On the Topography of Chemically Etched (000\bar{1}) Surfaces of ZnO

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Abstract

The pyramidally faceted etch topography of the (000\bar{1}) face of ZnO in 1 mol dm\(^{-3}\) HCl solution is discussed. It is shown that the topography can be regarded as a case of surface reconstruction to minimize surface free energy, with dissolution proceeding at the surface asperities.

Although the general nature of the topography of acid-etched (000\bar{1}) ZnO surfaces has been known for some time (Mariano & Hanneman, 1963; Heiland, Kunstmann & Pfister, 1963; Klein, 1965; Heiland & Kunstmann, 1969; Mariano & Wolff, 1968; Wolff, Frowley & Hietanen, 1964; Wolff, Das & Cocks, 1971), only in recent years, with the advent of scanning electron microscopy (SEM), have quite unusual aspects finally become apparent. Fig. 1 shows an SEM micrograph of an acid-etched (1 mol dm\(^{-3}\) HCl, 30 s, 323 K) (000\bar{1}) cleavage face of a vapour-phase-grown ZnO needle. The etched surface is sharply faceted in the form of an arrangement of highly regular six-sided pyramids. This brief note considers the origin of these features.

Two fundamentally different explanations for the presence of these pyramids can be considered. In the first the surface topography is regarded as being the result of preferential etching, i.e. of orientation-dependent dissolution rates. This approach can be formalized by use of the Frank kinematic theory of crystal dissolution (Frank, 1958, 1972; Frank & Ives, 1960). The second model supposes the observed topography primarily to be a surface reconstruction arising from rapid surface and volume diffusion processes, motivated by the requirements of minimizing the surface free energy. Earlier ideas of Gibbs (1928) and Wulff (1901) on the stable shapes of small particles have been extended by Herring (1950, 1951, 1952). Thus a plane surface can, in certain circumstances, minimize its surface free energy by breaking up into a hill-and-dale structure of small stable facets. Examples of this equilibrium type of faceting process arise at high temperatures [thermal faceting (Moore, 1963)], in sputtering (Chadderton, 1979a, b), as well as in certain heterogeneous chemical reactions having a high exothermicity (May, 1970).

Consider first the dissolution argument. It is established that a dissolving crystal of overall convex shape ultimately assumes a form in which it is bounded by fast-etching, curved surfaces (Cabrera & Vermilyea, 1958). More generally, the form of a crystal under dissolution control can be expressed in terms of Batterman's so-called reciprocity condition (Batterman, 1957) for which 'convex surfaces will on dissolution limit on fast-etching planes while slow-etching planes prevail on concave surfaces'. This result may also be deduced from Frank's kinematic theory of dissolution (Frank, 1958). We now apply the Batterman criterion to the question of the stability of intersections between facet planes (Irving, 1962). In the case of the faceted surface of ZnO, the valleys between pyramids represent concave intersections and the apices of the pyramids themselves convex intersections. Suppose that the pyramids – all are similarly oriented, with bases parallel to the \(a\) axis of the crystal – develop because their faces represent orientations of maximum etch rate compared with the much slower etching basal plane. This situation is shown schematically in Fig. 2(a), which illustrates the variation of etch rate with angle of rotation about a zone axis lying in an 'a' direction, starting from the orientation of the basal plane. It is easy to show from the reciprocity condition that the facet topography is unstable for the condition shown in Fig. 2(a) (Irving, 1962). Thus
Development of slow-etching basal plane orientations, concave intersections become rounded due to the development of slow-etching basal plane orientations, which is contrary to observation. On the other hand, the converse assumption (Fig. 2b) of minimum etch rate on the inclined surfaces and fast-etching basal plane orientations, although guaranteeing sharp concave intersections, results in a rounding of the apices of the pyramids due to the appearance there of fast-etching planes.

The proposal that the apices of the pyramids might be protected by some adsorbed impurity, as for an analogous situation in sputtering (Barber, Frank, Moss, Steeds & Tsong, 1973), is difficult to sustain here. The entire etched surface, including the pyramids, undergoes a general lowering during dissolution, and individual pyramids are not permanent features. They frequently disappear and are replaced. The overall sharply faceted topography, however, always remains the same.

One might envisage a certain combination of the etch rates (Figs. 2a and 2b), in which the basal-plane orientation represents a saddle point of relatively high etch rate, separated from low etch rate orientations by etch rate maxima (Irving, 1962). In this scheme both concave and convex intersections would remain sharp whilst the surfaces of the facets would be somewhat curved owing to the necessity to accommodate a change of orientation from high etch rate to low etch rate over the facet. Observation shows no visible curvature of the facets on ZnO.

In Herring's thermodynamic model, surface reconstruction occurs through diffusion processes which minimize the surface free energy of an initially plane surface (Herring, 1951). The inherent difficulty of dissolution kinetics - accounting for the origin of the facets - is thereby avoided. The most favourable facet orientations are provided by step-free low-index planes, which possess very sharply cusped minima in the Wulff polar plot of surface free energy (or more precisely surface tension) versus orientation (Herring, 1950, 1951, 1952). In the case of ZnO, facet orientations can be determined with a reasonable accuracy (≈1°) from measurements of the pyramid apex angles. We find in fact that the faces of the pyramids are relatively close in orientation to {1011} principal planes, although showing inclinations lower on the average by about 5°. These vicinal orientations of the facets, attributable to the presence of atomic steps, may be regarded as characterizing a steady-state approach to minimum surface free energy configurations. Minimal etch rate conditions, as in Fig. 2(b), should apply. Yet how can this latter requirement be reconciled with the presence of sharp asperities - apices of the pyramids? We propose that dissolution at the apex of a pyramid is continually reversed by rapid surface reconstruction. Herring estimates that edges and corners in the equilibrium shapes of crystals should be sharp to within a few tens of lattice spacings (Herring, 1951). The figure is very close to the experimental apex diameters in the present case (∼300 Å).

We wish now to consider the surface energies of the basal plane and the pyramidal surfaces of ZnO in terms of the bonding of the atoms on these surfaces. It is generally accepted that the ideal structures of the (0001) and (0001) surfaces of ZnO involve layers made up of anions and cations respectively. The atoms in these layers are triply bonded to the lattice and expose single 'dangling' bonds. The stoichiometric {1011} cleavage plane contains equal numbers of surface cations with threefold and twofold coordination to lattice oxygen ions (Atherton, Newbold & Hockey, 1971). The adsorption of water or chloride ions on cationic surface sites stabilizes the ideal surface configuration of faces such as (0001), reducing the ratio \( \gamma = \varphi_c / \varphi_a \) of the energies associated with cations and anions in cation-anion bonds to a value less than unity (Wolff, Das & Cocks, 1971). The reduction in surface energy of {0001} and {1011} planes results in instability of {0001} planes with respect to {1011} orientations. It can be shown that for values of \( \gamma \leq \frac{1}{3} \) the equilibrium form of ZnO is a pyramid with a (0001) base and {1011} sloping faces (Wolff, Frowley & Hietanen 1964). It is in these circumstances that an initially flat (0001) surface may lower its surface energy by breaking up into facets with {1011} orientations.
The general material transport mechanisms by which a solid can undergo changes of shape minimizing its surface free energy are volume diffusion, surface diffusion along an interface, evaporation – condensation and plastic flow (Herring, 1952). Scaling laws which govern the kinetics of surface-tension-motivated morphology changes (Herring, 1950) show that surface diffusion is always the dominant transport process in sufficiently small scale changes. In the thermal faceting of metals, for example, surface diffusion appears to be rate controlling in faceting on a scale <20 λm (Flytzani-Stephanopoulos & Schmidt, 1979), the size range involved on the (0001) surface of ZnO. Volume diffusion of defects in ZnO, such as interstitial zinc, becomes significant only at temperatures of 570–670 K (Thomas, 1957).

Now consider the section through the (0001) etch surface of ZnO shown in Fig. 2(c). During dissolution the profile of the facets is supposed maintained near equilibrium by surface diffusion of material from the valleys to the surface peaks. A slowing down of this reconstruction should result in rounding of the peaks by dissolution as shown in Fig. 2(b), not the rounding of valleys in Fig. 2(a). Experiment demonstrates that when the availability of water at the (0001) etch surface is restricted by solution diffusion limitations, an originally sharply faceted surface undergoes polishing through rounding of the surface peaks (Cope, 1981).

Finally, a comment on the greater depth of etching and higher facet density evident at the edges of the (0001) etch surface in Fig. 1. Corners in the equilibrium form of a crystal are points of maximum surface energy in the Wulff polar plot just as crystal faces are cusped minima (Wolff, 1967). Regions of higher surface energy arising in this way at the prism face boundaries of the (0001) surface may be the cause of the observed increased faceting and attack.

References


