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MISORIENTATION DEPENDENCE OF DIFFUSION INDUCED GRAIN BOUNDARY MIGRATION (DIGM) IN ORIENTED Cu (Zn) BICRYSTALS

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Abstract - Diffusion induced grain boundary migration (DIGM) has been studied in the Cu(Zn) system using Cu bicrystals with initially symmetrical tilt grain boundaries (GBs) of the $\langle 011 \rangle \{011\}$ type produced by diffusion bonding. The misorientation has been varied systematically over the range from 10.1 to 171.9°. Measurements of the GB velocity showed it to have a strong dependence on the misorientation angle. The morphology of DIGM has been studied by optical microscopy. As a special morphological phenomenon, faceting has been investigated at a symmetrical $\Sigma 19a/26.52^\circ \langle 011 \rangle \{011\}$ GB.

1. Introduction - Under certain conditions GBM in a pure metal can be caused by the diffusion of a solute element into the metal along the grain boundary. As this occurs an alloyed zone (AZ) forms behind the migrating GB as the result of the solute atoms incorporating themselves in the zone left behind the migrating boundary [1-4]. These zones can develop in the form of bowed boundary segments during DIGM at various places along the GB. These bows in the grain boundary generally distribute themselves in both directions in the grain interiors. Further, with reference to the morphology, both an ordinary and an oscillating GB migration in which the grain boundary migrates either forwards or back and forth respectively, is observed for DIGM. The transition from ordinary to oscillating GB migration occurs at $T \approx 770$ K in the Cu(Zn) system.

Closely related to DIGM is another metallurgical process, diffusion induced recrystallization (DIR), a reaction in which fine grains with increased foreign atom concentration nucleate on the specimen surface and grow according to the DIGM mechanism. The growth of the DIR grains in the z direction perpendicular to the specimen surface is essentially determined by the annealing time t. In addition to DIR, facet formation at various GBs in the surface region ($z < 5 \mu\text{m}$) also occurs. For this phenomenon the segments which have migrated appear to align themselves on certain crystallographic planes.

2. Experimental Methods - The materials used to make the synthetically prepared bicrystals were single crystals of high purity Cu (5N8), which were grown by the Bridgman technique. The single crystals were stress relief annealed for 15 hours at 1273 K after being grown from the melt. Subsequently, they were oriented by the Laue back reflection technique and cut into 3 mm thick slices by spark erosion. After appropriate preparation the slices were diffusion bonded at 1323 K for 15 hours. Rectangular samples with the dimensions $4.5 \times 3.0 \times 2.5 \text{ mm}^3$ were then cut out parallel to the $\langle 011 \rangle$ diffusion direction. With this procedure well defined bicrystals of the $\langle 011 \rangle \{011\}$ type were prepared, where $\langle 011 \rangle$ is the tilt axis and $\{011\}$ are the planes between which the tilt angle θ is measured. The angle θ was systematically varied over the entire range from 10.1 to 171.9°. Before being given the DIGM anneal, the bicrystals were again stress relief annealed at 1223 K in order to avoid GB migration due to internal stresses. For the DIGM anneal the samples along with the Zn source, which was in the form of turnings of a Cu-30 wt.% Zn alloy were placed in an evacuated quartz capsule. An undesired uptake of O_2 during the experiment was avoided by placing a Ta foil, high purity graphite and an Ar-20% H_2 mixture in the reaction capsule. After the DIGM anneal the samples were quenched in water.

Metallographic specimen preparation proved to be difficult, on the one hand, because the single crystal Cu material was very soft and, on the other hand, because of the relatively slight penetration of DIGM into the sample interior (μm range). The following metallographic specimen preparation procedure proved itself to be the most suitable. First, the specimens were ground with 4000 grit SiC paper in such a way that no great pressure was applied to the sample. Polishing was carried out first with $3 \mu\text{m}$ and then with $1 \mu\text{m}$ diamond paste under light pressure using a velvet cloth. Subsequently the samples were etched with a solution containing 1.5 ml distilled water, 2 ml conc. NH_4OH and 0.25 ml aqueous H_2O_2 solution for about 5 - 10 s. Here the etchant always had to be freshly prepared.

Since the dependence of GB migration on the depth z below the specimen surface is of special interest, an exact determination of the depth was carried out. This was successfully done with the aid of a Vickers hardness impression, which was placed in the center of the specimen before the polishing procedure. From the difference between the diagonals of the hardness impressions before and after the polishing procedure (d_1 , d_2) the depth z could be exactly determined using the relation,

$$z = 0.143 (d_1 - d_2),$$

which is based on the geometry of the Vickers 136° pyramidal indenter. Light microscopy (LM) proved to be more than adequate for the study of the morphology of DIGM and DIR as well as for the measurement of GB migration distances.

3. Experimental Results - For the study of the morphology and kinetics of DIGM metallographic specimens of surfaces parallel and perpendicular to the $\langle 011 \rangle$ diffusion direction were prepared. On all specimens studied a fine grained DIR layer interdispersed with twins was observable after the DIGM anneal at $T = 693$ K for various annealing times t . This layer (Fig.1) covered the entire specimen surface. Electron microprobe studies showed the DIR grains on the specimen surface to have a Zn concentration of about 22 wt.% Zn. For further investigation this fine grained layer had to be removed by polishing. When this was done the surface layer and thus the number of DIR grains decreased with increasing depth below the specimen surface until finally only the DIGM reaction region was observable. In the region lying between the surface with 100% DIR and the depth at which no DIR is observed DIR grains as well as DIGM reaction seams exhibited approximately the same Zn concentration.

The reaction fronts (RFs) migrated randomly into both crystal halves, which indicates in general that the GBs were highly symmetric (Fig.2). Metallographic specimens perpendicular to the $\langle 011 \rangle$ directions exhibited depth profiles of GBs, which had migrated, having three different forms (Figs.3a-c).

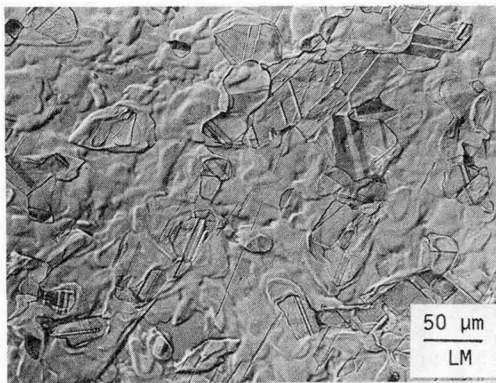


Fig.1 DIR. Entire sample surface covered with fine grained alloy layer. 1030 h at 693 K.

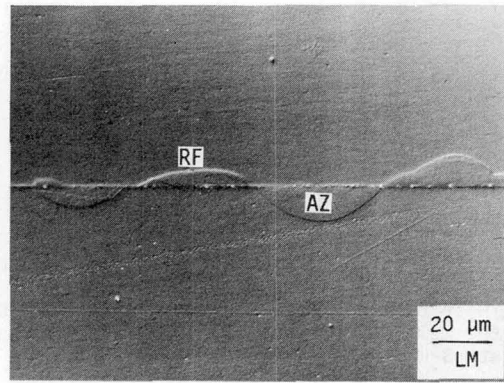


Fig.2 DIGM. GB segments migrate randomly into both crystallites. 244 h at 693 K, $z = 35 \mu\text{m}$.

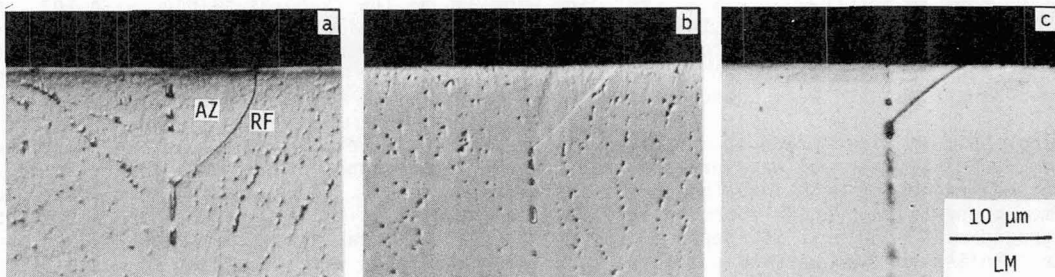


Fig.3 Three different shapes of DIGM depth profiles: concave (a), straight (b) and convex (c). RF - reaction front, AZ - alloyed zone. 503 h at 693 K.

For the determination of the GB migration rate v , w - t diagrams with w as the average seam width along the GB for constant z were drawn. The slopes of the resulting straight lines corresponds to the steady state migration rate v for a given depth z (Fig.4). In addition, for the determination of the depth dependence of v , w - z diagrams for constant annealing times t were drawn (Fig.5). The w - t curves obtained with their aid (see Fig.4) show that v can be viewed as constant over the entire depth range studied. The dependence of the v values determined in this manner on the misorientation angle θ is presented in Fig.6.

Additionally, concentration profiles were determined which gave the Zn concentration as a function of the distance to the specimen surface. With the aid of wave length dispersive X-ray analysis the Zn content in the reaction regions was determined for the various depths. The concentration profiles show an exponential decrease with increasing depth (Fig.7). Within a seam no regularity in the concentration distribution was observed. The grain boundary diffusivity was determined using the mass balance equation [5] which yields the following analytical relationship:

$$\log x(z) = \log x_0 - \frac{1}{\sqrt{s\delta D_b} \ln 10} \sqrt{v} z. \quad (1)$$

In this equation $x(z)$ is the solute atom concentration immediately behind the GB at a depth z , x_0 is the solute atom concentration in the seam at the surface, v is the migration rate, s is the segregation factor, δ is the width of the GB and D_b is the grain boundary diffusion coefficient. The dependence of the $s\delta D_b$ values determined from Eq.(1) on the misorientation angle θ is also given in Fig.6.

The formation of the facets presents a special case of morphological development in which the final position of grain boundaries, which migrated during the formation of DIGM seams, corresponds to special crystallographic planes. This phenomenon is especially striking for the $\Sigma 19a/26.52^\circ \langle 011 \rangle \{011\}$ boundary, for which facets can even be observed on the specimen surface. Special studies of this phenomenon have shown that the marked triangular shape of the facets quickly is lost through a rounding-off of the apex of the triangles with increasing depth z ($0 < z < 2 \mu\text{m}$) below the surface. Below $z \approx 6 \mu\text{m}$ facets cannot be distinguished from ordinary DIGM seams (Fig.8).

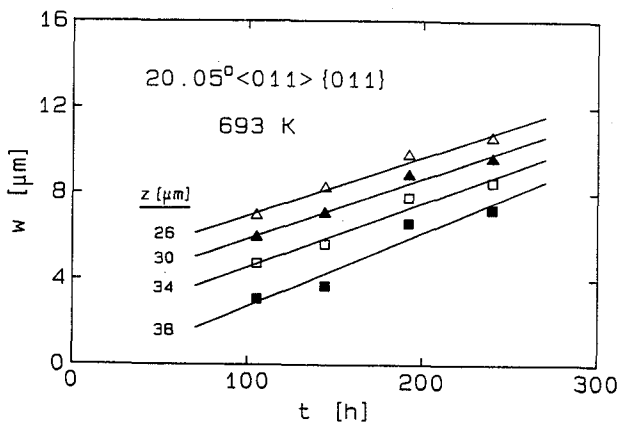
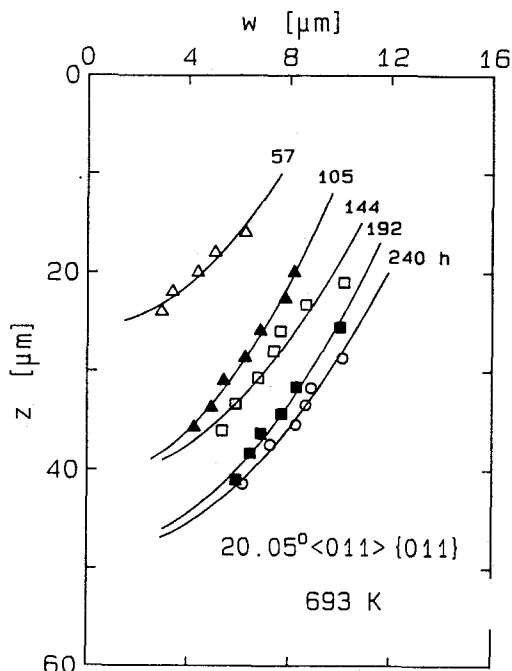


Fig.4 Seam widths as a function of annealing time at 693 K for various depths below the specimen surface. $\Sigma 33a/20.05^\circ \langle 011 \rangle \{011\}$ GB.

Fig.5 Seam widths as a function of the depth z below the specimen surface at 693 K. $\Sigma 33a/20.05^\circ \langle 011 \rangle \{011\}$ GB.



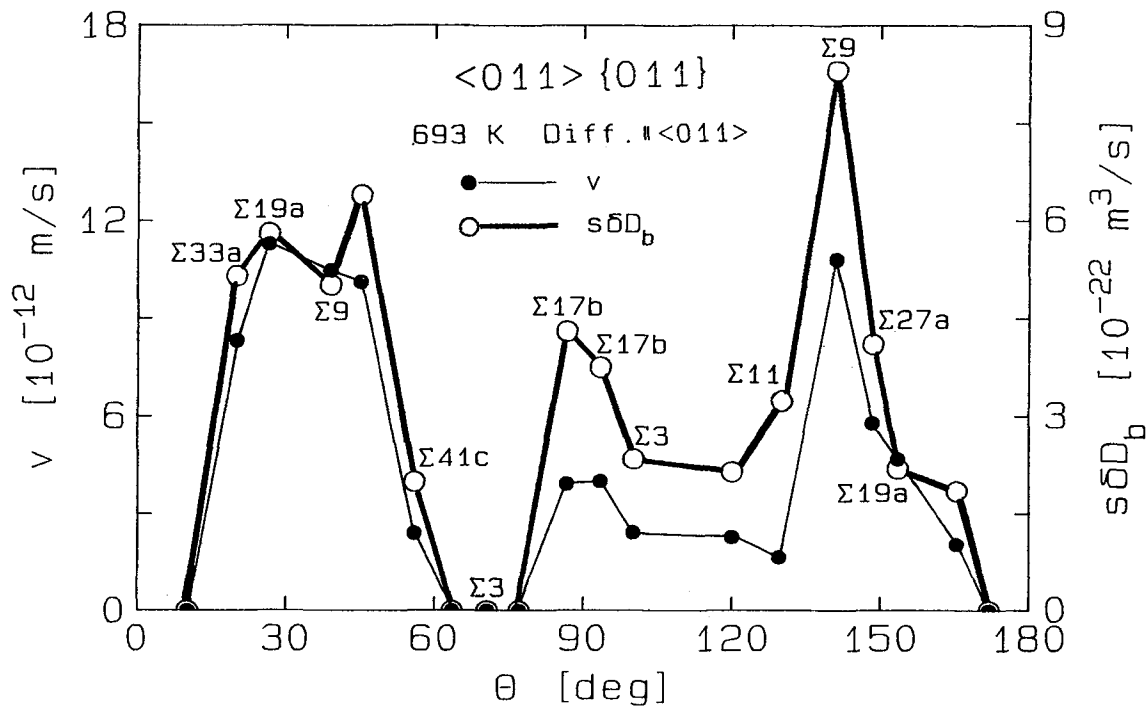


Fig.6 Migration velocity as well as grain boundary diffusivity as a function of misorientation angle at 693 K. The diffusion takes place parallel to the <011> tilt axis.

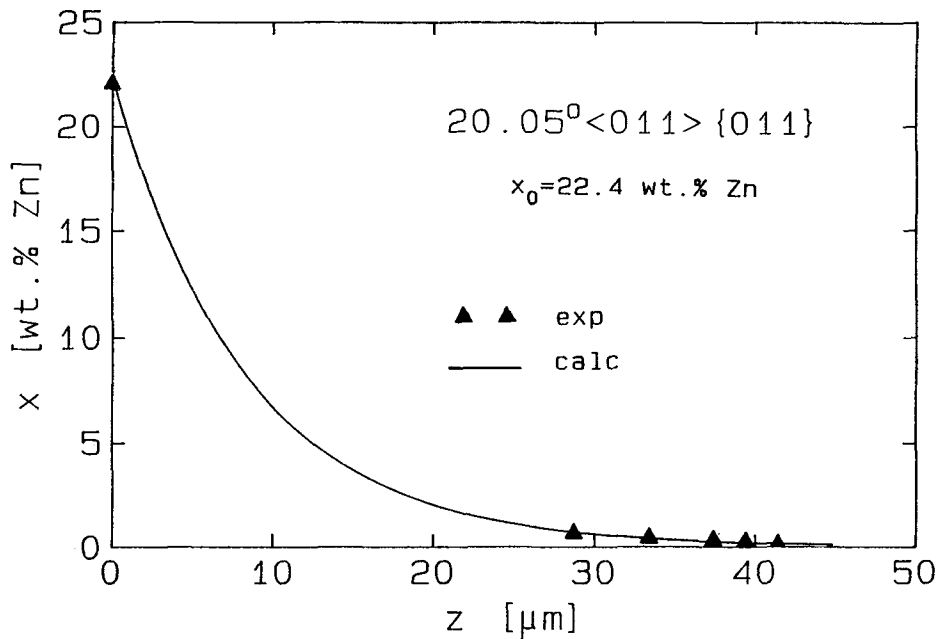


Fig.7 Zn concentration profile. Σ 33a/20.05° <011> {011} GB, 240 h-at 693 K.

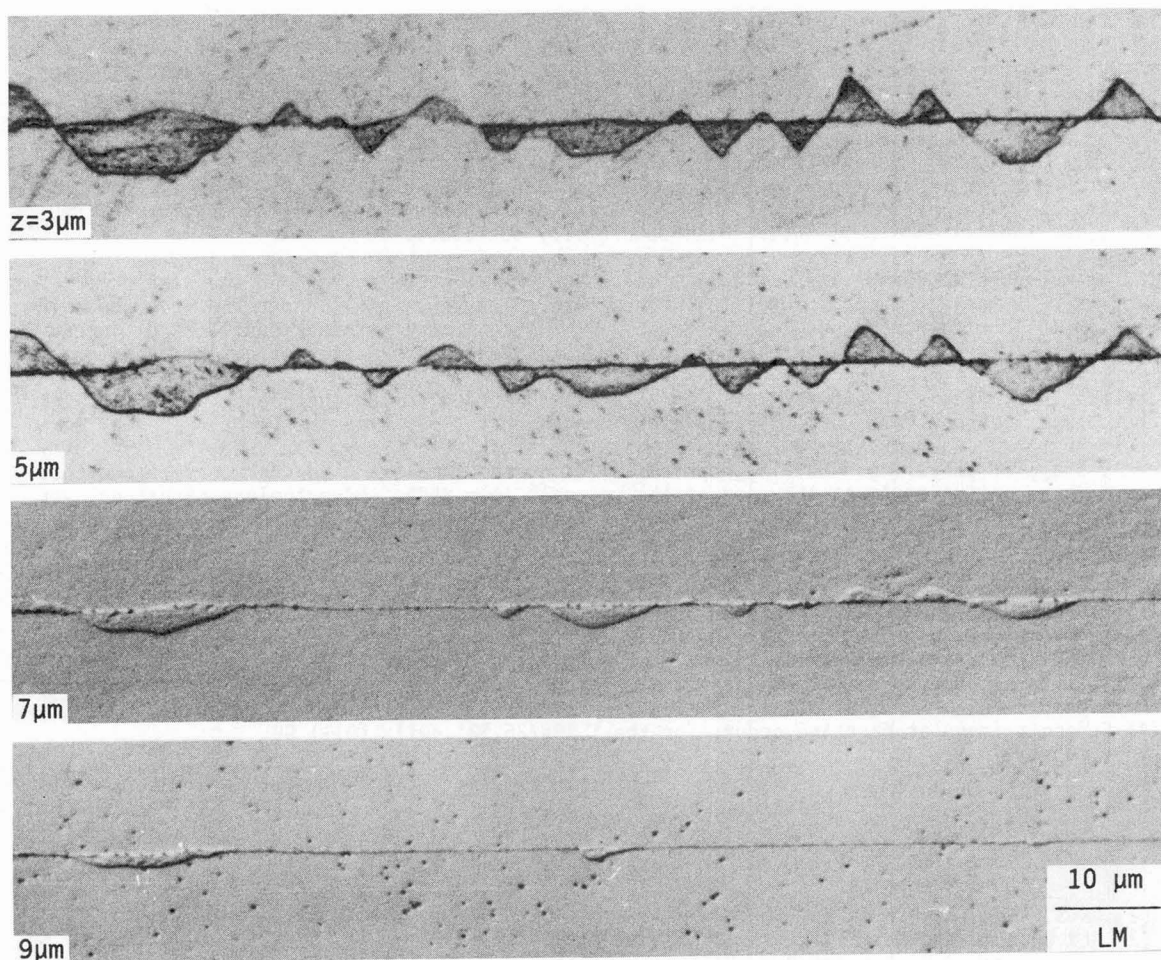


Fig.8 Facets. Change of the morphological appearance of facets with depth below the specimen surface. $\Sigma 19a/26.52^\circ \langle 011 \rangle \{011\}$ GB, 3 h at 693 K.

4. Discussion - Because the DIR layer penetration into the specimen interior to some depth z does not allow the observation of the DIGM reaction region and thus presents a complicating factor for DIGM measurements, an attempt was made to suppress DIR. After the sample preparation described in Section 2 the bicrystals were additionally chemically polished for various lengths of time ($t = 5 - 20$ min) with a solution of equal volume percentages of H_3PO_4 , HNO_3 and CH_3COOH before the DIGM anneal. As a result it was found that each GB type exhibited very different etching behavior. In contrast to $\Sigma 19a$ -GBs grooves could be observed to form quickly ($t = 5$ min) at $\Sigma 9$ -GBs. This made further use of these boundaries impossible. For boundaries which showed no groove formation after 20 min, it was possible in our studies to suppress the DIR reaction up to an annealing time of 24 h maximum whereas Chen and King [6] did not observe any DIR even after annealing for 48 h.

In Fig.5 the measured w - z values were described by a power function because nearly all profiles exhibited the shape presented in Fig.3a. For the evaluation of the w - t curves (Fig.4) the w - z data for $t = 51$ h were disregarded because the determination of the w - t dependence over a larger temperature range could not be carried out with them. The velocities v obtained from the slopes were constant considering the measurement uncertainty for the depths z studied (about $\pm 0.2 \mu m$). The dependence of v on θ presented in Fig.6 shows clearly that GBs in the small angle region ($\theta \leq 10^\circ$) did not exhibit any migration until after annealing for times of 5000 h. In the high angle region the $\Sigma 3$ twin boundary likewise shows no migration tendency after 5000 h. This is probably due to the short periodicity distance of its structural units and the low energy associated with it. This structural influence of the $\Sigma 3$

structural units determines likewise the migration behavior of GBs whose misorientation angle θ deviates up to about $\pm 10^\circ$ from that of the $\Sigma 3$ GB. Analogous to those in the small angle regions GBs with $\theta \geq 171^\circ$ also do not exhibit any tendency to migrate after $t = 5000$ h.

As can be seen in Fig.6 the calculated $s\delta D_b$ values, with the exception of the value for the $45^\circ \langle 011 \rangle \{011\}$ GB, behave analogously to the v values in their variation with the tilt angle θ . However, while the expected cusp [1] in the v - θ curve at $\theta = 38.94^\circ$ ($\Sigma 9$) could not be seen, it is clearly visible in the $s\delta D_b$ - θ curve. Further, the very high values of $s\delta D_b$ and v for the 141.06° ($\Sigma 9$) $\langle 011 \rangle \{011\}$ GB are very noticeable.

The measured Zn concentrations (Fig.7), which are ≤ 1.5 wt.% Zn, are on the same order of magnitude as those given in Ref.[8]. They are, however, small compared to those in Refs.[9,10]. On the one hand, the different tilt axes and, on the other hand, the difference in bicrystal fabrication techniques may have contributed to the different observations.

The origin of facets (Fig.8) presents an interesting morphological phenomenon, whose origins and causes cannot yet be completely explained. Short time experiments ($t = 30$ min) have shown that the facets already possess their characteristic triangular shape in the very early stage of annealing. Metallographic studies on the same grain boundary have shown that there is a unique angle at the apex of the triangle ($\alpha \approx 85^\circ$). Nevertheless it has not yet been explained if different habit planes or if planes of the same type cut the $\langle 011 \rangle$ specimen surface.

5. Conclusions - The results can be summarized as follows:

- (1) DIR could not be suppressed at the longer annealing times.
- (2) The GB migration rate v as well as the GB diffusivity $s\delta D_b$ are strongly dependent on the misorientation angle θ and vary analogously with θ .
- (3) The Zn concentration in the reaction regions decreases exponentially with increasing depth.
- (4) Strong triangular faceting occurs for the $\Sigma 19a/26.52^\circ \langle 011 \rangle \{011\}$ GB.

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