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redactie

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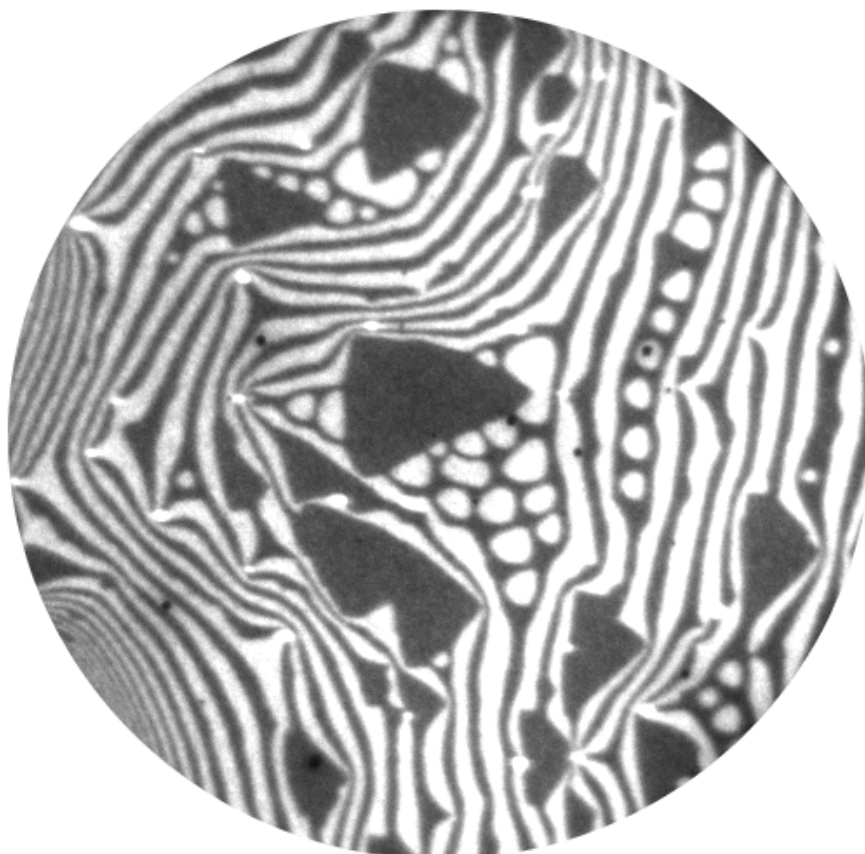
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Omslagfoto/Cover

De omslagfoto laat een Lage Energie Electronen Microscopie (LEEM) plaatje zien van een bismuth overlaag structuur op een Cu(111) substraat. De heldere gebieden van de zebrastructuur zijn bedekt met een vloeibare Bi monolaag en de donkere gebieden bestaan uit een oppervlaktelegering van Bi met het koper substraat. Het plaatje is gemaakt tijdens een experiment waarbij door verwarming de oppervlaktelegering zijn long-range order kwijtraakt. Dit leidt tot de vorming van de driehoekige domeinstructuren die de zebrastructuur in het getoonde plaatje onderbreken.

De figuur is aangeleverd door Raoul van Gastel en Bene Poelsema van de Universiteit Twente en Daniel Kaminski en Elias Vlieg van de Radboud Universiteit Nijmegen.

Electronische verzending FACET

Indien U deze FACET niet via de reguliere mailing aan de NVKG-leden heeft ontvangen, vragen wij U om aan de [redactie](#) van de FACET een geldig emailadres door te geven, danwel kenbaar te maken of U de FACET in papieren vorm wilt blijven ontvangen.

De FACET verschijnt uiteraard ook nog altijd gelijktijdig met de emailversie op de website van de NVKG. De meest recente FACET kan daar te allen tijde uit het FACETtenarchief gedownload worden. Net zoals de vorige

elektronische FACETten, bevat ook dit exemplaar weer handige, automatische links voor web en e-mail.

Redactioneel

Voor u ligt de eerste FACET van het jaar 2008. Zoals U in de linkerkolom ziet zijn tijdens de afgelopen jaarvergadering bij Avantium in Amsterdam, de diverse voorgestelde bestuurswijzigingen door de ledenvergadering bekrachtigd. Daarnaast zijn tevens plannen gemaakt voor kristalgroeiactiviteiten voor dit jaar en ten aanzien daarvan bevat deze FACET een belangrijke wijziging. Het geplande kristalgroei-symposium van 23 mei a.s. op de Universiteit Twente gaat niet door omdat het voor verscheidene van de bij de NVKG betrokken onderzoeksgroepen samen blijkt te vallen met andere belangrijke evenementen. In plaats daarvan wijzen we U in deze FACET op het mede door de NVKG gesponsorde symposium 'Chirality and Crystallization', wat op 20 juni aan de Radboud Universiteit gehouden zal worden, zie ook de aankondiging verderop in deze FACET.

Een vast item op deze plek is de oproep voor input voor de FACET. Wat kunt u bijdragen ?

- Aankondigingen van lezingen, symposia en congressen (niet alleen de activiteiten die u zelf organiseert, maar ook activiteiten waarover u langs andere weg bent geïnformeerd)
- Verslagen van (kristalgroei)-conferenties
- Artikelen (mag ook heel kort zijn!) over een opmerkelijke ontdekking
- Advertenties: bijvoorbeeld i.v.m. vacature
- Omslagfoto's (met toelichting). Telkens zal de beste ingezonden foto op de omslag van de FACET worden afgedrukt samen met een korte toelichting aan de binnenzijde van het blad. Bovendien zullen de foto's op de fotogalerij van onze webstek worden gepost.

De drempel voor uw bijdragen is *zeer laag*: aanleveren kan per brief, fax, [e-mail](#), of telefoon. En we staan natuurlijk open voor alle direct of indirect met de NVKG verwante onderwerpen. De volgende FACET verschijnt volgens schema begin mei 2008.

[Raoul van Gastel](#)

Symposium

CHIRALITY AND CRYSTALLIZATION

Friday 20th June 2008

Radboud University Nijmegen

Kindly sponsored by:

Synthon BV

Institute for Molecules and Materials
Nederlandse Vereniging voor Kristallografie
Nederlandse Vereniging voor Kristalgroei

Understanding how the single-handedness of biological molecules came about has been of interest to scientists since Pasteur first separated mirror-image crystals of ammonium tartrate. Chirality is important in molecular recognition and as such would seem to be a prerequisite for the origin of life as well as for the efficacy of many pharmaceutical compounds.

This one-day symposium intends to give an overview of important aspects in the chiral separation of molecules via crystallization up to the latest discovery involving abrasive grinding applied to a racemic solid phase in contact with a racemizing solution leading to an enantiopure solid state with a 100 % yield.

Keynote lectures will be given by

Prof. G. Coquerel (University Rouen)

Prof. M. Lahav (Weizmann Institute)

The symposium fee is 25 Euro, which includes coffee, lunch and drinks afterwards. Students, NVK and NVKG members pay 15 Euro.

To register: Send an e-mail with your details (name, address, affiliation, amount due) to E.Salem@science.ru.nl. Please transfer the symposium fee to bank account number 231247834 in the name of 'FNWI', Nijmegen, include your name and the code '6200425'.

See also the website: <http://www.crystallography.nl/ccs.html>

Background image by Loes Modderman

Synthon



Recente proefschriften

Dr. Menno Deij

“Modeling Crystal Growth of Organic Materials, Nucleation, Steps and Morphology”

Promotor: prof.dr. E. Vlieg

Co-promotor: dr. H. Meekes

Verdedigd op: 9 januari 2008

Summary

This thesis is the result of four years of research into modeling of crystal growth of organic materials. New methods were developed to study crystal growth, because older methods, which are widely used, do not give satisfactory results for complex systems. The methods were developed with general applicability, speed and relevance to industry in mind. They therefore do not focus on a single problem, or a small subset of problems, but try to be as general as possible, while still offering new and fundamental insights in the problems of interest.

In this thesis the focus is on modeling of three important aspects: nucleation, the role of steps during growth, and the final morphology of crystals. The first subject, nucleation, is very important in polymorphism. As different polymorphs may form during crystallization, and usually only one is desired, the nucleation phase is critical for the formation of the desired polymorph. The research on nucleation, reported on in this thesis in Chapters 4 and 5, consists of the development of a new method where the probability that a small cluster grows out to a macroscopic crystal is simulated using Monte Carlo crystal growth simulations. These simulations, based on a random Monte Carlo process, allow for the determination of the cluster growth probability, both as a function of initial cluster size and as a function of driving force. Using such simulations, nucleation rates for different polymorphs can be calculated, thus giving insight in the nucleation behavior of all polymorphs simulated. Ultimately this will lead to an a priori product quality prediction, when the results of the simulations are combined with process simulations to obtain

particle size distributions and product polymorphic fractions.

When a crystal is growing, the relative growth rate as a function of crystal orientation determines the final shape. The growth rates can be obtained from Monte Carlo crystal growth simulations, where crystal growth is simulated both as a function of crystal orientation and as a function of driving force for crystallization. These simulations then allow for a prediction of the final crystal shape, or morphology, as a function of driving force. These simulations, however, can take quite a long time and, more importantly, do not offer a fundamental understanding of the crystal growth processes taking place. A fundamental understanding of crystal growth, based in the first instance on 2D nucleation, is offered by the newly developed automated routine called Steplift, which calculates the lowest energy 2D nucleus for all connected net orientations from the crystal graph. During the development of this automated routine, the need to clearly define the way that step energies should be calculated in a general case led to the development of a new method for the calculation of step energies. The results of this new method, and the application of the Steplift routine to a number of organic materials are described in Chapters 2 and 3. The role of steps during crystal growth, as is fleshed out further in Chapter 1, further adds to the importance of looking in detail at step structures during crystal growth.

From the Steplift routine crystal growth rates can be computed, as a function of crystal orientation as well as driving force, leading to the prediction of crystal morphology, which is the third subject of this thesis. Using the newly developed Steplift routine as well as the already existing Monte Carlo growth simulation methods, the prediction of crystal morphology is studied for a number of different ‘real-world’ systems in Chapters 7, 8, 9 and 10.

Thus, in Chapter 7, the two very different crystal habits of a yellow dye used in the photographic industry is studied using Monte Carlo simulations. The next chapter deals with Venlafaxine, an anti-depressant

pharmaceutical, which has three different polymorphs. In a comparison of established and new morphology prediction methods, it is found that the BFDH and attachment energy model do not suffice for the correct prediction of the crystal morphology. Monte Carlo simulations are used, with either 2D-nucleation or spiral growth mechanism, to correctly model the morphologies observed experimentally. The last two chapters, 9 and 10 deal with another pharmaceutical, Ondansetron. The crystal structure of this molecule was unknown, and in Chapter 9, using different experimental methods, it was found that the crystal structure is a solid solution of enantiomers. The extreme needle-like morphology of Ondansetron is modeled using step energy calculations and Monte Carlo simulations, which clearly show that the needle-like morphology can be explained from the fact that a family of faces in the same crystallographic zone has a substantially higher 2D-nucleation barrier, compared to faces outside of that zone. This, in turn, explains the experimentally observed needle-like morphology from the large difference in growth rates for the faces in the zone, and those outside the zone.

The remaining chapter, Chapter 6, puts forward a new theoretical approach to the rational design of habit modifiers. This approach is again based on the Monte Carlo crystal growth simulations, now expanded with routines to monitor the creation and annihilation of growth sites on the growing crystal surface. Using the statistics thus obtained from the growth process, a method is proposed to quantify the importance of growth site configurations to the growth process. These contribution values of all possible growth site configurations, which are different for each orientation simulated, allow for the identification of a subset of configurations that have both a high and a selective contribution to the growth of a single face. When these configurations can be identified, they can be used as the starting point of a process of rational design of tailor-made additives, able to modify the crystal morphology in the desired way.

Dr. Ton van Niftrik.

"The epitaxial lift-off method, III/V materials and HF etch process studies"

Promotor: prof.dr. P.K. Larsen

Co-promotor: dr.ir. J.J. Schermer

Verdedigd op: 23 januari 2008

Summary

The epitaxial lift-off (ELO) process is a technique that allows the separation of a single crystalline film from the substrate it was deposited on via the etching of an intermediate AIAs release layer. For this purpose, the extreme selectivity of hydrofluoric acid (HF) for AIAs over GaAs is employed. Application of this technique is interesting for the optoelectronics industry, because it can result in cost reduction by reuse of the substrates. This is of particular importance for intrinsically large-area, thus expensive, devices like high efficiency III/V solar cells, and the integration of III/V based components with, for example, silicon-based devices. Additionally, the use of thin-film devices potentially results in a more efficient transfer of generated heat from device to carrier or heat sink. The ELO process is only suitable for large-scale industrial utilization if the area of the released film is sufficiently large and the lateral etch rate sufficiently high. Therefore, this process has been under investigation during the last decades.

A starting point in this research is a model, originally developed in 1987 by Yablonovitch *et al.* This model derives a theoretical expression for the ELO etch rate, based on the assumption that hydrogen is formed during the etching of AIAs with HF, and that the out-diffusion of this hydrogen through the narrow crevice between substrate and epilayers is the limiting factor of the process. Using this model, maximal lateral etch rates in the order of several micrometers per hour are predicted for the typically applied experimental conditions, whereas the actual experiments conducted at the Radboud University yielded etch rates of several tens of millimetres per hour. This indicates that either the assumptions made to derive the model are incorrect or that the ELO

etch rate is influenced by additional factors such as the possible occurrence of ordering or strain in the release layers not yet accounted for in the model. In this study the possible influence of these additional factors as well as the correctness of the assumptions are evaluated.

To test the possible occurrence of ordering in the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ release layers, $\text{Al}_x\text{Ga}_{1-x}\text{As}$ films are analysed using surface X-ray diffraction at the European Synchrotron Radiation Facility in Grenoble. These experiments as described in chapter 3 indicate that there is hardly any ordering in the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ release layers, so that this is not a factor of concern with respect to the ELO process. In chapter 4, it is demonstrated that the main assumption of the model, namely the production of 3 moles of hydrogen per mole of AIAs etched, is actually wrong. By a systematic investigation of solid, solution and gaseous reaction products, it is determined that gaseous arsine instead of hydrogen is produced during the ELO process together with dissolved and precipitated aluminium fluoride compounds.

In order to determine the influence of strain on the AIAs etch rate, planar AIAs layers are etched while subjected to a controlled bending of the sample. In chapter 5, it is shown that the etch rate can be increased significantly by bending the sample, which actually reduces the intrinsic compressive strain in the AIAs layer which is induced by its lattice mismatch with respect to the GaAs substrate. So the presence of strain is a factor to be considered in ELO process studies. Besides the application of an external force, strain can also be introduced by an intrinsic force, *e.g.* as a result of epitaxially grown layers with different lattice constants. In chapter 6, the influence of intrinsic strain on the ELO process is determined as a function of the composition variation of two $\text{In}_x\text{Ga}_{1-x}\text{As}$ or two $\text{GaAs}_{1-y}\text{Py}$ layers surrounding the AIAs etch layer. For this purpose a weight-induced ELO (WI-ELO) setup is employed in which a plastic foil is mounted on the epilayer and a weight is used to provide the necessary curvature. It is observed that the ELO etch rate maximizes for

structures which put a minimum amount of strain on the AIAs release layer.

In Chapter 7, a new model is derived to describe the ELO process. This model is based on the idea that the overall etch rate in this process is determined both by the diffusion rate and the reaction rate of a certain species in the process. For this so-called diffusion and reaction related model (DR-model), it is assumed that HF limits the overall etch rate in the ELO process and that the reaction products, being AsH_3 and aluminium fluoride complexes, are quickly removed from the etch front. The DR-model is tested by several series of experiments. These showed that the ELO process rate dependence on the composition of the $\text{AIAs}_{1-y}\text{Py}$ release layer can be accounted for by the reaction rate related part of the model and that the ELO process rate dependence on the thickness of the release layer is in agreement with the diffusion rate related part of the model. In contrast to the Yablonovitch model, it is found that the DR-model yields ELO etch rates which are in quantitative agreement with those obtained experimentally. Furthermore, the experiments revealed that the ELO etch rate is highest for $\text{AIAs}_{1-y}\text{Py}$ release layers with a release layer thickness of 10 nm and a P content of 2% – 3% *i.e.* the composition for which the layer is lattice matched compared to its surrounding GaAs layers. For these release layers a maximum etch rate was obtained of 47.6 ± 0.8 mm/hr at 71.2 °C.

In chapter 8, it is found that the etch rate increases linearly with the total HF concentration of the etch solution, which is in accordance with the DR-model. This result and composition calculations of HF solutions show that the first step in the etch process of AIAs with an HF solution most probably takes place by chemical attack of undissociated HF on AIAs surface bonds. After subsequent reactions with HF, this gives rise to the formation of AsH_3 and (hydrated) AlF_3 . Furthermore, it is shown that the ELO process rate decreases slightly if the partial oxygen pressure in the ELO setup is reduced from 1 down to about 0.05 atm, but that for an oxygen pressure very close to zero (0.003 atm) a sudden drop in etch rate takes

place. The abrupt decrease in etch rate was argued to be related to surface passivation by elemental arsenic, which is formed by the reaction of AIAs with H⁺. An oxygen-poor atmosphere may allow the build-up of elemental arsenic on the surface, thus slowing down the AIAs reaction with HF. Oxygen, by quickly removing arsenic as As₂O₃, keeps the surface active.

Based on the research, described in this thesis, it can be concluded that, in contrast to the Yablonovitch model, the DR-model yields ELO etch rates which are in quantitative agreement with those obtained experimentally. However, some issues such as the exact nature of the deposits found on both the thin-film and substrate after completion of the etch process require further research in order to fully comprehend the mechanisms of the ELO process.

AANKONDIGING CONGRESSEN EN SYMPOSIA

NVKG Kristalgroeisymposium,
23 mei 2008, Universiteit Twente, organizer: R. van Gastel
!!!! GAAT NIET DOOR !!!!

Symposium “Chirality and Crystallization”,
Vrijdag 20 juni 2008, Nijmegen,
Zie de symposium website voor verdere details.....

ISIC-2008,
14-17 september 2008, Maastricht
Zie de ISIC-17 website voor verdere details.....

JANE 2008, Japan-Netherlands Seminar on Crystal Growth
19-23 October 2008, Sapporo, Japan
Organizers: E. Vlieg and Y. Furukawa

NVKG Jaarvergadering,
14 November 2008, Friesland Foods, Deventer
Meer informatie in de volgende FACET