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Crystal growth / Croissance cristalline

Foreword

Without single crystals, the development of our advanced technology would have been stopped around the 1950s: no silicon for microelectronics, no modern computers, no solid-state lasers, frequency doubling or scintillators for medical scanners, no nuclear radiation or pollution detectors would exist… Chemistry also would not be able to produce many modern drugs and fine chemicals without the recent advances in understanding nucleation and growth of precipitates from a nutrient phase. In biology, modern protein crystal growth allows X-ray analysis of bigger crystals, giving a more precise reconstruction of their chemical structure and then of their biological function.

Crystal growth is an interdisciplinary domain aiming to understand how the (almost) perfect piling of atoms and molecules proceeds and can be reproduced and improved. It classically includes studies in seed nucleation, growth kinetics, crystallographic defect formation, growth of new phases, crystal characterization, and applications. On the technological point of view, the development and control of crystal growth processes, which extends from nano-powders to huge silicon crystals of almost one ton, is the exclusive concern of entire laboratories and institutes. The associated worldwide industrial activity employs some 50 000 people directly involved in the growth of crystals.

The present dossier in *Comptes rendus Physique* collects a panel, that I chose as large as possible, of researches performed in France in the field of crystal growth. This geographical bias has been essentially motivated because I felt the necessity to demonstrate the quality of these researches at a moment when our national community shows structuration difficulties. I hope that our readers outside France will pardon this restriction, for which I am totally responsible.

The first paper, signed by **Z. Hammadi and co-workers**, presents a major step in nucleation researches, with simultaneous theoretical and practical objectives. By mastering the production of reproducible micro-droplets, the authors have demonstrated the possibility to control, spatially and in time, a single nucleation event. After analysis of the effect of confinement, they show that this experimental technique opens the way to a better understanding and control of nucleation.

F. Bonneté is interested in understanding how biologic macromolecules can crystallize in spite of their very large entropy and weak bonding interactions. By studying the effect of solution physicochemical parameters, she shows that it is possible to choose positions, in the phase diagram, giving the best crystals according to the objective. Applications of these studies concern improvement of X-ray diffraction structure analysis of proteins as well as protein purification.

Nanostructures are likely to present many potential applications. However, their growth mechanism remains mysterious in many cases. The paper by **J. Eymery et al.** evidences for the first time the unexpected result that semiconductor and metal nanowires grow by similar mechanisms. Several growth regimes are identified and characterized. Also in the case of growth mechanisms, but in the field of thin crystalline film deposition, the paper by **X. Xu and co-workers** presents a very nice computation of the various instability modes and develops conclusions on the effect of film thickness and process parameters, especially substrate patterning, on the instability.

The growth of bulk diamond crystals resisted to human fury for decades and it is only in the last years that plasma assisted chemical vapor deposition allowed synthesis of reasonably good crystals. **A. Tallaire and his team** have written a comprehensive review of this technology and the associated problems, including recent achievements. This will be for sure a reference paper in the field. An aspect of crystal growth that necessitates constant, difficult and rarely successful work is the growth of new phases and new chemical compounds with the aim of providing those astounding physical properties that are typical of single crystals as a consequence of Curie's principle. **M. Prakasam and his co-workers** give an example of this type of work, which is presently pushed by the necessity to stop growth from lead oxide flux and find new production technologies. They show that ferroelectric crystals can be grown with good quality from lead-free melts.

Grown-in crystallographic structural defects such as dislocations, point defects or micro-bubbles have been studied extensively in the past decades. However, the loss of single crystallinity because of the occurrence and development of sub-grain boundaries, grain boundaries, or twin boundaries has received little attention. This issue presents three papers devoted to these defects. In the first one, **G. Faivre et al.** study the kinetic of sub-grain boundaries as a function of growth conditions and show a specific behavior close to the plane–cellular transition. Such a kind of fundamental understanding is needed for the general description of the development of the grain structure in a multi-crystalline ingot. By using classical nucleation and kinetic theories, **T. Duffar and A. Nadri** propose a general model of grain boundary kinetics in Si multi-crystals based on

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the morphology of the grain–grain–liquid groove. Some aspects of this model receive an impressive confirmation through in-situ observation of the solidification of Si thanks to a synchrotron X-ray beam. These careful experiments and painstaking exploitation, thanks to the work of **A. Tandjaoui and co-workers**, evidence two kinetic mechanisms of twinning.

As shown by the previous paper, development of newest, original, more precise and sensitive characterization techniques is needed for improvement of our knowledge of crystal growth mechanisms. The last paper, by **J. Baruchel**, in collaboration with his co-workers and several research teams, describes the new capabilities associated with the development of synchrotron X-ray sources and gives several examples of the various characterizations that can be achieved on various materials.

It appears that crystal growth research is very active in many fundamental as well as technological directions and is far from being elucidated in many cases. As shown by the varied contributions, it concerns materials as different as proteins, nanowires, thin semiconductor layers, bulk diamonds or optical crystals and huge Si multi-crystalline ingots. Anyhow, the similarities of concerns and approaches in the growth of so different materials are striking. It is amazing to observe how old topics gain a renewed interest because new technologies simultaneously need better growth understanding and provide better analyzing tools. A typical example, well documented in this issue, is given by the growth of multi-crystalline silicon: indeed, 15 years ago, all specialists would have declared that absolutely everything is known in silicon crystal growth, as evidenced by the perfection of the crystals produced industrially. However, the growth of less pure material for photovoltaic applications suddenly brought about a number of new questions and, hopefully, X-ray characterization techniques improved in between and allow elegant answers to these questions. In conclusion, because of its wide spectra of applications and fundamental concerns, the need of researches in crystal growth will continue to increase and to motivate excellent specialists in the future, in France as well as in all other countries.

Finally, I would like to thank the colleagues who generously accepted to deliver high-level contributions to this issue and the international referees who agreed to review these papers and, in most cases, suggested constructive improvements.

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