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Crystal Growth Methods and Mechanisms

Abstract

Various methods of crystal growth are reviewed, considering solid, melt, solution, and vapor phase growth methods, as well as more exotic methods. The commonalities between the mechanisms of these different methods is also considered. Recent developments in the theory of near-equilibrium crystal growth are examined more in-depth, and an experiment is proposed towards an empirical understanding of the genesis of screw dislocations, integral to spiral growth patterns which predominate at near-equilibrium conditions. The experiment measures the formation of these dislocations in gold crystals grown from solution, on a substrate that has no initial dislocations. This is achieved by using a gold-functionalized Langmuir-Blodgett film for a substrate, as compared with a normal cloven gold substrate.

Introduction and Background

Crystalline matter is distinguished by its ordered structure. Specifically, is is a pattern composed of subunits (usually molecules) arranged in such a way that the environment of each unit is the same (consequently, each unit must be the same) [6]. Classically, crystallinity is closely linked with the solid phase of matter [6][21], but liquid crystals have gained widespread acceptance in the scientific community [9][18] and there has been recent interest in "colloidal crystals", which are colloids that emulate the structure of traditional crystals, but which can have different properties because of their scale [1][8][16][18][34][42][52].

Because of the broadening of the scope of what is considered crystalline, the process of crystal growth is also a growing topic, but it is hoped that just as new forms of crystal are analogous to the old, new crystals grow in analogous ways to classical ones. Indeed, they are being used as model systems to better understand crystal growth [18][52].

There are, in general three methods of crystal growth: solid growth, melt growth, and vapor growth [38]. Due to the extensive body of literature however, I will distinguish here melt growth and growth from solution, and also discuss some stranger methods, and generalizations that can be made about all of them.

Generalities

Traditionally, crystallization occurs at a thermodynamic phase boundary. However, conditions conducive to crystal growth are not necessarily enough to guarantee a crystal will begin to grow: crystals grow layer-by-layer or *epitaxially*. Consequently, they require something to grow on: either an impurity or a seed crystal. Under certain conditions, these seeds will form spontaneously in a process called *nucleation*. This is generally desirable, but the conditions under which it occurs are not necessarily the best for crystal growth [2].

After the nucleus forms, the growth process is driven by several instabilities in the system. If the system is near-equilibrium, classical crystals will form, but if it is not more complicated, dendritic structures may form [27]. Because the bonds crystals form are *anisotropic*, that is directionally specific,

crystals do not form spheres (as might be expected), but rather have faces, which may grow at different rates, giving a crystal a distinctive shape or *habit* [40][41][46][47]. There is a good theory that explains epitaxial crystal growth by assuming that each layer must be individually nucleated, but it gives growth rates that are orders of magnitude too small. An explanation involving a screw dislocation was put forwards, leading to the spiral growth mechanism, and this has since been borne out by experiment [14][39]. Such defects and impurities, while possibly undesirable in a finished crystal, have profound effects on the crystal growth process [4][10][45][51]

Recently, advanced techniques such as Atomic Force Microscopy (AFM) have allowed the direct observation of the crystal growth process, generally confirming the last century of theory [39][48][54]. Additionally, colloidal models have been serving as more easily observed physical models as well.

All crystallization processes can be classified by a dimensionless entropy factor called the Jackson α-factor. In general, the factor is strongly related to the strength of a crystal's habits [38].

Solid Growth

Solid growth processes include annealing and growth from gels. In any crystalline material, there are potentially multiple grains, which are essentially separate crystal structures. Annealing is a process that "grows" one grain at the expense of others, and is usually done by holding the material at an elevated temperature for an extended period of time [38]. Crystal growth from a gel is a reactive process, where one reactant diffuses through a gel containing the other reactant. It can produce large, high-purity single crystals [20].

Melt Growth

Melt growth is a freezing process in which a liquid self-organizes into a solid crystalline structure. Normal freezing will not usually produce single crystals, but processes such as the Kryopoulos or the Czochralski process avoid this difficulty by introducing a seed crystal [38]. The Bridgman technique is also similar, but more intricate [49]. Because these single crystals are essential to the manufacture of semiconductor chips, melt growth is a well-studied area, with extensive theoretical and experimental studies [13][15][24][25][31][35][55][56]. Melt growth also includes the zone melting or floating zone technique, in which a heater is moved along a sample. As the heater moves, it melts the area underneath it, which is small enough that it solidifies as part of the previous grain [38]. This technique also has the potential to produce high-purity, large single crystals of semiconductor material, and so is similarly well-studied [7][12][29][33][36][56].

Growth from Solution

Growth from solution is similar to growth from melt except that the concentration of the material is now a concern. If a melt is cooled below its freezing temperature but no nuclei are present, it is called *supercooled*. If a solution is cooled below the solubility of the solvent, it is called *supersaturated*, and is more "eager" to crystallize [11][17][23]. Additionally, mass transfer through the medium is an important consideration in solutions: more concentration drives the crystallization, but increased viscosity slows it [2][23]. Probably the best studied solution is sucrose-water [2].

Vapor Growth

The "third" general method of crystal growth is from the vapor phase. The case of sublimation is equivalent to growth from melt, as in the formation of dry ice from carbon dioxide [21]. Vapor transport is a method where the gas-phase material is passed through a tube and forms crystals on the container walls. It is analogous to growth from solution in many respects [5]. Finally, crystals may be precipitated by gas-phase reactions [38]. Some more exotic mechanisms can also be classified here, such as the "Vapor-Liquid-Solid" mechanism of single crystal growth [53].

Other Methods

While all methods generally will work the same as these, there are some instances where special treatment is merited. For example, biomineralization is a process where some microbial organisms sequester metallic side-products, which crystallize inside the organism like pearls [3][30][43]. Or in the case where naturally-formed minerals are studied, where the mechanisms may be understood, but cannot be controlled [22][44]. Atmospheric and oceanic ice crystals are of similar concern.

Usually crystallization is used a separation process, such as when producing ultrapure materials, but it has other uses. Protein crystallization is a delicate process that allows for structural analysis by x-ray crystallography. Because the purity of the crystals formed is of great importance for this procedure, it is desirable to grow these crystals in a microgravity environment, such as in orbit [19][37][50].

Better understanding of crystal growth mechanisms will also lead to greater ability to synthesize nanomaterials [26][32].

Proposed Research

Let us return to crystal growth at a screw dislocation, if only for its elegance: theory limits the rate of crystal growth by the necessity of re-nucleating each layer, but a screw dislocation presents a new edge on each layer, bypassing this need. This allows for crystal growth that is orders of magnitude faster than theory predicts, but with a guaranteed defect. This theory is the Burton-Cabrera-Frank (BCF) theory, and is closely related to periodic-bond-chain (PBC) theory.

However elegant the theory is, it is useless if it cannot be made to agree with experiment. The research conducted by Pina, Becker, and Risthaus [39], highlights some limitations of the BCF and PBC theories at near-equilibrium crystal growth processes. Because the "direction" of the screw dislocation changes with each layer, and the crystal is anisotropic, the screw dislocation's influence is confined to an ever-shrinking spiral, which itself is highly anisotropic.

Although Pina, Becker, and Risthaus provide tools and theory to model this process, they do not formalize their developments in the publication. It is proposed that the best conditions for the formation of a screw dislocation are found by experiment, and then that a complete model of near-equilibrium crystal growth is formally formulated.

Experimental Plans

It is desired to find empirically the rate at which screw defects from spontaneously, and so it is

necessary to exclude the influence of pre-existing defects in the substrate. In the paper by Pina, Becker, and Risthaus, barite was grown on a cloven barite substrate, which does not account for potentially pre-existing crystalline defects (it was not intended to). However, line defects like dislocations necessitate a three-dimensional structure; a two-dimensional structure would preclude such a defect. Thus using a self-assembled gold Langmuir-Blodgett film on a liquid surface as a substrate would guarantee freedom from these defects. Ensuring the purity of the solution could avoid many other defects. Such a substrate could however, still exhibit vacancies, impurities, grain boundaries, and topological defects unique to two-dimensional crystal structures [28]. The hope is that the influence of these other defects is not comparable to that of a pre-existing screw dislocation, but controls with cloven gold surfaces should also be run.

Then, these films (and their corresponding controls) should be exposed to different concentration and temperature conditions for equal amounts of time. These conditions should be chosen to be near equilibrium, so that spiral growth still dominates, but also to be as far apart from each other as possible. After, the density of spiral growth locations in an area for each sample can be counted manually under an AFM.

The density of these locations indicates the tendency for spiral defects to spontaneously arise under the corresponding conditions, the final piece of the near-equilibrium crystal growth theory. Armed with these calculations, and the corrections to BCF and PBC theory proposed by Pina, Becker, and Risthaus, a complete model of near-equilibrium crystal growth can be made, and compared with macroscopic crystal growth experiments.

Conclusions

Crystal growth is an enormous topic with myriad applications. Although it is well-studied, its ubiquity provides ever more opportunity for application and exploration, and even in the well-studied parts of the field there are gaps in our knowledge.

Acknowledgments

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