Self-Organized Growth of Crystallographic Macropores in Multicrystalline Zn by Nanoscale Sculpturing

M.-D. Gerngross, M. Baytekin-Gerngross, J. Carstensen, and R. Adelung
Institute for Materials Science, Kiel University, 24143 Kiel, Germany

The self-organized formation of crystallographically oriented macropores in multicrystalline Zn is presented in the present paper. These pores are obtained by pulsed-potential electrochemical etching in an aqueous KCl electrolyte. They exhibit the typical characteristics of crystallographically-oriented pores like growth along certain crystallographic directions, formation of pore domains, branching of pores, and intersections of pores, as observed for e.g. III-V semiconductors such as InP. The pore walls of the pores in Zn are entirely composed of metallic Zn unlike the amorphous metal oxide ones observed in other metals like Al (AAO) or Ti (TiO2). The main pore growth direction in Zn is along [0001]. The branching of side pores occurs along [1210] and [1210] in 90° angles from the root pore forming a pore geometry reminding remotely on a monkey puzzle tree. Because of their crystallographic nature of the pores they grow under various angles into the multicrystalline Zn surface depending on the underlying crystal orientation. Like this they form a perfectly suitable structure for mechanical interlocking with polymers. When filled with polymer, the root pores together with the branched side pores act as ideal hooks anchoring the polymer in Zn solving the well-known problem of poor adhesion of polymers and paint on Zn surfaces.

The growth of porous structures by electrochemical etching was first found for Si and Ge in 1956 by Uhlir1 followed by GaAs.2 After the parallel discovery of luminescence of porous Si by Canham3 and Lehmann4 research activities in the field of pore growth in semiconductors by electrochemical etching received a tremendous boost5–12 which still continues.13–15 In semiconductors two basic pore types have been observed, currentline-oriented pores and crystallographically-oriented pores. In short, the growth direction of currentline-oriented pores follows the direction of current flow regardless of crystallographic planes, while the crystallographically-oriented ones follow certain crystallographic directions.

Alongside with the investigations of pore growth in various semiconductors pore formation by electrochemical etching of metal substrates was first observed on Al by Masuda16 and later on Ti.17,18 The common ground of these metals is their ability to form extremely stable metal oxides as well as the development of passivating surface layers based on these oxides. These features are fundamental requirements for the formation of metal oxide pores.

Zn also fulfills these requirements. That is the reason, why Zn is mainly used in industry as corrosion-protection coating for other metals, mostly steels and iron-based alloys. The benefit of the Zn coating is that Zn is here preferentially chemically attacked instead of the host metal because of its lower standard potential with respect to the host metal. The Zn coating itself is considerably protected against corrosion due to the good adhesion between the Zn corrosion products and the metallic Zn coating. Due to its importance for application the corrosion and dissolution behavior of Zn was widely investigated for aqueous acidic media, especially chloride based electrolytes,19–22 also for aqueous alkaline media.23–26 Besides these, studies investigating the corrosion and dissolution behavior under various environmental conditions were conducted, emphasizing here the extensive of Odnevall27–29 and the book of Zhang30 which is the reference in the field of Zn electrochemistry and corrosion. In terms of the resulting Zn surface morphologies all studies performed so far exhibited no formation of pores in Zn till very recently pore growth in Zn was reported by electrochemical nanoscale sculpturing.31 The decisive idea of the nanoscale sculpturing concept is to specifically adjust the intermediate formation of an oxide layer on the metal surface and its subsequent controlled dissolution. The present work further extends this research showing structural and chemical properties of the electrochemically nanoscale sculptured Zn pore structures, exploiting their characteristic features as well as providing insights into the pore growth conditions. These results are discussed with respect to characteristic features of crystallographically-oriented pores in III-V semiconductors, in particular in terms of pore growth along certain crystallographic directions,32–34 pore domain formation,34–36 branching of pores from the pore walls37,38 and the pore tips,38 as well as the intersection of pores at the pore tips, but stopping at the pore walls.39

The most preeminent application of such porous Zn structures can be found in the field of adhesion and joint formation between Zn and other materials, such as polymers and paints. When completely filled by the polymer, the Zn pore structures act as hooks in the polymer establishing an extremely robust connection between the polymer and the Zn substrate. As a proof of principle such a cyanoacrylate/porous Zn joint is presented in this paper. Besides adhesion and joint applications, such Zn pore structures might also be employed as anode material in Zn-air batteries due to the tremendously high surface area.

Experimental

For this work multicrystalline Zn sheets, commercially available from Goodfellow (778-414-12), are employed. These sheets show a purity of 99.95% with a thickness of 100 μm ± 10 μm and possess the surface finish and mechanical state “as rolled”. Prior to electrochemical pore etching, the Zn sheets are mechanically polished with a grit 4000 silicon carbide grinding paper until a mirror-like surface finish is achieved, rinsed in acetone, and air-dried.

The electrochemical etching setup is depicted in Fig. 1. It consists of a Teflon-based electrochemical etching cell in a four electrode configuration. Inside the etching cell, but far away from the Zn sample surface, a large area Pt counter electrode (CE) is positioned. The position of the reference electrode (RE) is in the nearest proximity to the Zn sample surface without touching it. The sense electrode (SE) is an Al stripe and in direct contact with the front side of the Zn sample. The Zn sample itself is the working electrode (WE) and externally connected over an Al stripe which is mechanically pressed on the back side of the Zn sample. For all samples the etched area is circular with a diameter of 1 cm and a resulting area A of 0.785 cm². The
Figure 1. Electrochemical etching setup. Electrochemical etching single-cell in a four electrode arrangement with the Pt counter electrode (CE), Pt pseudo-reference electrode (RE), Al sense electrode (SE), and the working electrode (WE). The electrolyte inlet and outlet are schematically illustrated.

Figure 2. Crystallographically-oriented pores in Zn after electrochemical nanoscale sculpturing. I SEM top view on the porous surface a) as macroscopic overview, b) in higher magnification at a different position with pore domain boundaries separated by dotted lines and red arrows as indicators for pore growth direction, c) high magnification image of the pores growing non-parallel to the surface normal, and d) high magnification on young pores growing perpendicular to the surface normal. The blue dotted lines outline the distorted hexagonal pore shape in the proximity of the pore tip and the red dotted lines the rhomboidal pore shape at the pore opening.

A further zoom in on the porous Zn surface is given in Fig. 2b. Here, one observes already clear signs of order in the pore arrangement. Within distinct areas in the dimensions of several tens of microns neighboring pores grow parallel aligned to each other into the depth under the same angle with respect to the surface normal of the Zn substrate. In addition, there are no signs of a preferential dissolution of the Zn grain boundaries. Based on the finding in porous semiconductors like GaAs such pore areas are typically called pore domains. As a guide for the eye the white dotted lines in Fig. 2b indicate the boundaries of the pore domains, the red ones the growth direction of the pores within the domain. The growth angle of the pores is different for each pore domain and varies between parallel to the Zn surface normal to almost perpendicular to the Zn surface normal. The formation of pore domains in Zn can be conclusively explained taking into account that the Zn sheet is multicrystalline exhibiting grain sizes that seem to directly correspond to the lateral dimensions of the formed pore domains. Also in this context the strongly differing pore growth angles can be explained by different crystallographic orientations of the surface-near Zn grains. This means the crystallographic pore growth direction is the same for all pores and only appears to be different due to the different crystallographic orientations of the underlying Zn grain which is also found e.g. for crystallographically-oriented pores in Si.

Figures 2c and 2d offer a close look on the local pore distribution within two different domains. Within a pore domain one observes a random pore arrangement. This is a commonly found property of self-organized grown crystallographically-oriented pores, as observed e.g. in Ge and III-V semiconductors. The pores in Zn exhibit a wide pore diameter distribution starting from around 100 nm (see top left corner of Fig. 2c) up to several microns (see left side of Fig. 2c). This is in contrast to crystallographically-oriented pores in e.g. III-V semiconductors where the pore diameter is typically constant.
Like the pore diameter also the distance between neighboring pores within one pore domain can vary from less than hundred nanometers (see Fig. 2c) up to the lower micron range (see Fig. 2d). An intergrowth of neighboring pores is also possible as shown in the center of Fig. 2c. One can understand the wide pore diameter distribution as a direct consequence of the electrochemical growth conditions. The frequent anodic potential pulses initiate the nucleation of new pores in the Zn grains and also enable the growth of already nucleated pores. Therefore, the pores with smaller diameter nucleate rather toward the end of the electrochemical etching process, while the pores with a pore diameter in the micron range nucleated rather in the beginning. Thus, a more homogeneous nucleation of the pores at the beginning of the etching process would directly affect the distribution of pore sizes in such a way that the full width half maximum of the pore size distribution drastically narrows down. A more homogeneous nucleation could be e.g. obtained by electrochemically inducing defects homo- geneously distributed over the surface, e.g. by a very high voltage spike at the beginning of the etching experiment, very similar to the concept used for the growth of crystallographically-oriented pores in III-V semiconductors. Another property of the crystallographically-oriented pores in Zn is the tapered pore diameter as shown in Fig. 2d. At the pore opening the pores show a much higher pore diameter known from crystallographically-oriented pores in e.g. III-V semiconductors. The tapering of the pore diameter is also accompanied by a change in the cross-sectional shape of the pores. At the pore tip and the nearest proximity to it the pore has a distorted hexagonal pore shape (see the red dotted lines in Fig. 2d) with typically about 90° for the acute angles and around 130° for the obtuse ones. In contrast to the pore tips the pore openings and the remaining parts of the pore exhibit a rather rhomboidal shape (see the blue dotted lines in Fig. 2d) with a typical acute angle of around 64° and an obtuse angle of about 116°. Based on this observation the original pore shape seems to be the hexagonal shape. It appears that the obtuse sides of the hexagon are only meta-stable and dissolve during the pore growth transforming the hexagonal pore shape into a rhomboid further away from the pore tip. The dissolution of the meta-stable obtuse sides of the hexagon seems to occur stepwise leaving parallel aligned facets in the nanometer range in the shape transition zone. In the end the rhomboid is formed by expanding the acute sides of the former hexagon further till they touch again. Beside the tapering and the pore shape transformation the pore walls, especially in Fig. 2d, also exhibit nanometer-sized, plate-like features being attached to them. The nature of these will be discussed later in the text.

Branching is a typical phenomenon observed for crystallographically-oriented pores in semiconductors, especially in III-V semiconductors. It can occur directly at the pore tips or out of the pore walls. Figure 3a presents a close view on a pore arrangement within a pore domain. It shows that branching of pores is a pore feature also observed for the pore growth in Zn. The red dotted circles enclose exemplarily such side pores freshly nucleated in the pore walls starting to grow out of them. The high density of such branched side pores illustrates that branching out of the pore walls is a very common event in the growth process of crystallographically-oriented pores in Zn. Thus, the branching probability from the pore wall is rather high. This is in strong contrast to the equivalent phenomenon in III-V semiconductors. There the probability of branching from the pore walls is rather low. To analyze the Zn pore structure in cross-section cleaving of the Zn substrate would be highly desired, but is almost impossible due to the high ductility and mechanical softness of Zn. Therefore, the Zn pore structures are analyzed indirectly by fabricating a cyanoacrylate cast of the Zn pores and subsequently dissolving the remaining Zn substrate. Figure 3b presents such a cast of the pores in Zn looking into the depth is the result. A very similar situation is also observed for the growth of crystallographically-oriented pores in Ge.

Figure 3. Crystallographically-oriented pores in Zn after electrochemical nanoscale sculpturing II. a) SEM top view on the porous surface showing nucleating side pores in the pore walls (exemplarily enclosed by the red dotted lines), SEM view on the pore cast showing b) the pore shape close to the pore tips including the side pores, inset: high magnification on single pores with branched side pores, c) two pores intersecting each other at the pore tips, and d) SEM top view on a pore intersecting another pore through its pore wall.
under the condition that the two actively growing pores meet directly at their pore tips. If an actively growing pore reaches the pore wall of another pore the intersection is prevented by the space charge region surrounding the pore walls stopping the dissolution of the pore wall. For crystallographically-oriented pores in Zn the intersection behavior is slightly different. Figures 3c and 3d show that intersection at the pore tips as well as intersection at the pore walls is possible. In Figure 3c the intersection of pores directly at their pore tips is depicted (enclosed by the red dotted circle). The two pores intersect under an angle of approximately 90° and continue their growth in their former direction. The intersection through the pore walls is given in Fig. 3d. Here, a pore continues its growth (bottom center to center of Fig. 3d) directly through an already existing pore forming an interconnected pore arrangement. The behavior of branching from the pore walls as well as the intersection behavior of the pores in Zn can be explained in terms of pore wall passivation. In semiconductors a strong protection of the pore walls against further dissolution is provided by the space charge region around the pores. As a metal Zn cannot form such a protective space charge region around the pores. The passivating coating obtained from the cathodic pulses seems to be not strong enough to completely passivate the pore walls, so that a nucleation of side pores is possible as well as the intersection of pores through the pore walls.

The chemical composition of the pore wall in Zn and the influence of the pores on the crystal structure are investigated by XRD and EDX elemental mapping. The Zn specimen has been investigated by XRD prior to and after electrochemical pore formation. The corresponding diffractograms are presented in Fig. 4a with the ICSD 421014 Zn powder diffractogram as reference. Comparing the diffractograms of the untreated Zn specimen before and after electrochemical pore growth, one observes six peaks. No additional peaks or amorphous halos originating from e.g. Zn oxides, hydroxides or chlorides etc. are detected for the porous Zn specimen. Both diffractograms show the same six peaks, five of them very distinct and sharp and one broadened. They all can be assigned to crystalline Zn exhibiting the typical hexagonal crystal structure of Zn. In the order of appearance the six peaks are assigned as Zn{0002}, Zn{1010}, Zn{1011}, Zn{1012}, Zn{1013}, and Zn{1120}. The Zn{1120} peak is the broadened peak. The sharp and distinct shape of the first five peaks is an indicator of rather large coherently scattering areas and therefore rather big Zn grains. Clear signs of texturing are observed in the diffractogram of the untreated Zn specimen. Comparing it to the Zn powder reference the Zn{1010} peak is very pronounced, while the Zn{1011} and Zn{1120} peaks are suppressed. Comparing the Zn sheet prior to and after pore formation, differences in the peak intensities of the six peaks are observed. After pore formation the diffraction pattern of the Zn specimen exhibits very high similarities with the Zn powder diffractogram. This might be explained by the electrochemical pore etching that caused a removal of the surface-near rolling texturing so that a randomly oriented grain structure is left. The diffractogram also shows that the pore walls do not consist of crystalline Zn oxide, hydroxides et cetera.

The composition of the pore walls is further investigated using EDX elemental mapping on selected areas of the porous Zn surface. Figure 4b shows such an exemplarily selected area with pores growing under a very high angle into the Zn grain (with respect to the surface normal) and the corresponding elemental maps (Figs. 4c–4e). Such pore geometry is chosen for obtaining the maximum signal intensity from the pore walls. Figure 4c depicts the elemental Zn distribution within the investigated porous area showing high amounts of counts over the entire surface with pronounced topography dependence at deep pores. This topography dependence is also observed in the O- and C-maps and originates from the signal shading of overlapping pore walls of deep pores. The O-map in Fig. 4d shows a highly reduced amount of counts compared to the Zn-map. The source of the O-signal might originate from the nanometer-sized, plate-like features attached to the pore walls as shown earlier in Fig. 2d. Compared to the O-map, the C-map in Fig. 4e shows even a lower amount of counts. The C-content is most likely not an intrinsic feature of the pore walls, but appears to be a measurement artifact originating from C-deposition from the SEM chamber atmosphere during the EDX measurement due to frequent electron beam scanning. From the results obtained from the XRD and EDX analysis the pore walls in Zn seem to entirely consist of metallic Zn being only covered by a non-closed layer of nanometer-sized, plate-like Zn oxide.

**j-t characteristics during etching and single loop voltammogram.**—The j-t characteristics during the pore growth in Zn are exemplarily shown in Fig. 5a and 5b. One observes an exponential decline in both current densities, the anodic as well as the quasi-cathodic, over time originating from a diffusion limitation in the process of pore growth as well-known from the pore formation in e.g. III-V semiconductors. Figure 5b provides these j-t characteristics in higher time resolution exhibiting a time behavior of the anodic current density during the anodic potential phase that can be described by an exponential function with a negative exponent and a relaxation time of roughly 800 ms before the potential is switched.
to the quasi-cathodic potential. During this phase of quasi-cathodic potential most likely a deposition of reaction products from the anodic dissolution reaction occurs in the proximity of the pore tips as well as on the pore walls being probably the reason for the time behavior of the anodic current density during the anodic potential phase.

To further elucidate the situation single loop voltammograms are performed. Figure 5c presents such a single loop voltammogram performed on an untreated Zn sheet exhibiting three distinct regions. The boundaries of these regions are marked by the dashed blue and purple lines. The regions are defined only based on the characteristic changes in the I-V slope of the voltage back sweep. This appears reasonable, because for the back sweep e.g. the electrolyte composition with the presence of dissolution products and the activation of the Zn surface etc. are much closer to the actual pore growth conditions present during the pulsed potential process used for the already shown pore growth. Region I expands from $-1.5 \text{ V}$ to about $-0.8 \text{ V}$, region II from about $-0.8 \text{ V}$ to about $0.1 \text{ V}$, and region III from about $0.1 \text{ V}$ to $1 \text{ V}$. The surface morphology of the Zn sheet after performing a complete single loop voltage sweep is depicted in Fig. 5d. One observes the formation of pores in the Zn sheet as exemplarily indicated by the purple arrows. These pores appear to be much bigger in diameter and less distinct in their shape compared to the pores obtained from the pulsed potential process (see Figs. 2 and 3). The development of side-pores is not observed. The pore walls and the unporous Zn surface are highly covered by nanometer-sized structures. Partially, the pores are also overgrown by hexagonal flake structures (blue arrows) consisting of Zn oxychlorides as revealed by EDX analysis. Most likely these structures form in the last stage of the voltage back sweep in region I below $-0.8 \text{ V}$. Thus, the quasi-cathodic potential in the pulsed potential etching process is reduced to $-0.6 \text{ V}$ to prevent the formation of such hexagonal flake structures on the Zn surface. Region II appears to be the sweet spot of pore formation in Zn, while above $0.1 \text{ V}$ (region III) the Zn dissolution reaction becomes intensified without the formation of pores as observed after performing only the forward voltage sweep. It seems to be decisive for the growth of distinct crystallographically-oriented pores in Zn to find the right potential conditions and single loop voltammetry can help to identify these parameters for a given electrolyte.

**Growth directions and model of crystallographically-oriented pores in Zn.—** As shown in Figs. 2 and 3 the growth of the crystallographically-oriented pores follows certain crystallographic directions. In Fig. 6a the crystallographic directions of interest for describing the pore growth are schematically shown with an actual pore as underlying. To better visualize the pore shape the hexagonal pore shape is outlined by the blue lines, the rhomboidal one by the red lines. The blue arrow represents the main pore growth direction, the black arrow the growth direction of the side pores and the red arrow the direction of pore widening toward a rhomboidal pore shape.
It is commonly accepted that the fast crystallographic growth directions are usually also the fast crystallographic directions for dissolution. According to, these fast growth directions in Zn are $<1\bar{1}00>$, $<1\bar{2}10>$, and $<0001>$ in the order of velocity. The schematic outline of the pore body in Zn pores is presented in Fig. 6b. For the sake of clarity the side pores are omitted in this schematic. The distorted hexagonal pore tip is given in blue and the rhomboidal pore opening of the pore in red. Figure 6c shows the projection of the pore along the main pore growth direction including the side pores (black triangles). The allocation of distinct crystallographic directions to the growth directions of the crystallographically-oriented pores in Zn is based on the observed pore characteristics, the crystallographic direction dependences in hexagonal crystals, and the statement of the fast dissolution directions in crystals. It is well-founded to ascertain the main pore growth along the $<0001>$ direction, since the $<0001>$ direction is the only one that allows for growth of branches perpendicular to the growth axis and being enclosed by pore walls forming a distorted hexagon. There are six crystallographically equivalent $<1\bar{2}10>$ directions (black arrows) in hexagonal crystals all pointing toward the corners of the hexagon. The red arrows represent the six crystallographic equivalent $<1100>$ directions pointing toward the center of each hexagonal facet. These two direction sets are the remaining two fast growth directions in Zn needed for crystallographically describing the development of side pores and the transformation of the pore shape from hexagonal to rhomboidal. In the notation of Kittel for hexagonal crystals, the growth directions of branched side pores can be allocated to the $<1210>$ and the $<12\bar{1}0>$ direction, because only these two directions show the matching two-fold symmetry for the side pores and cannot be overgrown by pore widening along the $<1010>$ and $<1\bar{1}01>$ direction (transformation to rhomboidal pore shape).

Although the relevant growth directions needed to describe the growth of the crystallographically-oriented pores are identified, the reason for the taper of the pore diameter as well as the shape change of the pores from the pore tip to the pore opening have not been fully discussed yet. One can associate these two phenomena directly with the passivation of the pore walls that occurs during the quasi-cathodic potential pulses during the electrochemical nanoscale sculpturing process. During the cathodic potential pulse the pore walls are passivated by depositing nanometer-sized plate-like structures on the pore walls, as observed in Fig. 2d. These consist most likely of e.g. reaction products from the Zn dissolution, such as Zn-hydroxychlorides, as observed by Neufeld in. Depending on the crystallographic orientation of the pore wall surface the growth rate of these passivating structures might differ, so that on pore walls with a certain crystallographic orientation the growth of these structures is preferred compared to others. Thus, the pore walls exhibiting reduced coverage with these passivating structures face a reduced protection against dissolution during the anodic potential phase and therefore are attacked easier compared to the pore walls with improved coverage. From this follows that the pore walls evolve kinetically out of the etching and passivation conditions which is in good agreement to the formation of crystallographically-oriented pores in InP and GaAs whose pore walls are formed from $<112>$ planes with $<111>$A planes as natural etch-stop planes.

The precise interplay between etching and passivation conditions and their match up following the concept of nanoscale sculpturing are the decisive point in the crystallographic pore growth in Zn. The passivation has to be adjusted in such a way that it is strong enough on the pore walls, so that the pore walls are maintained during the anodic pore growth phase, but not too strong, so that pore growth can progress at the pore tip and is not prevented by the passivation. The same is true for the etching conditions. The etching strength needs to be strong enough, so that the dissolution reaction at the pore tips results in further pore growth during the anodic phase, but not too strong, so that the pore walls are not dissolved during the same. For this interplay and match up the electrolyte composition and electrolyte temperature play a decisive role, besides the electrochemical parameters.

The used concentration of 0.1 mol/l KCl fulfills this requirement for the Zn dissolution reaction, while the temperature of 50 °C supports the passivation built-up on the pore walls during the quasi-cathodic reaction in the aqueous electrolyte. Introducing a diffusion limitation into the electrochemical system is a standard method to achieve a high control over the reaction kinetics of the occurring electrochemical reactions. In the present electrolyte this diffusion limitation is achieved by adding PEG 3350 to it. Exemplarily, reducing only the KCl electrolyte concentration to 0.05 mol/l results in a drastically lower pore density and the pronounced growth of needle-like Zn-oxide based structures on the pore walls, while a KCl concentration increase to 0.15 mol/l leads to thinner and smoother pore walls with hardly any pore wall coverage of nanometer-sized plate-like structures. An increase of the electrolyte temperature to 65 °C causes a similar effect as the reduction of the KCl concentration. Reducing the electrolyte concentration...
temperature down to 35°C decreases the pore density, increases the pore size, and also reduces the pore length. Increasing e.g. the anodic pulse potential to 0.1 V results in thinner pore walls, while a reduction to —0.1 V leaves thicker pore walls. All these results indicate that single process parameters cannot be changed independently without direct consequences for the match up of the passivation and etching conditions and thus, the pore growth conditions. Thus, changing e.g. the KCl concentration involves also an adjustment of the electrolyte temperature, viscosity, and the electrochemical etching parameters (pulse amplitudes, pulse lengths), so that the etching and passivation conditions are matched again.

Adding all these points to the crystallographic model all phenomena related to the growth of crystallographically-oriented pores in multicrystalline Zn can be explained conclusively.

**Mechanical interlocking with polymers.**—The concept of mechanical interlocking relies on the interlocking of two materials with each other without the need of forming chemical bonds between the two materials. In Fig. 7a a photograph of an ethyl-2-cyanoacrylate / porous Zn composite is depicted. The silver, shiny part is the untreated Zn sheet, other without the need of forming chemical bonds between the two materials, paints etc. as needed for a huge variety of applications.

**Conclusions**

In summary, the present paper has shown the self-organized growth of crystallographically-oriented macropores in multicrystalline Zn by nanoscale sculpturing. The pore formation and growth are obtained by pulsed potential switching between anodic dissolution and quasi-cathodic passivation of the developing pore walls. These pores exhibit characteristic features typically observed for crystallographically-oriented pores in semiconductors like pore growth along certain crystallographic directions, formation of pore domains, branching and intersection of pores.

The main direction of pore growth is along the <0001> with branching in [1120] and in [1210] directions. The pores are tapered with a hexagonal pore shape at the pore tip transforming into a rhomboid for the pore body. The pore diameter at the pore opening shows a wide size distribution from around 100 nm up to several microns depending on the total etching time and the time of pore nucleation. The resulting pore depth shows the same time dependence and ranges from several hundred nanometers up to several tens of microns. The pore walls in Zn entirely consist of Zn with only an ultra-thin, non-closed layer of nanometer-sized, plate-like structures that consist of Zn oxides unlike the conventionally found pores in metals like AAO with amorphous metal oxide pore walls.

It has been also shown that this porous Zn structure is perfectly suited for establishing high-strength joints between Zn and various polymers based on the concept of mechanical interlocking. The high amount of side pores as well as the random pore distribution with pores growing under various angles with respect to the Zn surface normal on a multicrystalline Zn substrate act as a two-level interlocking structure making a delamination of the polymer component from the porous Zn surface nearly impossible. The transfer of such porous Zn structures to Zn galvanized steels could be a suitable pathway to solve the commonly encountered adhesion problem between Zn surfaces and polymers, paints etc. as needed for a huge variety of applications.

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