SELECTED TOPICS IN SOLID STATE PHYSICS

Editor. E P. WOHLFARTH

The Growth of Crystals from Liquids

BY

J. C . BRICE

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PREFACE

In the preface of a previous book (Brice (1965b)) crystal growth was described as a craft. That is still a good description. The processes involved cannot yet be completely predicted, but the original art is becoming more scientific and is being much more widely studied. When the time came to revise the previous book, it was clear that almost every section must be rewritten. Solution growth at both high and low temperatures has many similarities to melt growth. The opportunity was therefore taken to include descriptions of solution growth so that the present work covers growth from all types of liquids.

The aim of this monograph is to give a simple account of the scientific principles of and the methods for the growth of single phase crystals. No attempt is made to cover the field of composite growth. The treatment of interface stability therefore omits much interesting but complex theory. Similarly because attention is concentrated on bulk crystals, steady state transport is usually assumed and only scant attention is paid to transient effects.

The book can be split roughly into four parts. The first of these, which comprises the first chapter and parts of the second, is introductory. The remainder of the second chapter and chapters 3 and 4 cover the theoretical aspects of the subject. The third part of the book – chapters 5 to 10 – describes the practical aspects of growth from liquids. The final part, chapter 11, is essentially a postscript which attempts to gather together some of the ideas put forward in the previous chapters and to present them in a wider context.

These parts of the book can be used in various ways. Someone

interested primarily in techniques could read chapters 1 and 5 followed by any desired combination of chapters 6 to 11. Similarly, someone interested mainly in the theoretical aspects could read chapter 1 (omitting §§ 5 to 7) and then chapters 2, 3 and 4. It is hoped however, that the majority of readers will attempt to read most of the book, because techniques can be better applied if the limitations imposed by the theory are known, and theory with no idea of practical application is likely to be sterile.

Any book must reflect the interests and prejudices of the author. This one is not an exception. However, his views have been modified by much discussion with many workers in the field. In the text an attempt is made to give credit to those to whom it is due, but it is doubtful whether this has been done completely. The author's colleagues at Mullard Research Laboratories (Messrs J. Chadwick, O.F. Hill, M.J. King, E.J. Millet, J.L. Page, P.A.C. Whiffin and particularly P.W. Whipps) have done much to correct the errors and eliminate the misplaced enthusiasms in the original draft and have freely contributed much of the data used to illustrate the various points. Similar help has been given by colleagues in other Philips Laboratories, including Professor A. Rabenau and Dr U. Gross (Aachen), Dr W. Tolksdorf and Dr D. Mateika (Hamburg), Mr J.J. Brissot (Paris), Mr J. Goorissen, Dr C.J.M. Rooymans, Dr J.M. Robertson and Dr W. Albers (Eindhoven).

The author is also grateful to Mr R.T. Harriden and Miss C. McCarriston who prepared the figures and to Mrs B. Ingram who typed the manuscript.

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LIST OF MOST IMPORTANT SYMBOLS; PREFERRED UNITS

A	Radius, mm
A	Area, mm^2
A	Constant defined in the text
a	Radius, mm
B	Constant defined in the text
b	Burgers' vector, mm
C	Concentration, mm^{-3}
C	Specific heat, joules per gram atom or molecule
c	Specific heat, joules per gram
D	Diffusion coefficient, $cm^2\ sec^{-1}$
E	Energy, joules
F	Free energy, joules $mole^{-1}$
F_v	Free energy per unit volume, joules mm^{-3}
f	Linear growth rate, mm sec^{-1} or mm hr^{-1}
G	Shear modulus, dynes mm^{-1}
g	Acceleration due to gravity, 9810 mm sec^{-2}
H	Enthalpy, joules $mole^{-1}$
h	Planck's constant, 6.624×10^{-27} erg sec
h	Heat transfer coefficient, mm^{-1}
i	General number or symbol
j	General number or symbol
K	Thermal conductivity, watt $cm^{-1}\ C^{-1}$
K	Segregation coefficient
K	Mass action constant
k	Boltzmann's constant, 1.38×10^{-16} erg C^{-1}
k	Distribution coefficient

L	Length, mm
L	Latent heat, joules g^{-1}
l	Length, mm
M	Molar weight, gram
m	Number
m	Slope of liquidus
N	Number
N_0	Avogadro's number, 6.02×10^{23}
n	Number
P	Pressure, dynes cm^{-2}
Q	Flux
R	Gas constant, 8.314 joules $mole^{-1}$
r	Radial distance, mm
S	Entropy, joules $mole^{-1}$ C^{-1}
s	Height of liquid column, mm
T	Absolute temperature, K
t	Time, sec
u	Number of nearest neighbours
V	Volume, mm^3
v	Velocity, mm sec^{-1}
w'	Number of nearest neighbours in the same plane
w	Interaction energy, joules $mole^{-1}$
X	Atom fraction
x	Distance (parallel to growth axis), mm
y	Distance, mm
z	Distance (vertically), mm
α	Coefficient of linear expansion, C^{-1}
β	Coefficient of volume expansion, C^{-1}
γ	Surface free energy, ergs cm^{-2}
γ	Surface tension, ergs cm^{-2}
γ_i	Activity coefficient of ith component
δ	Boundary layer thickness, mm
ε	Emissivity, watts cm^{-2} C^{-4}
ε	Evaporation constant, mm sec^{-1}

η	Viscosity, poise
θ	Angle, radians
θ	Relative temperature, C
λ	Atomic spacing, mm
λ	Wavelength, mm
ν	Frequency, Hz
ρ	Resistivity, Ω cm
σ	Molecular diameter, mm
τ	Time constant, sec
τ_c	Critical shear stress, dynes mm^{-2}
ϕ	Free energy per particle, joules
ω	Rotation rate, radians sec^{-1}

Suffixes

A	Of *A*
B	Of *B*
d	Dislocation
e	Equilibrium
G	Gas
i	Of the *i*th component, at the interface, interstitial
L	Liquid
M	Molar
m	Melting
P	Pressure
S	Solid, solute, solution
T	Thermal
V	Volume, vapour, vapourization
0	Equilibrium or limiting value

CONTENTS

PREFACE v

CONTENTS vii

LIST OF MOST IMPORTANT SYMBOLS; PREFERRED UNITS . . xi

CHAPTER 1. BASIC CONCEPTS 1
1. Introduction 1
2. Methods of growth from the melt 4
3. Methods of growth from solution 8
4. Other methods for the growth of crystals 10
4.1. Crystal growth in the solid state 10
4.2. Crystal growth from the vapour 12
5. Phase relations 14
6. Growth kinetics. 17
7. Transport effects 22

CHAPTER 2. SOLIDS, LIQUIDS AND GASES 26
1. Introduction 26
2. Binding forces in solids 26
3. Crystal lattices 28
4. Equilibrium defects 30
5. Non-equilibrium defects 33
6. Impure solids 40
7. The solid–liquid transition 42
8. Sublimation and evaporation 44
9. Phase relations 46
9.1. Major components 47
9.2. Minor components 53
10. The estimation of relevant physical properties 64
10.1. Background 64

10.2. Specific heats 65
10.3. Phase transitions 70
10.4. Viscosities 70
10.5. Diffusion coefficients 71
10.6. Thermal conductivities 73
10.7. Thermal expansion 73
10.8. Surface tension 75
10.9. Emissivities 76
10.10. Solutions 77
10.11. Conclusions 77

CHAPTER 3. GROWTH KINETICS 78
1. Introduction 78
2. The driving force 79
3. Crystal morphology 81
4. Possible types of interface 85
5. Nucleation 89
6. Growth on rough sharp interfaces 97
7. Growth on perfect sharp singular interfaces 103
8. Growth on imperfect sharp singular interfaces 110
9. Diffuse interfaces 117
10. Some conclusions about growth mechanisms 119
11. The interface segregation coefficient 120

CHAPTER 4. TRANSPORT PROCESSES 128
1. Introduction 128
2. Boundary layer theory 129
3. Transport in bulk liquids 138
4. Transport in solids 143
5. Transport effects at growing interfaces 150
5.1. The steady state growth rate 150
5.2. Effective segregation coefficients 154
5.3. Non-steady state effects 158
6. Interface stability 160

CHAPTER 5. GENERAL TECHNIQUES 171
1. Introduction 171
2. Constructional materials 171
3. Methods of heating 175

4. Temperature measurement 180
5. Temperature control. 183
6. The production of slow movements 190
7. Methods for attaching seed crystals 192
8. Containers 194
9. Atmospheres 197
10. Starting materials 201
11. Methods of assessment 202

CHAPTER 6. MELT GROWTH IN CRUCIBLES 207
1. Introduction 207
2. General considerations 209
3. Apparatus for normal freezing 211
3.1. Crucibles 211
3.2. Furnaces 214
4. Apparatus for zone methods 218
5. Techniques for volatile materials 220
6. The control of perfection. 223

CHAPTER 7. PULLING FROM THE MELT 226
1. Introduction 226
2. Some basic concepts. 228
2.1. The shape of the liquid surface 228
2.2. The interface shape 230
2.3. Static heat flow. 231
2.4. Dynamic heat flow 232
2.5. The rate of growth 233
3. Apparatus 234
4. Volatile materials 240
5. Some modifications to the method. 244
5.1. The growth of dendrites 244
5.2. Pulling shaped crystal 245
6. The addition of dopants 247
7. The control of perfection. 252
7.1. The control of crystallographic quality. 253
7.2. The control of homogeneity 255

CHAPTER 8. MELT GROWTH WITHOUT CRUCIBLES . . . 258
1. Introduction 258
2. The Verneuil technique 259

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3. Floating zone refining 265
3.1. Stability of floating zones 265
3.2. Means for producing molten zones 269
3.3. Other apparatus requirements 274
3.4. The control of perfection. 277
4. The submerged-arc fusion method. 279

CHAPTER 9. LOW TEMPERATURE SOLUTION GROWTH . . 282
1. Introduction 282
2. Solvents 284
3 Other general considerations 288
4. Slow cooling methods 290
5. Evaporation methods 293
6. Temperature gradient methods 295
7. The control of perfection. 297

CHAPTER 10. HIGH TEMPERATURE SOLUTION GROWTH . . 301
1. Introduction 301
2. Properties of typical solvents 302
3. Slow cooling methods 308
4. Evaporation methods 317
5. Temperature gradient methods 319
6. Some special methods 324
7. The control of perfection. 327

CHAPTER 11. THE SELECTION OF METHODS 330
1. Introduction 330
2. Technical choices 330
3. Available experience. 331
4. Economic aspects 333
5. Optimization 335
6. Some conclusions on crystal growth 337

REFERENCES 338

AUTHOR INDEX 363

SUBJECT INDEX 377

CHAPTER 1

BASIC CONCEPTS

§ 1. INTRODUCTION

In an ideal crystal the surroundings of any atom would be exactly the same as the surroundings of every similar atom. Real crystals are not quite so perfect: they must always contain some defects and will usually contain some impurities. However, single crystals are solids in the most uniform condition that can be attained and this is the basis for most of the uses of crystals. For example, it leads to great uniformity and reproducibility of mechanical properties which are very desirable in the construction of highly stressed components – turbine blades, wire drawing dies and various bearings. However, perhaps the most useful feature is that uniformity can allow the transmission without scattering of both acoustic and electromagnetic waves and charged particles. This transparency which can be selectively modified by the controlled addition of impurities is the foundation of the modern electronics industry and has made possible devices like transistors, solid state lasers, quartz piezoelectric filters and a host of electromechanical and magneto- and electro-optical components.

To be useful in these various applications, crystals must have the appropriate properties, which depend on the particular substance and the impurities and defects present. The semiconductor industry for example, relies on pure materials with controlled additions of impurities: the presence or absence of dislocations (discontinuities in the crystal lattice) can have a profound effect on how these impurities behave during the processes required to make the device. Table 1.1 gives some examples of the uses of crystals.

TABLE 1.1

Some uses of crystals

Property exploited	Device[a]	Crystal
Uniformity alone	X-ray prisms	Lithium fluoride
	Neutron collimators	Metals
Uniformity giving reproducible mechanical properties and abrasion resistance	Turbine blades	Metals
	Gramophone styli	Sapphire
	Bearings	Ruby
	Tape recorder heads	Ferrites
	Wire drawing dies	Diamond
Uniformity eliminating scattering of electromagnetic waves	Lenses, prisms and optical windows	Alkali and alkaline earth halides
	Lasers*	Yttrium aluminium garnet
	Microwave filters	Yttrium iron garnet
Uniformity reducing charged carrier scattering	Transistors*	Silicon, germanium and gallium arsenide
	Diodes*	
	Thyristors*	
	Photocells	Cadmium sulphide
Uniformity reducing scattering of sound waves	Resonant filters	Quartz
	Delay lines	Lithium niobate
		Zinc oxide
Uniformity allowing exploitation of tensor properties	Nicol prism	Fluorite
	Ultrasonic transducers	Rochelle salt
	Gramophone pick-ups	Lithium sulphate

[a] The devices marked with an asterisk use crystals with controlled additions of impurities. In the case of complex structures, the necessary impurities can either be incorporated in a series of growth processes or can be added after growth by diffusion (Shaw (1972)) or by ion implantation (Mayer *et al.* (1970)).

At the present time crystals of nearly two hundred materials are commercially available. A survey of the methods of growth suggest that almost 80% are grown from the melt compared with roughly 7% from the vapour, 5% from low temperature solution, 5% from high temperature solution, 3% from the solid and only 2% by hydrothermal methods. In some cases huge quantities of crystals are grown annually (e.g. silicon, quartz, germanium, ruby and the dihydrogen phosphates of potassium and ammonium). Lists based on other criteria (for instance the volumes of the crystals produced, or their value) would therefore show less emphasis on melt growth. Although it would still occupy first place, the other methods would be seen to make much more significant contributions.

This chapter gives a brief introductory review of the methods by which crystals may be grown and the theory of the mechanisms which control their purity and perfection. This book deals only with growth from the melt and from solution. These methods are discussed in §§ 2 and 3, but for completeness, the other methods are reviewed briefly in § 4. Surveys of growth methods have been given by many authors (see for example, the books by Buckley (1951), Lawson and Nielsen (1958), Smakula (1962), Gilman (1963), Wilke (1963) and Laudise (1970) and the papers by Short (1957), Anon. (1965), White (1964, 1965a), Chinmulgund (1969) and Botsaris *et al.* (1969)). Representative examples of most methods can be found in the conference proceedings edited by Peiser (1967), Frank *et al.* (1968) and Laudise *et al.* (1972).

Some of the readers of this book will not want to consider in detail the theoretical aspects of crystal growth and will wish to omit chs. 2, 3 and 4. However, some knowledge of the processes occurring can be very useful and should lead to the growth of better quality crystals. The final three sections of this chapter therefore, give brief non-mathematical reviews of phase relations, growth kinetics and transport processes.

§ 2. METHODS OF GROWTH FROM THE MELT

All the methods of growth from a melt rely on cooling the liquid below its freezing point. This type of process normally produces a polycrystalline mass. However, if care is exercised one crystal can be made to propagate. The techniques by which this is done can be split into three rather arbitrary groups.

In the first group usually associated with the names of Bridgman (1925), Stober (1925) and Stockbarger (1936), the melt is contained in a crucible and is progressively frozen from one end. This can be achieved by:

(1) moving the crucible down a temperature gradient,
(2) moving the furnace over the crucible, or
(3) by keeping both the furnace and the crucible stationary and

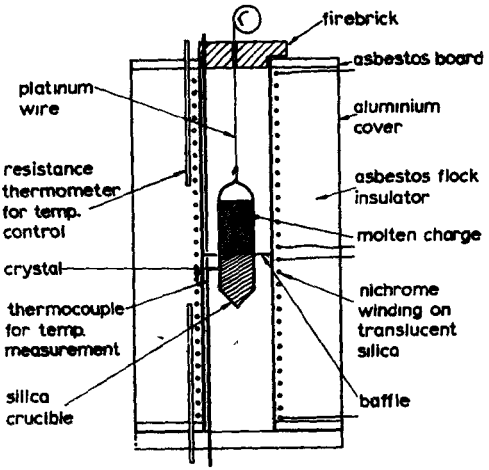

Fig. 1.1. The Bridgman technique. Apparatus of the type shown has been used with a wide range of materials with melting points up to about 1200 C. For higher melting materials, other crucibles and furnace windings can be used. Typical rates of lowering are in the range 5 to 100 mm hr^{-1}.

cooling the furnace so that the freezing isotherm moves steadily through the originally molten charge. Details of these methods are given in ch. 6. Fig. 1.1 gives an example of the type of apparatus used. In this example, as the crucible is lowered, solid forms first at the pointed tip of the crucible. If this tip is correctly shaped, usually only one crystal will be formed initially, and single crystal growth will generally continue if the conditions have been correctly chosen. The latent heat of solidification, which is evolved as the crystal grows, is removed by conduction through the crystal and the crucible. The principal characteristic of this method is that at least some part of the solid–liquid interface is in contact with the crucible. This has advantages (the shape of the crystal can be completely controlled by the crucible) and disadvantages (contact between the crucible and the crystal may result in the crystal being strained and the melt–crystal–crucible contact can result in the nucleation of new differently aligned crystals).

These disadvantages can be overcome by methods of the second group which were initially developed by Czochralski (1918) and Kyropoulos (1926). In these methods, the melt is contained in a crucible but the crystal is grown at the free top surface of the melt so that there is no contact between the crystal and the crucible. Fig. 1.2 shows a typical system. In the version due to Czochralski, the crystal is slowly pulled upwards as it grows, so that the solid–liquid interface is just above the level of the liquid surface. In the Kyropoulos version of the method, the melt temperature is lowered slowly causing the crystal to grow out from the seed into the melt. These methods which are discussed in detail in ch. 7, have the advantage that there can be no strains due to crystal–crucible contact, but the melt is still contained within a crucible and for very reactive materials it may be difficult to find a container which is not attacked by the melt.

In the third group of methods, crucibles are completely eliminated and the melt is supported by its own solid. The methods in this group were developed by Verneuil (1902) and Keck *et al.* (1953).

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