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ScienceDirect

Progress in Crystal Growth and Characterization of Materials 62 (2016) 203–211

www.elsevier.com/locate/pcrysgrow

Review

# The role of surface and interface structure in crystal growth

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Available online 3 June 2016

**Abstract**

Crystal growth occurs at the interface of a crystal and its growth medium. Due to the abrupt termination at the surface, at the interface the properties of the crystal will typically deviate from the bulk and this can affect the growth behaviour. Also the properties of the growth medium at the interface will typically differ from the bulk. In growth from solution, for example, the liquid will show ordering induced by the crystal surface or have a different composition. Here techniques to study such growth interfaces will be discussed together with examples of the effect that the properties of the interface can have on the growth.


*Keywords:* interface structure; X-ray diffraction; AFM

## 1. Introduction

The growth process of crystals and thin films depends on a large number of parameters, e.g. mass transport, supersaturation and additives that together determine the crystallographic structure, morphology and perfection of the crystal. The actual growth takes place at the interface between the crystal and the growth medium (vapour, solution, melt or even solid), and thus a full understanding of the crystal growth requires a detailed knowledge of the interface structure. In most cases the actual location where growth takes place is at the steps on the surface and their role cannot be overstated. Steps, however, will be covered elsewhere and this paper will mainly focus on the atomic-scale structure at interfaces and its consequences for crystal growth.

## 2. Surfaces and interfaces

At the surface of a crystal the environment is very different from the bulk and therefore at a surface structural rearrangements are expected to occur (see Fig. 1). The larger the difference with respect to the bulk environment, the larger these structural rearrangements will be. For this reason crystal surfaces in vacuum often show the most dramatic effects. As an example, at the surface of a metal crystal the atoms find themselves in an environment with lower charge density than the equilibrium conditions in the bulk. Therefore most metal surfaces show an inward relaxation (around 5%) as this increases the charge density. A so-called reconstruction is a more dramatic structural rearrangement in which the surface forms a new unit cell in which some atoms may even be removed (or added). Fig. 1c shows an example where every other atom at the surface is removed, giving a translational symmetry with twice the spacing as in the bulk. If there would be no change in the other direction along the surface, this is called a $(2 \times 1)$ reconstruction ('Wood notation'). For surfaces in vacuum a wide variety of reconstructions has been found, the most famous of

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http://dx.doi.org/10.1016/j.pcrysgrow.2016.04.010
0960-8974/

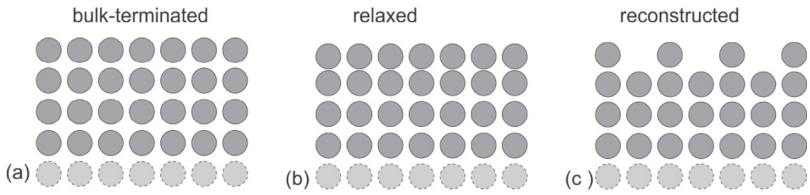


Fig. 1. At the surface of a crystal the atoms may stay in the same position as the bulk (a), but more often small structural changes, relaxations, occur (b). The surface may also reconstruct, involving significant atomic rearrangements and the formation of a larger unit cell.

which is the $(7 \times 7)$ reconstruction of the Si(111) surface [1]. In this covalently bonded crystal the termination at the surface cuts through many bonds and this is energetically very unfavourable. The reconstructed unit cell minimizes the surface energy by minimizing the number of dangling bonds and the strain by a surprisingly elaborate rearrangement.

When growing from a solution or melt, the transition from crystal to the growth medium is less dramatic and the rearrangements are typically smaller. Reconstructions do occur on crystal surfaces in solution, but much less frequently than in vacuum. In a solution or melt, however, structural changes will occur with respect to the structure in the bulk solution, both because of the change in environment at the interface and because the highly-ordered crystal structure will induce some order in the liquid as well. This order extends typically over 3–5 layers and the liquid is often called a quasi-liquid. This thin skin of partially-ordered liquid is the crystal-interface equivalent of the solvation shell found around dissolved molecules and ions in a solution. During growth of a crystal from solution, before a molecule (or atom) can enter the crystal lattice, it has to both get rid of its solvation shell and penetrate the quasi-liquid layer at the interface. Compared to bulk solution, the quasi-liquid layer will be less mobile and thus form a diffusion barrier. Depending on the strength of the interaction between crystal surface and the solvent, this barrier will vary in strength and thus different solvents can lead to different growth velocities for different surface orientations. This will lead to different growth morphologies. A simple example is rock salt (NaCl). When grown from water, NaCl forms cubes consisting of {100} facets. When grown from a water–formamide mixture with at least 10% formamide, an octahedral shape occurs, determined by {111} facets [2].

Quite often crystal growth yields crystals with well-defined facets. These are the directions of *slowest* growth, as all the faster directions 'grow out' of the morphology. These well-defined facets are the most stable and smooth interfaces with a low number of surface steps. The creation of steps on such a surface is relatively costly. Clearly, the free-energy cost of creating a step will depend on the solution and also this will determine the morphology. The easier it is to create steps on a specific facet, the faster it will grow and the less prominent it will show up in the crystal morphology. The number of steps on a crystal surface, i.e. the surface roughness, is thus highly relevant for crystal growth. For increasing temperature, the free-energy cost for creating a step decreases and for each surface a so-called thermal roughening temperature can be defined above which many steps occur. The specific facet will then disappear from the crystal morphology. The roughening temperature can be above the melting or decomposition temperature and in that case thermal roughening will not occur.

Crystallization is often used to purify materials, but additives may be added intentionally in order to modify the growth process. In the vapour growth of thin films of Ge on Si, for example, the lattice mismatch between Ge and Si leads to strain that is released by the formation of dislocations. By adding a layer of Sb as a surfactant that floats as a layer on top of the surface owing to its low surface energy, the mass transport of Ge is suppressed and the formation of dislocations is delayed [3]. The oldest example of the role of additives is from 1783, when Rome de l'Isle reported that the addition of urea to the aqueous growth solution changes the growth morphology of NaCl from cubic to octahedral [4]. This is the same effect as that of formamide, and the distinction between an additive (urea) and a solvent (formamide) is hard to make in this case.

## 3. Methods

When investigating a specific topic in science, most often no single method is available that provides all the answers and the surface/interface structure of growing crystals is no exception. In fact, this is an area that is still at the front of research as many things are not known yet due to the lack of suitable tools. Ideally, one would like to know the static and dynamic structure of the interface down to an atomic scale, including the step structure and for all possible growth environments. This is not (yet) possible, but a combination of existing techniques