

Growth of perfect and imperfect crystals in gel: A general view

D. S. Bhavsar

Research Laboratory, Department of Electronics, Pratap College, Amalner India

ABSTRACT

Crystals can be grown by various methods. Out of which some methods are simple and can be carried set any where such as gel method. Gel method is very simple and useful method to grow the crystals which are insoluble or slightly soluble. There are various parameters by which this method can be controlled. Once the optimum conditions were obtained, then the crystals can be grown with ease and ampoule of crystals can be obtained. In this paper, as an general idea to grow crystals has been described.

Keywords: Gel, growth of ideal crystals, growth of real crystals.

INTRODUCTION

The subject of crystal growth has held a high level of interest, both scientifically and technologically, for a very long period. Nearly all-basic solid materials of modern technology are made of crystals. Hence an understanding of how crystals are grown is an important aspect of the science of materials. With the growing need for large crystals free from flaws for application in spectroscopy, piezoelectric measurements and various other purposes in industries, which all can not be met with from the diminishing natural sources, the science of crystal growth and other related topics is now being more actively cultivated than ever in its history. Therefore, it is necessary to understand the theories of crystal growth. First prediction of crystal growth came from Gibbs (1878) in the case of natural mineral crystals.

MATERIALS AND METHODS

The gel method is simple and accurate method to grow the crystals. Gel can be prepared by taking the mixer of Sodium Metasilicate and Acid. Both should be taken in proper proportion. This can be done by measuring the pH of the mixer. The pH of the mixer should be such that the gel should set near about 8 days. In our laboratory we have grown various types of crystals by this method.

RESULTS AND DISCUSSION

Growth of Crystals

Many workers have made contributions to the understanding of growth of crystals. Gibbs's surface theory was developed further by Curie [1] and Wulff [2]. Volmer [3] suggested that growth of a crystal takes place by adsorption of atoms or molecules, layer-by-layer, on the crystal surface. This is referred to as the theory of 'layer-by-layer' growth. Later, other workers proposed several notable modifications of this theory. Well [4] and Buckley [5] gave a review of the historical development of theories of crystal growth.

Up to 1940, although physicists had a reasonable notion of how crystal grows, they were not able to explain as to how a crystal could initiate and build new layers easily at a lower degree of supersaturation. This problem led to a series of surprising discoveries and to a new picture of crystals. Physicists went back over their analysis and calculations, but they could find no answer that made any sense on the basis of the old concept, which they had at that time about the growth of crystals. The problem remains unsolved until in 1949 when an English Physicist F. C. Frank [6] suggested a new model. He pointed out that growth of a crystal could easily be accounted for if one supposed that layers were not laid independently, one upon the other, but were built in a spiral fashion by a continuous process. This could occur if the crystal contained an imperfection of the type known as 'screw dislocation'.

The present state of our theoretical knowledge leads to recognize the distinction between ideal (perfect) crystals and real (imperfect) crystals. By ideal crystals is meant a crystal in which each atom is symmetrically surrounded by neighboring atoms in a regular geometrical configuration. As against this, an imperfect crystal is the one in which relative positions of the atoms differ from those characteristics of an ideal lattice by amount comparable to the interatomic spacing. The models of growth of these two types of crystals are briefly described below.

Growth of ideal (perfect) crystals

Between 1920 and 1940 Kossel [7], Stranski [8], Volmer [9] and others had built up a conventional theory of growth of a perfect crystal. Its principal idea can be illustrated in Fig 1.1, which represents the surface of the simple cubic crystal. The crystal will grow by the addition of molecules at A, the so-called repeatable step, because the binding energy is greatest at this point. A molecule joining the surface at any other position, B, C, or D will be held by a smaller number of bonds. The binding energy at the repeatable step or kink is equal to the energy of evaporation of the crystal as a whole. When a whole line of molecules has been added to a monomolecular ledge, starting of a new line will follow a different process, since the first molecule to be added will be held by only two bonds, and finally when a whole monomolecular layer has been completed, the next molecule will only be held by one bond and launching of a new layer will involve an even longer delay than the starting of a fresh line. The process of starting a new layer is known as surface nucleation and it involves a small group adjacent sites. The mechanism described here results in the formation of succession of monomolecular layers (i.e. layer-by-layer growth). In other words the crystals grow by spreading of layers of constant thickness.

Experiments indicate that in growth from vapour, the rate of escape of molecules from a solid to the surrounding vapour depends upon the intensity of motion of molecules, i.e. on the temperature. The rate of their return from vapour to solids depends on the concentration of molecules in the vapor i.e. vapour pressure. For every temperature there is a saturation vapour pressure at which the rate of escape and the rate of deposition at a step balance under these conditions the crystals do not grow. It can grow only when the vapour is supersaturated. This suggests that after a layer on the crystal surface has been filled, continued growth becomes more difficult. It should take a degree of supersaturation to start a new layer. Calculations by Burton [10] et al. had indicated that the formation of islands or nuclei, large enough to start new layers so that crystal should grow required a supersaturation of at least 25 to 50 percent. But in 1931 the German Physicist M. Volmer and W. Schults [11] had reported the growth of crystals from vapour with a supersaturation of 1 percent or lower; indeed most regular and well faceted crystals are observed at lower supersaturation. Bunn [12], Forty [13], Williams [14] and others have extensively used growth by layer deposition.

Growth of real (imperfect) crystal.

In an attempt to explain the above-mentioned big disparity between theories and experiment the nucleation theory was re-examined and found to be correct. The discrepancy between theoretical and experimental results was accounted for by recognizing the fact that all real crystals have imperfections in their structure. More important among them are the Schottky defects, Frankle defects, dislocation, grain boundaries, stacking faults, etc. Out of these, dislocation plays an important role in the growth of the crystals. Frank [15] pointed out that emergence of dislocation on a face crystal produces on the face a ledge of height equal to the Burger's vector. If the crystal is pictured as growing by the attachment of molecules to the edge of this ledge, then no surface nucleation is needed since the ledge question is self-perpetuating and continues to be present on the surface so long as the dislocation line intersects the surface. As growth proceeds the ledge winds itself up in a spiral form. Several stages in the development of a spiral are shown in Fig. 1.2. Further, since the turns of the spiral will be close together, a large proportion of the molecules adsorbed on the surface will reach the edge before re-evaporating. This explains the growth of the crystals at low supersaturation.

Was Frank's [15] radically new picture of crystal growth correct? It did not have to wait long for confirmation. The first published experimental observation supporting the growth of crystals by the spiral mechanism was by Griffin [16] on beryl. Verma [17] and Amelinakx [18] simultaneously observed spirals on silicon carbide crystals. What is more, since then intensive examination of crystals under a microscope has brought to light various growth patterns, which can only be explained, indeed were predicted, by the screw dislocation theory.

The volume of experimental observations supporting the theory of spiral growth of crystals has increased considerably. A collected account of these observations can be got from Verma [19] and Joshi [20]. However, there were workers who expressed doubts about several aspects of screw dislocation theory. The step heights of growth spirals are often too large to be understood in terms of screw dislocations, Buckley [3] suggested that the formation of spirals is connected with microscopic events occurring in the vapour adjacent to the surface at the time of solidification. Jagodsinski [21] suggested that the high energy required for the creation of a screw dislocation couldn't be had from the crystal structure until the crystal has grown to a considerable volume. According to Jagodsinski, in the case of SiC crystals, screw dislocations play a role only in the later stages of growth. On similar lines Knippenberg [22] has also explained his results.

How do screw dislocations originate? Answer to this question is largely speculative. Dislocations can be formed by the application of external forces to the crystal or they may be caused by internal stresses. According to Frank [15] either the crystal begins to on a foreign solid, which may already be dislocated, or if early mode of growth is dendritic the arms of the dendrite will probably meet each other imperfectly and produce dislocations. Dirt particles picked during growth also may introduce dislocations.

Modern theory of crystal growth.

For generalized model of crystal growth one had to wait till, Temkin [23] who in a series of four papers emphasized that only a few structural characteristics of the interface often exhibited in properties like perfect wetting and poor wetting and not the binding energy between the molecules of the crystal and liquid, determine the growth of the crystal. This can be applied to any type of fluid-crystal phase transformation. These have appeared in the literature, a number of theories of crystal growth, Chernov and Muller-Krumvhaar [24], Mullin [25], Goodman [26, 27] and 1978), from these various theories one conclude that the rate of crystal growth will depend on the chance of an atom finding a site on a completed flat surface rather than the rate of which subsequent atoms are adsorbed at the layer which is thus started. Currently a unified microscope interface theory of multi-component crystal growth, comprising master equation approximation Saito and Muller-Krumvhaar [25], order parameter concept, Cherepanova [28], multiplayer sos-lattice interface model, Pfeiffer and Haubenreisseo [29], and statistical approximation scheme, Cherepanova [28], and Temkin [23] is in vogue. However, the basic questions, what is the growth mechanism and how is the nucleus formed, still remained unanswered, Wendt and Abhram [30], Hsu and Rahman [31].

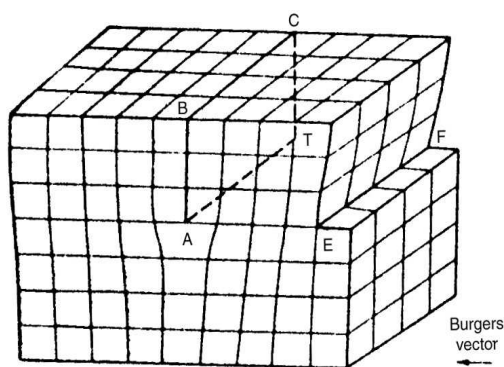


Fig. 1.1 (a) Edge dislocation

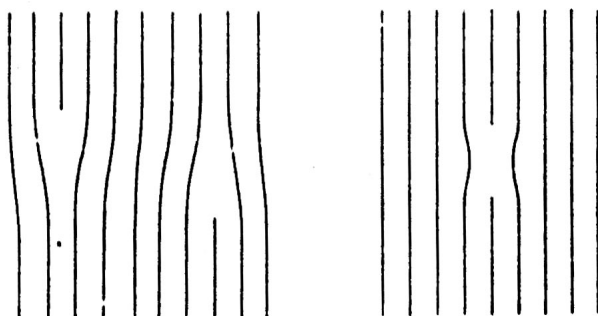


Fig. 1.1 (b) A positive and negative edge dislocation

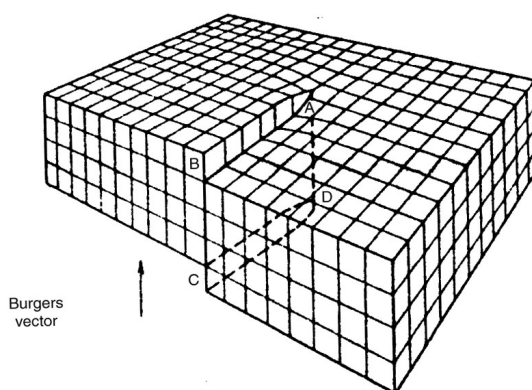


Fig. 1.2 Screw dislocation

CONCLUSION

In this paper as a theoretical part to grow the crystals by gel method has been described. It is possible to grow the real crystals by trial and error method. Once the optimum conditions obtained, it can be possible to grow the crystals rapidly. Large precautions should be taken while growing the crystals. Real crystals can be grown by this simple method which are insoluble or sparingly soluble in water.

REFERENCES

- [1] Curie, P., (1885), *Bull. Soc. France Minero.*, 8 ,145.
- [2] Wulff, G., (1901), *Krist.*, 34, 3449
- [3] Volmer, M. Z., (1922), *Phys. Chem.* 102, 288.
- [4] Wells, A. F. (1946), *Crystal Growth*, Am. Rep. Chem. Soc. London, 43, 62.
- [5] Buckley, H. E., (1951), *Crystal Growth*, John Wiley and Sons, New York.
- [6] Frank, F. C., (1949), *Disc. Faraday Soc.* No.51, P. 48
- [7] Kossel, W., (1927), *Nachr. Gen Wiss. Gottingen.*, 135.
- [8] Stranski, I.N., (1928), *Z.Phys.Chem.*, 136, 259
- [9] Volmer, M. Z., (1939), *Kinetic der Phasenbildung*, Dresden and Leipzig.
- [10] Burton, W. K. and Cabrera, N., (1949), *Disc. Faraday Soc.*, 5, 48.
- [11] Volmer, M.Z. and Schultse W. (1931), *Z. Phys.Chem. A* 156
- [12] Bunn, C. W. and Emmett, (1949), *Discuss Faraday Soc.*, 6, 119.

-
- [13] Forty, A.J., (1951), *Philips Mag.* 42, 670
 - [14] Willaims, A. P., (1957), *Phil. Mag.*, 2, 269, 3,343.
 - [15] Frank, F. C., (1951), *Acta. Cryst.*, 4 , 497.
 - [16] Griffin, L. J., (1950), *Phil. Mag.*, 41, 196.
 - [17] Verma, A. R., (1951), *Nature*, 167, 939.
 - [18] Amelinckx, S., (1952), *Nature*, 169, 841
 - [19] Verma, A. R., (1953), 'Crystal Growth and Dislocations' (Butterworth Publications, London)
 - [20] Joshi, M. S., (1959), Ph.D. Thesis, London University.
 - [21] Jagodsinski, H., (1954), *Neves Jahrb, Miner Monatsch*, 3, 49, *Acta. Cryst.*, 8 ,279.
 - [22] Knippenberg, W.P., (1963), *Philips Research Repli.* 18, 161
 - [23] Temkin, D. E., (1981), *J. Cryst. Growth*, 52, 319.
 - [24] Chernov, A. A. and Muooer-Krumbhaar H., Ed. Modern, (1983). *Theory of Crystal growth – Growth Properties and Applications*, Vol. 9, Springer.
 - [25] Mullin, J. W., (1977), *Crystallization*, 2nd Ed., Elsevier, Amsterdam.
 - [26] Goodman, C. H. L., (1974), *Crystal Growth Theory and Techniques*, Vol. 1 and 2, Plenum, New York.
 - [27] Goodman, C. H. L., (1978), *Crystal Growth Theory and Techniques*, Vol. 1 and 2, Plenum, New York.
 - [28] Pfeiffer, H., Haubenreisser, W., (1980), *Phys. Stat. Sol. (b)*, 101 , 253.
 - [29] Pfeiffer, H., Haubenreisser, W., (1980), *Phys. Stat. Sol. (b)*, 101 , 253.
 - [30] Wendt, H. R. and Abhram, F. F., (1978), *Phys. Rev. Letters*, 41, 1244.
 - [31] Hsu, C. S. and Rahman, A., (1979), *J. Chem. Phys.*, 71, 4974.