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# COMPARISON OF TEXTURE IN COPPER AND ALUMINUM THIN FILMS DETERMINED BY XRD AND EBSD*

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## ABSTRACT
X-ray diffraction (XRD) and electron backscatter diffraction (EBSD) are commonly used to perform texture analysis of thin films. However, due to principle differences in data acquisition these techniques can yield disagreeing results. In this paper, we aim to highlight possible error sources with given examples for aluminum and copper thin films.

## INTRODUCTION
Texture in materials has a large influence on many properties of thin films; it is customarily determined by neutron or X-ray diffraction by measuring pole figures and evaluating orientation-distribution functions (ODF) [1]. X-ray diffraction (XRD) has been the primary method for the characterization of texture for many years. Recently, alternative techniques for localized measurements have been developed, such as electron backscatter diffraction (EBSD). EBSD is a highly flexible method to measure grain sizes, grain size distributions and orientation maps [1][2], in order to bring the characterization of texture to the nanoscale level.
In this study, we compared measurements taken with XRD and EBSD for several selected cases of aluminum and copper thin films. We found that results obtained by both methods do not necessarily agree for the same sample. In the present paper, we highlight some possible sources of error and differences between these two techniques.

## EXPERIMENTAL DETAILS
*X-RAY DIFFRACTION*
A 2-circle X-ray powder diffractometer cannot give full information about the sample texture. For a closer examination of preferred orientations in a sample it is necessary to obtain pole figures, using a 4-circle goniometer. During a scan of this type (Fig. 1a), the sample normal is tilted outside of the diffraction plane (tilt angle $\Psi$, often also referred to as $\chi$) for a given Bragg reflection and rotated about the axis normal to its surface (rotation angle $\Phi$). The stepsize for $\Psi$ and $\Phi$ is typically 5°. In this way, the intensity of a particular Bragg reflection is measured for pairs of $\Psi$ and $\Phi$ at a fixed $\theta$-$2\theta$ position and is normally presented as a direct pole figure. By combining several (for cubic crystal symmetry at least three) direct pole figures of independent crystallographic orientations, an indirect (or inverse) pole figure can be calculated (Fig. 2). We performed measurements using a commercial 4-axis diffractometer at a voltage of 45 kV and a current of 40 mA. During the measurement the sample was tilted to 90° out of the diffraction plane and rotated 180° about the surface normal. Raw data were corrected for background

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intensity, defocusing and absorption (a more complete explanation of necessary corrections can be found elsewhere [1]). Pole figures were calculated using the a freely available software [3].

*ELECTRON BACKSCATTER DIFFRACTION*

The EBSD technique can be used to obtain both sizes and orientations of grains in a sample simultaneously. An advantage of EBSD over XRD is the ability to obtain measurements at a much smaller scale and to detect weak textures. During an EBSD measurement the sample was tilted 70° with respect to the incident electron beam (Fig. 1b). The surface was then scanned in a raster with an electron beam within an area of typically 20 μm × 20 μm. The diameter of the sampling volume defines the lateral resolution of the method, 40 nm – 50 nm in case of copper at 20 kV, with the smallest possible stepsize of 10 – 20 nm. Because of the steep angle of incidence and the limited penetration depth of electrons, the beam penetrates only a small distance (10 – 50 nm for copper) into the sample [4]. The primary electrons of the incident beam undergo very slight energy losses and then are inelastically scattered in all directions. These primary electrons can now be once more elastically scattered by sets of lattice planes, thus forming cones that are detected on a phosphor screen. The intersections of the rims of these cones with the screen result in a geometrical pattern of so-called Kikuchi bands. These images were automatically detected by a low-light CCD camera. With the help of a Hough (or Radon) transform, the pattern was indexed in real-time by commercially available image processing software that calculates the crystal orientation for each scanned spot. In this way, the instrument was able to detect not only full zone axes (intersections of Kikuchi bands), like [100] or [110], but also orientations at an arbitrary point in between. These data allowed for a number of further calculations: direct and inverse pole figures (Fig. 2) could immediately be generated, as well as a color-coded surface orientation map, providing images that make the size and shape of grains on the surface visible. Based on the collected data, it was also possible to statistically analyze grain size [2][5].

*COPPER SAMPLES*

Thin films of copper were grown by electrodeposition on single crystal Si (001) substrates with the native oxide layer of the wafers chemically removed by dilute (8 volume % conc.) hydrofluoric acid. Seed layers of copper with a thickness, *t*, of about 30 nm were thermally evaporated onto the substrate, serving as an anode in the plating process. However, thermal evaporation may have the undesired side effect that seed layers grown with this method will have a higher surface roughness than the substrate itself. As a result, thinner electroplated layers were also rough and problems with EBSD imaging arose, because the uneven surface had areas that could not be accessed by the electron beam, causing the image quality to drop. Hence, to achieve a smooth surface the seed layers of additional samples were grown by sputtering.
Samples were grown with a plating time of four minutes and a current density of 20 $mA/cm^2$, yielding films of about 4 μm in thickness. The solution was agitated by humidified argon gas at low pressure. To prevent surface oxidation, the samples were kept in a dry-box when not in use for measurements. Still, due to the high affinity of copper for oxygen, the oxidation process could not be completely stopped. Therefore, before EBSD measurements, the samples were cleaned with acetone in an ultrasonic bath followed by 10 seconds in dilute hydrofluoric acid (8 % volume conc.). During electroplating, conditions such as metal-ion concentration, additives and solution temperature were kept constant for all samples. Samples with grain size around 1 μm to few μm were desired for our examinations. Current density, solution agitation and plating time were varied to achieve this grain size. For example, a higher current density yields an

increased number of grain seed points on the substrate. This parameter and the agitation of the solution influence the rate of material transport towards the anode, because the region in front of the substrate is depleted of metal ions faster for higher current densities [6]. To keep grain growth slow, the solution agitation was kept at a low level to replenish the metal ion concentration near the substrate at a controlled low rate. Other copper samples included thin films from rolled copper foil (thickness ~5 μm).

*ALUMINUM SAMPLES*

Thin films of aluminum with a thickness of about 1 μm were sputtered on single crystal Si (001) wafer substrates. The sputtering process yielded highly textured samples with a smooth surface that were suitable for EBSD measurements.

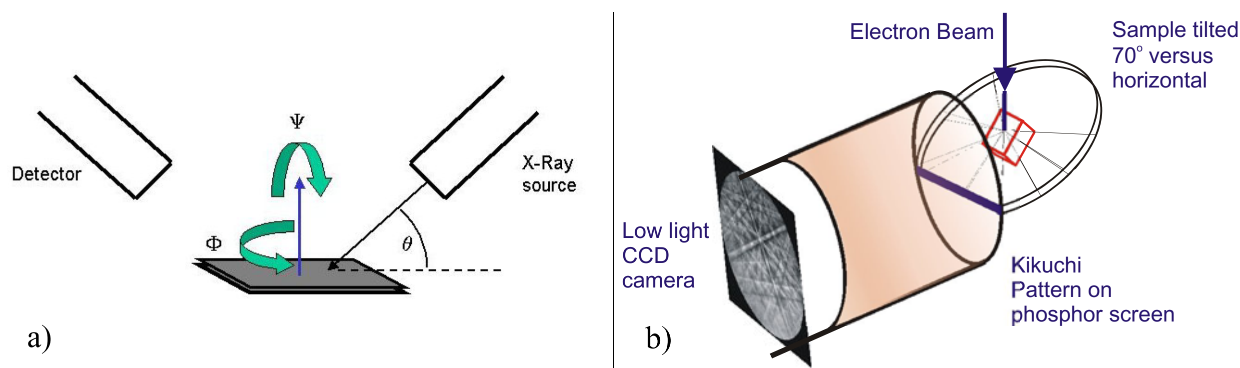


**Fig. 1** (a) Pole figure measurement by XRD. $\theta$:Diffraction angle; $\Phi$: Rotation angle; $\Psi$: Tilt angle. (b) Principle of an EBSD measurement.

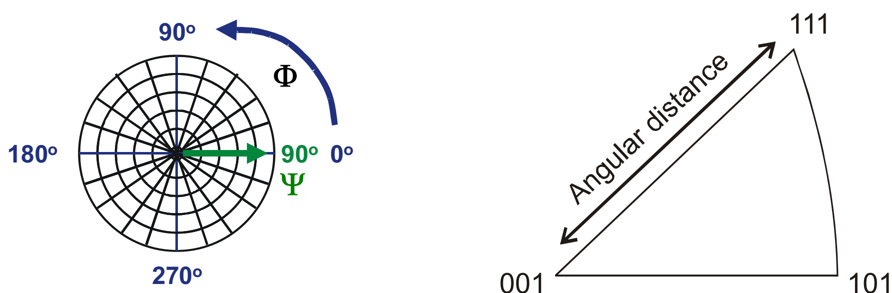


**Fig. 2** Construction of direct (left) and inverse (right) pole figures. A direct pole figure shows only information for *one* crystallographic direction. Combining the information from several pole figures of crystallographically independent directions will yield an inverse pole figure, which normally is a more useful presentation, especially for thin films.

## RESULTS AND DISCUSSION

To compare the textures determined by EBSD and XRD, we performed measurements on room-temperature-sputtered aluminum thin films, electroplated copper and rolled copper foil. We found that the results of the two methods are not always comparable and can, depending on the properties of the examined material, strongly differ. One reason for possible differences is a very different sampling depth for the two methods. EBSD collects information from only a shallow surface layer (sampling depth of tens of nanometer) in a sample. However, the spatial resolution is much higher than for XRD. On the other hand, X-rays are capable of penetrating considerably

deeper into the specimen (sampling depth of tens of micrometer), therefore yielding averaged information from a much larger volume.

Texture analysis of the aluminum sample ($t \approx 1$ μm) by XRD revealed a strong {111}-texture of the material, as shown in the left inverse pole figure (IPF) in Fig. 3a. When comparing with the right IPF, calculated from EBSD measurements, we found that the two methods yielded in this case nearly identical results. Reasons for this good agreement were that the sample is almost homogeneous through the thickness, *i.e.*, grain size and grain orientation didn't vary much between bulk and surface (we refer to the 'bulk' of the film as the volume outside the thin surface layer sampled by the EBSD method). As shown in Fig. 3b, we also found a very good agreement for the case of a thin foil of rolled copper. The high surface roughness of this sample was a problem for EBSD; however, due to the strong texture of the material (mainly {001}), the fraction of measurable surface was sufficient to yield a satisfactory IPF.

A different situation was found for copper samples 2 and 3. Both samples were electroplated films. For the sample referred to as Copper 2 the examinations by EBSD and XRD were performed immediately after plating to make sure that no self-annealing and oxidation of the surface would influence the measurement. The agreement of the two techniques in this case was still acceptable, but not as good as that for the first two samples (Fig. 3c).

Sample Copper 3 was left to age and stabilize in a dry-box for two weeks after plating. During this time the self-annealing process [7][8] took place. We found that it was necessary to remove the oxide layer by etching with dilute hydrofluoric acid, because non-etched samples showed EBSD patterns of poor quality. The XRD IPF showed several areas of slightly higher intensity, while for the EBSD IPF only one widely spread area of higher intensity was found (Fig. 3d). Compared to the other examples, the observed agreement between the two methods was rather poor in this case.

The most likely reason for this disagreement is the change of both grain size- and orientation-distributions after self-annealing and repeated twinning of grains. Surface-orientation mapping of Copper 3 by EBSD showed several bigger grains (4 μm – 5 μm in diameter) in a matrix of much smaller grains with random orientation; the grain size distribution followed a lognormal function. There are two important points to consider here. As seen by XRD, Bragg reflections diffracted by sufficiently small crystallites (approximately smaller than 100 nm) will be broadened and superimposed on the sharp and strong Bragg reflections diffracted by larger crystallites. Most commercial software packages track the maximum peak height as a function of $\Psi$ and $\Phi$ angles, and the pole figures obtained in this way are likely to be biased toward larger grains.

**Table** 1 Overview of sample properties in Fig. 3

| Sample | Preparation Method | Substrate | Thickness | XRD-EBSD agreement |
|---|---|---|---|---|
| Aluminum | sputtering | single crystal Si (001) | 1 μm | very good |
| Copper 1 | rolled foil | - | 5 μm | very good |
| Copper 2 *(examined directly after plating)* | electroplating | single crystal Si (001) | 5 μm | good |
| Copper 3 *(examined two weeks after plating)* | electroplating | single crystal Si (001) | 4 μm | poor |

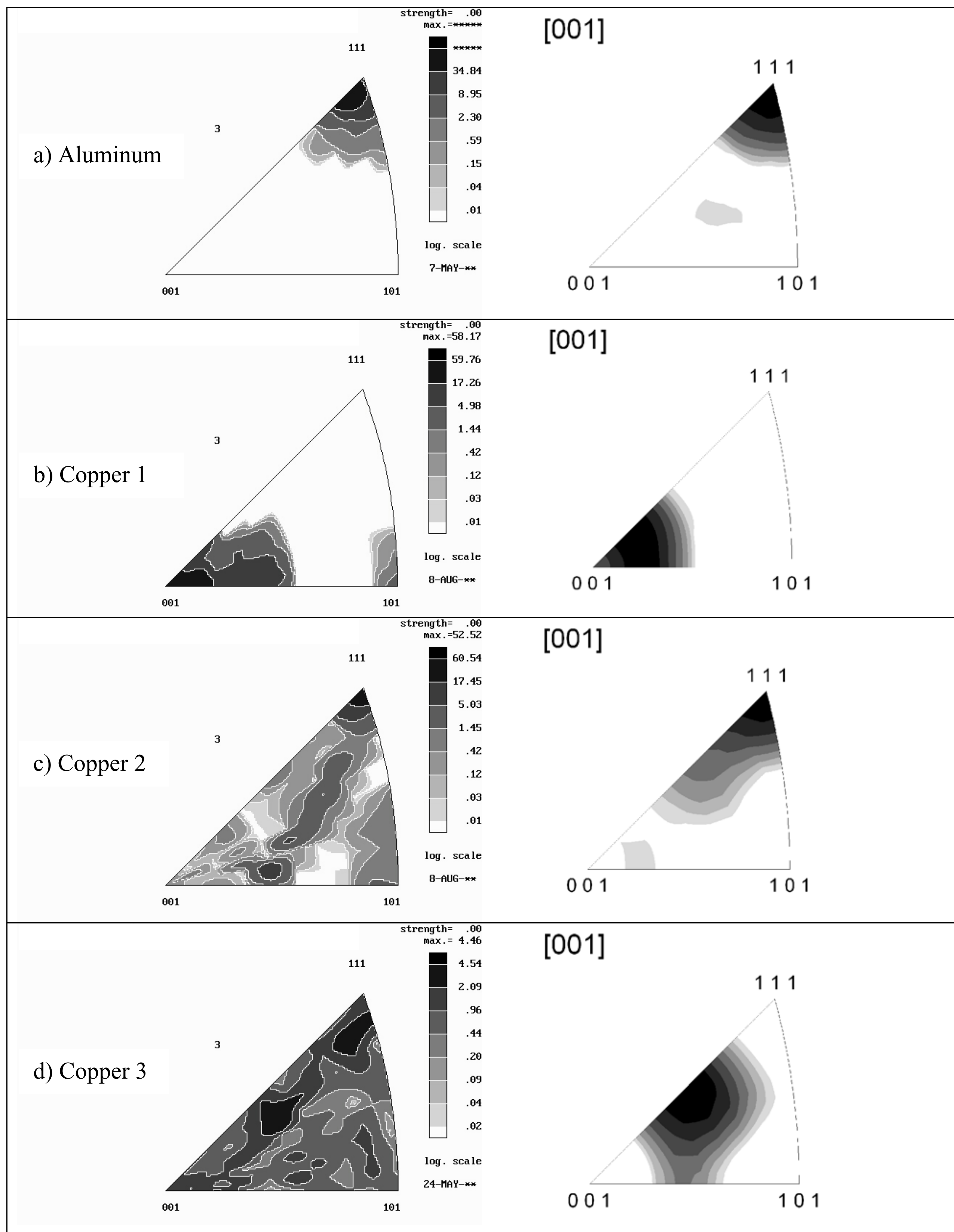


**Fig. 3** Comparison of inverse pole figures generated by XRD (left) and EBSD (right). See Table 1for sample details.

As there were relatively few large crystallites within the sampling volume of sample Copper 3, XRD pole figures will therefore show a significant texture. This bias can be avoided if integrated intensity (peak area) is used to construct pole figures instead of the maximum peak height. Another possible source of disagreement is the sampling of grains with different sizes by the EBSD technique, which becomes more critical for wider size distributions [9] Especially, it has to be made sure that a sufficiently large surface area is scanned to include enough grains for a good statistical description of grain size distribution and orientation. Additionally, it is expected that two techniques will give different results in cases of significant change of crystallite orientation and/or size distribution through the thickness of the thin film [10].

## SUMMARY

We examined the texture and grain size of thin films of electroplated copper, rolled copper foil and sputtered aluminum samples with the XRD and EBSD techniques. Direct and inverse pole figures were calculated based on the measurements of both methods, and possible sources of disagreement were pointed out. While for aluminum and rolled copper we found nearly identical results for both techniques, the results for self-annealed electroplated copper strongly deviated from each other.
The results show that the difference in basic detection principles of XRD and EBSD must be taken into account when comparing results obtained by these two techniques. In particular, obvious sources of error, caused by different properties between the surface and the bulk should be carefully examined. Differences can be for example caused by an alteration of the surface properties by etching and oxidation, as well as a nonhomogeneous crystallite orientation and size distribution through the thickness of the film. Furthermore, if XRD pole figures are constructed by use of the maximum peak height instead of integrated intensities of the reflections, the results will be biased toward larger crystallites that give sharp and strong diffraction lines. In regard to EBSD, proper care should be taken to sample a sufficient number of crystallites for all crystallite sizes, particularly for samples with broad distributions of crystallite size.

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