



Characterization of crystals by etching and mechanical properties

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Abstract : Crystals have gained an important role in modern technology because of their certain properties. Growing single crystals is not an easy task. It requires a complete knowledge of phase transition as well as solubility in different solvents. Before using a crystal in a device it is better to judge its thermal, optical and mechanical properties. It is also required to know the presence of defects, dislocations in the crystal. Generally mechanical properties are measured in terms of hardness measurement and defects present in the crystals are revealed by means of etching. In this paper we concentrate on how the mechanical properties are measured and how the defects are determined.

Keywords : Crystals, crystal growth method, hardness, etching

1.Introduction

Crystals have fascinated man because of their rarity and beauty since prehistoric times. For over 6000 years, humans have used crystals to adorn their bodies, to decorate their homes, and to benefit physical and emotional conditions. The delicately faceted surfaces of crystals have always been a source of fascination and delight. They seem to represent a degree of perfection that is not present in other forms of matter. In the realm of pure solid substances, they are the rule rather than the exception, although this may not be apparent unless they are observed under a microscope. Visual examination of crystals was able to establish a fairly mature science of crystallography.

In the language of science, a crystal or crystalline solid materials (such as atoms, molecules or ions) are arranged in a highly ordered microscopic structure, forming a crystal lattice that extends in all directions. There are several planes –called faces – which constitute the external boundaries of the solid. The multiple faces invariably display certain geometrical relationships to one another, resulting in a symmetry that attracts our attention and delights the eye.

A common method of growing large single crystals involves growth of the material from its solution. The growth methods may be classified according to their phase transition, as

Solid growth : Solid-Solid phase transition

Solution growth : Liquid-Solid phase transition

Melt growth : Liquid- Solid phase transition

Vapour growth : Vapour-solid phase transition

The common condition for all crystal growth process to occur is that the growing crystal must have lower free energy than the initial stage of the system. The selection of any crystal growth method depend much on the properties of the material and to a greater extent on the growth kinetics, requirements of size, shape, purity and economics. The various methods of crystal growth have been discussed in detail by various authors [1-3].

2. Defect characterization for use of crystals in devices :

Knowledge of the nature and distribution of defects in crystals is necessary because of their profound effects on the performance of electronic devices. In order to assess the quality of the crystals grown in the laboratory various techniques have been developed. These techniques include-

- i) Etching
- ii) Decoration technique
- iii) X-ray diffraction method
- iv) Birefringence
- v) Transmission electron microscopy

2.1.1 Etching technique :

Etching technique is a very simple and elegant technique to reveal dislocation sites in crystals and gives us an idea about the configuration and character of dislocations present in the crystal. Thermal, mechanical or chemical means may be used for etching.

Chemical etching is one of the important micromachining processes that is extensively used to produce microelectronic components for various applications. The process is simple, cost-effective and versatile which makes the method very popular [4-5].

Chemical etching is probably the first micromachining process; it was used to produce jewelry from copper by etching with citric acid solution in the Ancient Egypt around 2500 BC [6]. The process accepted as one of the key manufacturing processes after 1950's; one company (North American Aviation Inc., USA) etched aluminium for the production of rocket parts. The method was patented and named as "chemical milling" [7]. In the last half century, chemical etching and its various variations have been heavily used in aerospace, automotive, precision engineering, medical and optics industries. The process is also known in various names such as chemical machining, wet etching or etching [8-10].

In chemical etching the crystal is treated with a solvent or mixture of solvents in which the crystal is slightly soluble. As a result the surface of the crystal gets dissolved and depressions usually called pits appear at the sites where the dislocation intersect the surface. The pits can be observed under a optical microscope from which the nature and density of dislocation could be determined. Suitable dislocation density that can be assessed under microscope is less than $10^7/\text{cm}^2$ [11]. Impurities, vacancies also give etch patterns.

When a crystal is placed in an undersaturated solution of its own material or in some chemicals a double layer forms at the crystal liquid interface. This layer consists of specially adsorbed ions on the surface. The adsorption of ions or molecules of a reactant leads to the formation of adsorbed complexes on the crystal surface. These complexes subsequently dissociate into reaction products. Thus after the formation of an interfacial layer, further reactions between the crystal and the etchant depend on the solubility and solubility of the reaction products forming on the crystal surface. If the reaction product is highly soluble, the thickness of the layer may temporarily reduce and the dissolution process may be accelerated. The necessary condition for the formation of visible etch pits is the proper ratio of the three dissolution rates V_n (normal etch rate along the dislocation line), V_t (tangential etch rate across the surface) and V_p (rate of dissolution of the defect free surface). Etch pit formation takes place when $V_n > V_p$ and their contrast is determined by the ratio V_n/V_t . Gilman et al. [12] first pointed out that etch pits visible under an optical microscope is formed when $V_n/V_t > 0.1$.

2.1.2 Effect of different factors on etching:

i) Effect of additive : The effect of an additive and of its concentration in a solvent on the surface micromorphology and etch rates has been observed in many cases. With the change in the concentration of an additive in a solvent the morphology of dissolution etch pit changes. At different concentrations an impurity

in the same solvent reveals dislocation etch pits of different orientation. By adjusting the additive concentrations it is possible to obtain pits of same orientation and to know the relation between additive concentration and crystal solubility using the relation

$$\gamma_v = B^1 \ln c_{\text{imp}} - B^1 \ln c_{\text{imp}}^0$$

where B^1 and c_{imp}^0 are constants whose values depend on the nature of impurity and c_{imp}^0 denotes the impurity concentration required to produce pits of a particular orientation, γ_v determines undersaturation or solubility.

Effect of undersaturation : The effect of addition of water, acids and organic liquids, is related with the changes caused in the undersaturation of a medium with respect to the crystal. The dependence of the lateral etch rate on the volume ratio γ_v of an added solvent may be represented by the relation

$$v = v_0 \exp(b \gamma_v)$$

where v_0 is the etch rate in a solvent corresponding to $\gamma_v = 0$ and b is a constant whose value depends on the type of solvent added.

Effect of solvent : Etch pits can be produced by etchants composed from solvents in which a crystal is highly or poorly soluble. The contrast of dislocation etch pits decreases in the homologous series of organic acids and alcohols with the addition of a CH_3 group. However, the capability of slow solvents to reveal dislocation etch-pits is enhanced upon the addition of an inorganic salt or a solvent in which the crystal is more soluble.

Effect of etching time : The morphology of etch pits formed after prolonged etching in an etchant corresponds to the morphology of pits formed after short etching durations in the etchant containing a lower amount of the additive. The time dependence of v_t and v_n in slow solvents and in etching solutions containing impurities, and the change in the morphology of etch pits on prolonged etching, are attributed to the time dependent adsorption of inhibiting species and solvent molecules at the newly created surface.

Effect of stirring : Stirring of an etchant invariably leads to a change in the morphology of dislocation etch pits. The effect of stirring on the etch rates is expected when the dissolution process is diffusion controlled as a result of reduced undersaturation near the etching surface, such that the rate of kink nucleation is reduced.

Effect of temperature: The morphology of dislocation etch pits often changes with a change in etching temperature. Dissolution rates always increase with an increase in the temperature of etching in an etchant. This dependence follows an Arrhenius-type equation ,

$$V = A \exp(-E/KT)$$

Where v denotes the etch rate, A is the pre exponential factor, E is the activation energy. The activation energy depend on the nature of additive, concentration in the solvent, stirring of etchant.

3. Hardness measurement:

The concept of material hardness has been tracked historically by Walley starting from biblical time and proceeding until the 1950s, with pictorial emphasis given to the earliest 19th century design of testing machines and accumulated measurements [12]. Walley's review leads up to David Tabor setting a new course via science connection with his seminal 1951 book *The Hardness of Metals* [13] and further leading, for example, to a later 1973 conference proceedings on *The Science of Hardness Testing and Its Research Applications* [14]. The subject has gained increased importance with the relatively recent advent of orders of magnitude greater force and displacement measuring capabilities available with modern nano-indentation test systems. A review was presented in 2013 of the complete elastic, plastic and, when appropriate, cracking behaviors that can be monitored for crystals, polycrystals, composites and amorphous materials under suitable probing indentation [15]. A substantial reference list was included in the review of conferences and books produced until that time. As will be seen in the current updated collection of research and review articles, no crystal can be too soft or too hard within its environment to escape measurement with a suitable probing indenter applied using appropriate test conditions.

The metals handbook defines hardness as “resistance of metal to plastic deformation, usually by indentation”. However, the term may also refer to stiffness or temper, or to resistance to scratching, abrasion, or cutting. It is the property of a metal which gives it the ability to resist being permanently deformed, when a load is applied. The greater the value of hardness, the greater resistance it has to deformation. In mineralogy the property of matter commonly described as the resistance of a substance to being scratched by another substance. In metallurgy hardness is defined as the ability of a material to resist plastic deformation. Hardness tests are commonly carried out to determine the mechanical strength of materials and it correlates with other mechanical properties like elastic constants and yield stress [16]. The hardness test has proved to be a valuable technique in the general study of plastic deformation [17]. The resistance of a crystalline body to elastic or plastic deformation is dependent on the bonding forces between the atoms. Materials in which the molecular chains are bound together by weak van der Waals forces and hydrogen bonding are soft whereas crystals composed of atoms or molecules with strong ionic or covalent bonding are hard in nature. Hardness of crystal is a complex property, which depends on a large number of factors such as impurities, dislocations, vacancies, temperature and composition. [18].

Hardness measurement can be defined as macro, micro and nano scale according to the forces applied and displacement obtained. Measurement of the macro-hardness of materials is a quick and simple method of obtaining mechanical property data for the bulk material from a small sample. Microhardness is the hardness of a material as determined by forcing an indenter such as Vickers or Knoop indenter into the surface of the material under 15 to 1000 gm load; usually, the indentations are so small that they must be measured with a microscope. Nano indentation tests measure hardness by indenting using very small, on the order of 1 nano-Newton, indentation forces and measuring the depth of the indentation that was made.

Conclusion

Crystals have attracted man because of their beauty and rarity. The significance of that beauty for a technological society and for the development of scientific knowledge has only begun to be realized, however. The basis of the beauty is now known to be things as symmetry, structural simplicity and purity. These characteristics endow crystals with unique physical and chemical properties which have already been used to cause a major transformation of the electronics industry and systems based on it.

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