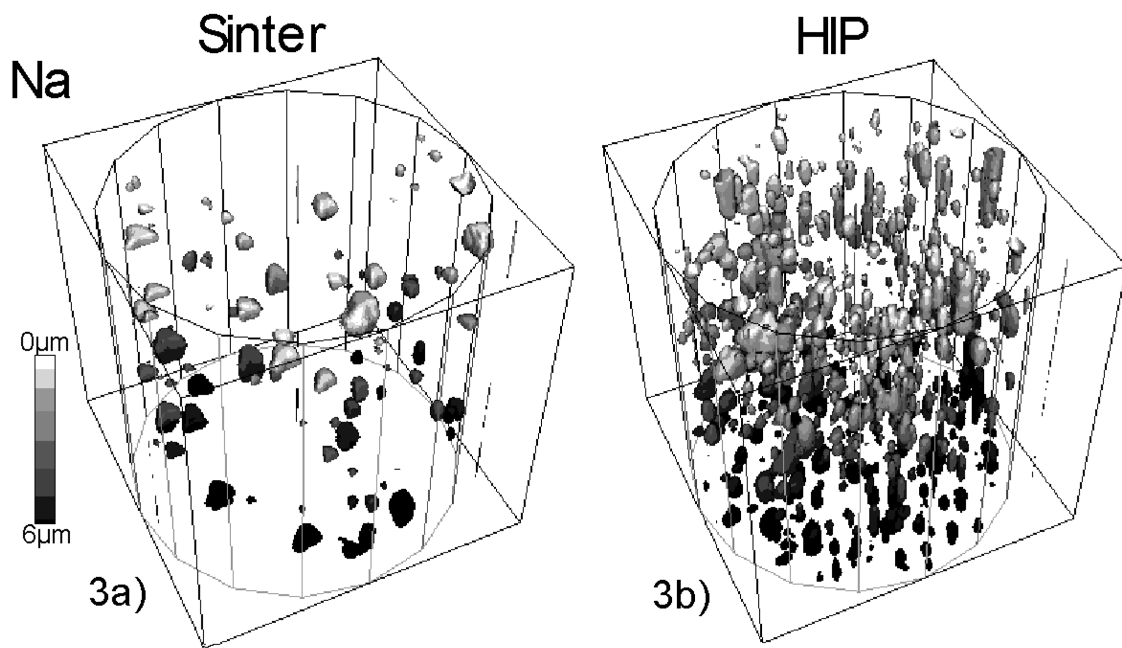

Fig. 3: 3d- images, left from sintered chromium, right from HIPped chromium: Na distribution (O_2^+ PI, 2µA, 150 x 150 x 6µm)

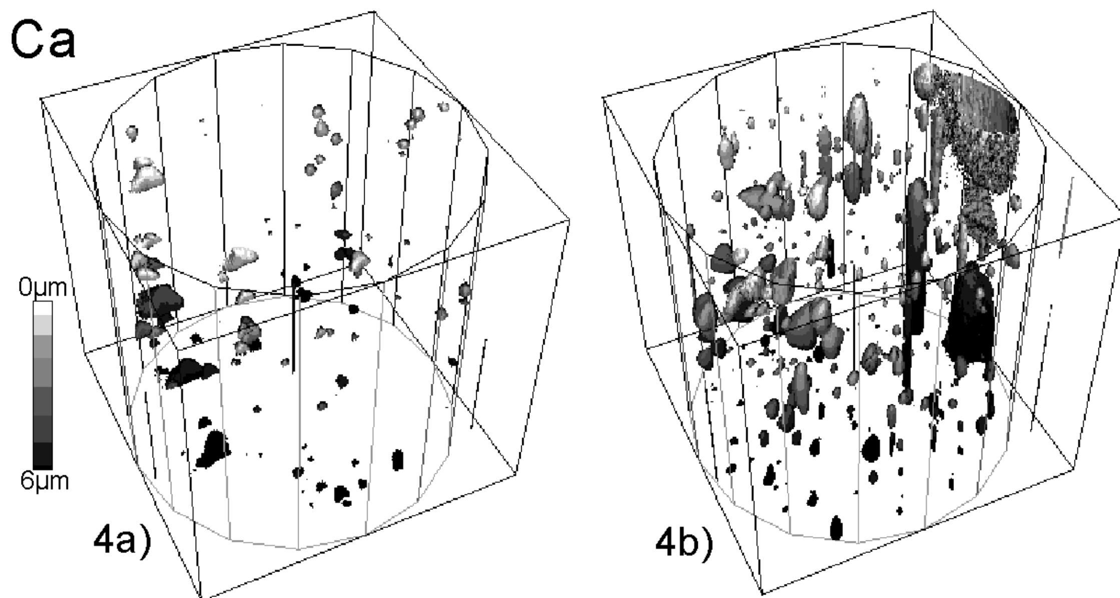

Fig. 4: 3d- images, left from sintered chromium, right from HIPped chromium: Ca distribution (O_2^+ PI, 2µA, 150 x 150 x 6µm)

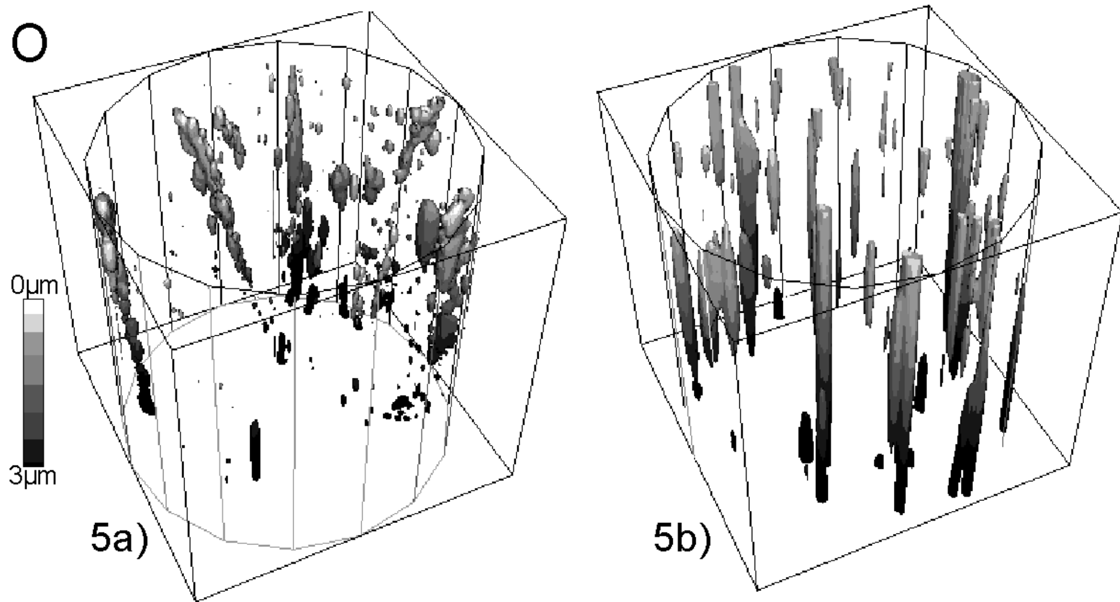

Fig. 5: 3d- images, left from sintered chromium, right from HIPped chromium: O distribution (Cs^+ PI, 50nA, 150 x 150 x 3µm)

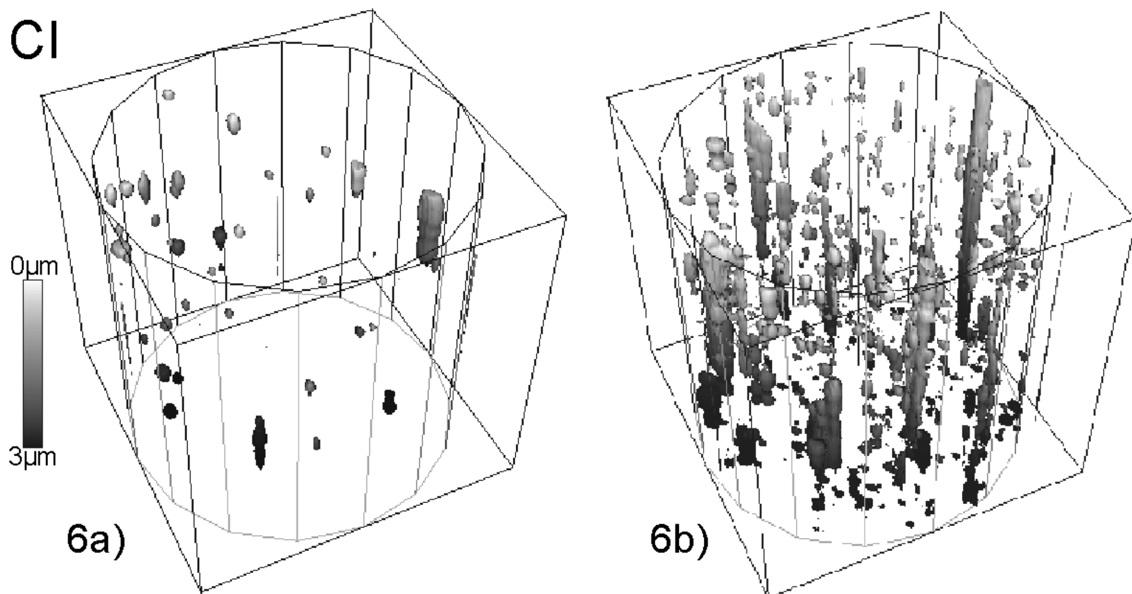

Fig.6.: Cl distribution (Cs^+ PI, 50nA, 150 x 150 x 3µm)

To obtain quantitative information GDMS bulk analysis was applied, which indicated that the average concentration of impurities is significantly higher in the HIPped chromium. The spatial distribution of trace elements is also important for the sputter deposition of the metal, because inhomogeneously distributed contaminants result in particle emission during the sputter process [2]. For the visualization of the obtained analytical data we used isosurface representation, that means that only those volume elements are drawn which correspond to an assigned intensity. 15 different element distributions were examined, 4 of them are presented. Fig. 3 and 4 show differences in the sodium

and calcium distribution. In the HIPped sample, a large amount of small precipitates occur whereas the sintered chromium shows fewer precipitates with similar volume. In the calcium image of the hot isostatic pressed chromium a large precipitate was detected whereas the sintered sample seems to be less contaminated and more homogeneous. Figure 5 illustrates the distribution of oxygen. Specially the grain boundary enrichment is better visible than in the 2d images (Fig.1.c and 2.c). The chlorine distribution (Fig.6) also exhibits major differences between HIPped and sintered chromium.

3. Conclusion

Different produced sputter targets result in different concentration and distribution of contaminants. Summarizing it can be said that sintered chromium is more homogenous and less contaminated, which can be explained by the ability of the trace elements to evaporate during the production process. SIMS supports microelectronics as well as metallurgical industry in order to optimize manufacturing processes and properties of materials.

References

[1] P. Wilhartitz, R. Krismer: “3d SIMS analysis of ultra high purity molybdenum and tungsten“, Fresnius J. Anal. Chem.(1995) 353: 524 – 532

[2] H. Hutter, C. Brunner, P. Wilhartitz: “3d characterization of trace element distribution in chromium”, Mikrochim. Acta 122, 195-202(1996)