Crystals

Growth, Morphology, and Perfection

How do crystals nucleate and grow? Why and how do crystals form such a wide variety of morphologies, from polyhedral to dendritic and spherulitic forms? These are questions that have been posed since the seventeenth century, and are still of vital importance today, both for modern technology, and to understand the Earth's interior and the formation of minerals by living organisms. In this book, Ichiro Sunagawa sets out clearly the atomic processes behind crystal growth, and describes case studies of complex systems from diamond, calcite, and pyrite, to crystals formed through biomineralization, such as the aragonite of shells, and apatite of teeth. It will be essential reading for advanced graduates and researchers in mineralogy and materials science.

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Foreword to the English translation

The English version of this book was prepared based on translation by the author of the Japanese version; however, a few modifications have been made to assist the reader. The photographs appearing as plates at the front of the Japanese edition have been moved to the appropriate pages in the text, and references and suggested reading were moved to follow each chapter.

In preparing the English version, several individuals have assisted the author. Professor Andrew Putnis arranged the publication of the English version, and Professor Alan L. Mackay read through the manuscript and gave useful suggestions from a scientific standpoint. Dr. Sally Thomas and Irene Pizzie very carefully checked the manuscript and improved the English. The author sincerely appreciates their contributions. The permissions granted by many authors to reproduce figures from their various books and journals is gratefully acknowledged.

Preface

Crystals are solid materials having regular atomic arrangements characterized by periodicity and anisotropy. These properties are universally present, irrespective of whether the crystal is inorganic or organic, in living systems or in the inanimate world. Crystals exhibit various external forms, as represented by the elaborately varied dendritic forms of snow crystals or the hexagonal prismatic forms of rock-crystal. This variety of shape has stimulated scientific curiosity since the seventeenth century, since when intensive efforts have been made to understand the reasons why and how crystals can take a variety of forms.

The forms that crystals take result from the way in which crystals grow. The mechanism of growth is recorded in various forms in each individual crystal, regardless of size. The same crystal species may show different crystal forms (for example, polyhedral, skeletal, and dendritic), depending on growth conditions. Spiral growth step patterns, which record the growth process at the nanometer scale, have been observed on crystal faces. In single crystals, fluctuations in growth rates during the growth process are recorded as variations in perfection and homogeneity, such as growth sectors, growth banding, and three-dimensional distribution of lattice defects such as dislocations. The texture and structure of minute polycrystalline aggregate also record the growth history. These fluctuations are observed not only in crystals formed by inorganic processes, but also in those formed in living organs like bones, teeth or shells, or in calculus formed in various organs through the excretion of unnecessary components. To understand the phenomena occurring in complicated and complex systems, in which the growth process is unobservable *in situ*, we must regard the characteristics exhibited by crystal forms (morphology of crystals) as very important sources of information.

Our understanding of the atomic process and the mechanism of crystal growth progressed greatly during the latter half of the twentieth century. Various techniques have been developed that will produce bulk single crystals and thin films with high perfection and homogeneity by strict control of the growth parameters.

Various crystalline materials with desired properties have been synthesized, and this has driven the utilization of single crystals in the production of semiconductor, opto-electronic, piezoelectric, and pyroelectric materials.

Understanding crystal growth mechanisms is just as important in the field of industrial crystallization, where a large quantity of minute crystals with well controlled sizes and forms are required, such as in pharmaceuticals, chemical seasonings or photographic emulsion, and even proteins. By coupling intellectual curiosity with the demands from industry, we have reached the point at which we can understand, at the atomic level, the mechanisms that determine crystal form, perfection, and homogeneity, at least in simple systems. It will be the task of researchers in the twenty-first century to deepen our understanding of phenomena that occur in more complicated and complex systems.

The main purpose of this book is to present the route that we need to take in order to decipher the phenomena and history occurring in complicated and complex systems, based on our present day understanding of simple and single systems. It is also hoped to present the root of the science and technology of crystal growth to those who are already actively involved in growing bulk single crystals and thin films using industrially established growth techniques.

The findings summarized in this book have been achieved through research activities by the author during half a century's work at the Geological Survey of Japan, Tohoku University, and the Yamanashi Institute of Gemmology and Jewellery Arts. Throughout this scientific career, a deeper understanding has been achieved thanks to my joint efforts with colleagues, and postgraduate and undergraduate students. I have unforgettable memories from individual research works, and, although no names are mentioned, I wish to express my sincere thanks to all those that have been involved. My thanks are also due to Ikuo Hirayama and Hideya Fukase of Kyoritsu Shuppan Co., for their overall support in publishing this book.

This book is dedicated to my wife, Michiko, and those unnamed others who have supported my research activities behind the scenes.