FACET

NIEUWSBRIEF VAN DE NVKG

14 maart 2011

nummer 1

FACET

Nieuwsbrief van

de NVKG, sectie van

de KNCV en de NNV

redactie

dr. Arie van Houselt

Redactieadres

dr. A. van Houselt

Catalytic Processes & Materials

Universiteit Twente

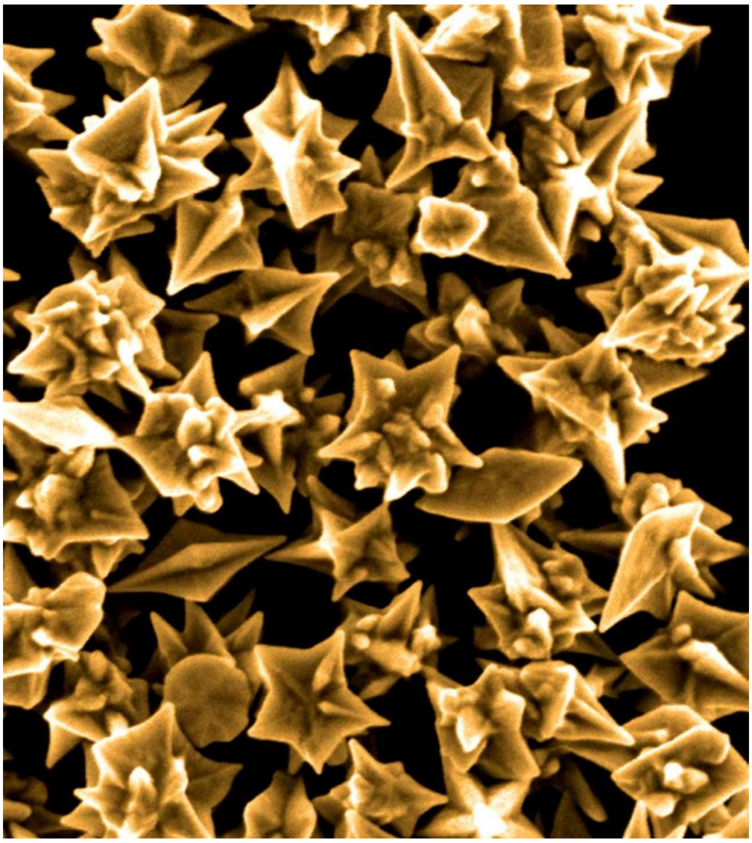
Postbus 217

7500 AE Enschede

tel (053) 4892999 (3033)

fax (053) 4894683

A.vanHouselt@utwente.nl



INHOUD: PAGINA:

Redactioneel en mededelingen	2
Congressen en symposia	4
Jaarverslag NVKG 2009-2010	6
Symposium jaarvergadering 2010	7
Crystal Growth Berlin meeting	8
Recente proefschriften	9

Secretariaat NVKG

dr. Rolf Keltjens (nvkg.secretariaat@gmail.com)

Bestuur NVKG

dr.ir. Joop ter Horst (TUD)	voorzitter
dr. Rolf Keltjens (Synthon)	secretaris
dr. Hans te Nijenhuis (Panalytical)	penningmeester
dr. Arie van Houselt (UT)	FACET/WWW
dr. Pieter Vonk (DSM)	lid
dr. Hugo Meekes (RU)	lid
dr. Marcel Rost (UL)	lid

Omslagfoto/Cover

Stervormige deeltjes van goud kunnen eenvoudig langs colloïdale weg worden gemaakt, zoals te zien op de elektronenmicroscopie-opname (SEM). Door de relatieve hoeveelheden goud en reducerend ascorbinezuur in oplossing te variëren kunnen we de lengte van de 'stralen' variëren. Verhogen van de hoeveelheid ascorbinezuur leidt tot afvlakken van de scherpe punten, en daarmee tot de vorming van meer isotrope deeltjes. We maken gebruik van multikristallijne groeikiemen; de getwinde structuur is essentieel voor de vorming van de nanosterren. Verandering van de kiem-dichtheid in de groeioplossing stelt ons in staat om de absolute grootte van de deeltjes te variëren.

De optische eigenschappen zijn sterk afhankelijk van de vorm en grootte van de nanodeeltjes. De karakteristieke optische resonantie is daarmee instelbaar over een breed spectraal gebied, van zichtbaar tot nabij infrarood. Mogelijke toepassing van deze deeltjes, onder andere in biologische sensoren, maken gebruik van de versterking van het elektromagnetische veld rond de scherpe punten van de sterren.

De figuur is aangeleverd door Waqqar Ahmed en Stefan Kooij van de Universiteit Twente. Voor meer informatie klik hier.

Electronische verzending FACET

Ten behoeve van de verzending van de FACET is het van belang dat de NVKG beschikt over een geldig emailadres. 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.

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, na enige onderbreking, de eerste FACET van het jaar 2011. Vanaf dit moment zal de FACET vaker uitkomen als nieuwsbrief, met daarin gegevens over symposia en andere activiteiten die van belang kunnen zijn voor iedereen die kristallen groeit of bestudeert. Zo vindt u in dit nummer aandacht voor het jaarsymposium van de NVKG in 2010 en treft u overzicht van toekomstige activiteiten aan.

Onveranderd blijft dat uw bijdrage voor de FACET zeer wordt gewaardeerd. 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, zoals in dit nummer van de hand van Elias Vlieg op pagina 8
- 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.

Arie van Houselt

Congressen en symposia

De NVKG is de komende tijd betrokken bij de organisatie van zowel de International Workshop on Industrial Crystallization (BIWIC18) als bij de gezamenlijke voorjaarsvergadering van de NVKG en de British Association for Crystal Growth (BACG). Verder treft u aankondigen aan van ISIC18 en ACCGE-18.

BIWIC - 18th International Workshop on Industrial Crystallization
7-9 September 2011, Delft, The Netherlands

Organization:	Joop ter Horst (biwic2011@tudelft.nl)
Website:	www.3mE.tudelft.nl/BIWIC2011
Abstract deadline:	15 March 2011
Paper deadline:	15 June 2011

The BIWIC is the International Workshop on Industrial Crystallization. This year's workshop will be held **7-9 September 2011** in Delft, the Netherlands. It will be organized by the Intensified Reaction & Separation Systems group of the Department for Process & Energy, Delft University of Technology in conjunction with the DACG.

The BIWIC is an informal 2 day workshop with around 100 participants. In a pleasant atmosphere, the current state of the art in Industrial Crystallization is discussed during scientific sessions and even more so during the social events.

The conference starts at Wednesday evening 7 September with an informal get-together in the Vermeer Centre Delft. The scientific program takes place on Thursday 8 and Friday 9 September in the Berlage room at the Faculty of Architecture of the Delft University of Technology. On Thursday, before the conference dinner, the now already traditional annual soccer game will be played.

DACG Spring meeting / BACG Annual Conference
Our annual DACG spring meeting will be held in conjunction with the BACG 2011 Annual Conference
10-12 July 2011, University College London (UCL), UK

Website:	www.bacg.co.uk
Abstract deadline:	1 April 2011

The British Association for Crystal Growth (BACG) is pleased to announce that the 2011 Annual Conference will be held at University College London (UCL) from **10-12 July 2011** jointly with the Dutch Association for Crystal Growth (DACG) and in partnership with the British Crystallographic Association (BCA) Industrial Group.

ISIC18: 18th International Symposium on Industrial Crystallization
13-16 September 2011, Zurich, Switzerland

Website:	www.isic18.ch
Abstract deadline:	14 February 2011
Organizer:	Marco Mazzotti (isic18@ethz.ch)

ISIC18 is organized by the Working Party on Crystallization (WPC) of the European Federation of Chemical Engineering (EFCE). The ISIC series has traditionally provided a unique opportunity for international exchange between scientists and engineers of all disciplines, academia and industry, and between novice and expert. ISIC18, held in the conference facilities of ETH Zurich, the Swiss Federal Institute of Technology in Zurich, aims at honouring and continuing such tradition.

The Eighteenth American Conference on Crystal Growth and Epitaxy will be held jointly with the **15th Biennial (US) Workshop on OMVPE, July 31 - August 5, 2011 in Monterey, California**

Website: http://crystalgrowth.us/accge18/index.php
Abstract deadline May 2, 2011
Late news/poster deadline: June 11, 2011.

The **Eighteenth American Conference on Crystal Growth and Epitaxy, ACCGE-18**, will provide a forum for the presentation and discussion of recent research and development activities in all aspects of bulk crystal growth and epitaxial thin film growth, with sessions integrating fundamentals, experimental and industrial growth processes, characterization, and applications. Contributed papers will be accepted in all relevant areas. In addition to focused sessions listed in the call for papers, other sessions will be organized based upon the topical distribution of contributed papers. The conference will include both oral and poster sessions.

The **Fifteenth Biennial Workshop on Organometallic Vapor Phase Epitaxy (OMVPE-15)** brings together specialists in the OMVPE field from industry, academia, and government laboratories, in an informal atmosphere, and scenic surroundings. The workshop is an excellent opportunity to present and discuss new results in the OMVPE field, as well as providing a venue for recent entrants to the field to familiarize themselves with OMVPE science and technology. The format of the conference is designed to maximize interaction between OMVPE specialists, and with the wider crystal growth community represented at the ACCGE.

For further information, please contact AACG Administrator at AACG@comcast.net

Jaarverslag NVKG november 2009 – november 2010

Secretariaat:

Dr. Marcel J. Rost
Kamerlingh Onnes Laboratory
Leiden Institute of Physics
Leiden University
(Niels Bohrweg 2, 2333 CA Leiden)
Postbus 9504, 2300 RA Leiden
The Netherlands
Phone: (+31) 71 - 5271883
E-mail: rost@physics.leidenuniv.nl
Web: http://www.physics.leidenuniv.nl/rost

Ledenbestand:
Het ledenaantal is momenteel ongeveer 130.

Bestuur:
De taakverdeling binnen het bestuur was als volgt.

Dr. ir. J.H. ter Horst	Voorzitter
Dr. M.J. Rost	Secretaris
Dr. M. Deij	Penningmeester
Dr. A. van Houselt	FACET en web-pagina
Dr. P. Vonk	Lid
Dr. H. Meekes	Lid
Dr. P. van Hoof	Lid

Het bestuur heeft twee maal vergaderd in het verslagjaar.
Besluitenlijsten van de bestuursvergaderingen worden gepubliceerd in de FACET.

Verenigingsblad
Het verenigingsblad FACET zal voor het eind van 2010 verschijnen. Het blad is bedoeld om de communicatie tussen onderzoekers en gebruikers van kristallisatie in Nederland te bevorderen. Het blad bevat onder meer samenvattingen van relevante proefschriften, 'mooie' plaatjes uit kristalgroeionderzoek en data van congressen en activiteiten die voor kristalgroeiers interessant zijn. Initiatieven, besluiten en plannen van de NVKG worden in de FACET gepubliceerd. De FACET wordt zoveel mogelijk elektronisch verspreid. Leden van de NVKG worden uitgenodigd kopij in te leveren.

Webpagina
Op de webpagina www.dacg.nl wordt informatie gegeven over de structuur en activiteiten van de NVKG. Verder zijn alle nummers van FACET sinds 2000 in elektronische vorm beschikbaar en worden links naar de Nederlandse onderzoeksgroepen op het gebied van kristallisatie en naar buitenlandse zusterverenigingen gegeven. Suggesties voor aanvullingen zijn welkom en kunnen aan Raoul van Gastel worden doorgegeven.

Jaarvergadering en excursie 2009
Deze zijn gehouden op vrijdag 13 november 2009 bij Panalytical in Almelo. De organisatie was in handen van Hans te Nijenhuis van Panalytical en Raoul van Gastel (UTwente). De jaarvergadering met ongeveer 25 deelnemers was een succes.

Kristalgroeisymposium 2010
Het kristalgroeisymposium is vooral bedoeld om jonge onderzoekers kennis te laten nemen van elkaars werk. Het jaarlijkse kristalgroeisymposium is dit jaar vervangen door een symposium over Crystal Nucleation in Delft,

georganiseerd door Joop ter Horst en Hugo Meekes. Met meer dan 80 deelnemers en de gastsprekers Allan Myerson (MIT), Naomi Chayen (Imperial College London) en Stéphane Veesler (CINAM-CNRS Marseille) werd het een groot succes.

Jaarvergadering en excursie 2010
Deze zullen worden gehouden op vrijdag 12 november 2010 bij Synthon in Nijmegen. De organisatie is in handen van Rolf Keltjens (Synthon), Joop ter Horst (TU Delft) en Hugo Meekes (RU Nijmegen).

KNCV/NVKG dissertatieprijs 2010
De dissertatieprijs wordt eens per twee jaar uitgereikt. De prijs wordt mede gesponsord door de KNCV. De prijs wordt tijdens de jaarvergadering uitgereikt aan een jonge onderzoeker voor hoogstaand wetenschappelijk onderzoek op het gebied van de kristalgroei. In 2010 zal er weer een dissertatieprijs worden uitgereikt.

Ondersteunende activiteiten
De NVKG stimuleert dat voor kristalgroei belangrijke congressen in en/of mede door Nederland georganiseerd worden. Daartoe geeft het bestuur advies en ondersteuning aan leden die bij de organisatie van evenementen als ISIC, BIWIC, JANE en andere kristalgroeimeetings betrokken zijn. De NVKG is aangesloten bij de internationale kristalgroeiorganisatie IOCG. Veel leden bezoeken de driejaarlijkse ISSCG zomerscholen en ICCG congressen.
Verder geeft de NVKG soms bescheiden financiële ondersteuning aan wetenschappelijke symposia en andere activiteiten die van belang zijn voor de kristalgroeiwetenschap.

Symposium en jaarvergadering NVKG 2010

Op 12 november 2010 was Synthon gastheer van het jaarlijkse symposium van de NVKG. Zoals altijd was het doel de kennis en inzichten met betrekking tot kristalgroei te vergroten en daarnaast het contact tussen onderzoekers die gebruik maken van kristalgroei te vergroten en te intensiveren. Terugkijkend op die vrijdag in november, kan worden gesteld dat aan die doelstelling ruimschoots werd voldaan.

In het knusse en comforabele Facility Point gelegen naast Synthon, konden ruim 35 leden hun wetenschappelijke hart ophalen aan een 7-tal lezingen, verzorgd door zowel industriële als academische onderzoekers. Na een korte inleiding door Rolf Keltjens (Synthon) over Synthon en enkele voorbeelden waarbij kristallisatieprocessen voor Synthon een grote rol speelden, werd het tijd voor een wat fundamentelere kijk op kristallisaties en nucleatie mechanismen. De spits werd afgebeten door Somnath Kadam (TU Delft) die de optimale parameters (MSZW etc.) voor kristallisaties op grotere schaal vaststelde op kleine schaal met behulp van Avantium's Crystal16™. Hij toonde aan dat er een duidelijke relatie bestaat tussen die twee schalen: de kleinste MSZW waargenomen op 1 ml blijkt goed overeen te komen met het gedrag op 1 liter schaal. De parameters en *in situ* imaging stellen een single nucleus mechanisme voor. Vervolgens presenteerde Ernst van Eck (RU Nijmegen) fraaie resulaten voortkomend uit de hechte samenwerking tussen de Nijmeegse universiteit en Synthon. Interessante verschijnselen in de XRPD patronen van Odansetron en Prasugrel bleken te kunnen worden verklaard met hulp van de complementaire technieken XRPD en ss-NMR als een gedeeltelijke wanorde (*solid solution* gedrag). Uiteraard kwamen de uitzonderlijke resultaten over Venlafaxine (dissertatie Zjak van Eupen) ook aan bod.

Na een korte maar krachtige jaarvergadering werd de NVKG/KNCV dissertatieprijs uitgereikt aan Wim Noorduin, die helaas niet aanwezig kon zijn. Hugo Meekens deed vervolgens in een enthousiaste lezing uit de doeken waarom Wim Noorduin dit jaar de terechte winnaar van deze prijs was. *Single chirality through crystal grinding* heeft heel wat teweeg gebracht in de (pharmaceutische) wereld. Er werd zelfs een relatie gelegd met het voorkomen van chiraliteit in de natuur!

Vervolgens was het Gerard Hofland (Feyecon carbon dioxide techniologies) die liet zien dat met superkritische CO_2 polymorfie, deeltjesgrootte en morfologie kunnen worden gestuurd in kristallisatieprocessen. Daarnaast wordt CO_2 ook gebruikt als sterilisatie medium, vluchtig zuur, extractiemiddel en als droogmiddel voor natte kristallen. De TU Twente werd vertegenwoordigd door Ahmed Waqqar met een lezing over goud nanodeeltjes. Na gedegen onderzoek blijkt het verbluffend eenvoudig te zijn om de grootte en vorm van vertakte goud nanodeeltjes te controleren door onder andere de verhouding tussen goud en ascorbinezuur te variëren. Tot slot was het Nico Sommerdijk (TU Eindhoven) die zich op de grens (en er soms even overheen!) begaf van de huidige mogelijkheden wat betreft microscopie. Een foto van zijn enthousiasmerende voordracht staat hiernaast. In zijn lezing getiteld *CryoTEM in biomemetic mineralisation; transient phases and prenucleation clusters* nam Nico het publiek mee naar de basis (oorsprong) van het kristallisatieproces: een hoogwaardige afsluiting van een mooie serie lezingen!

Na een korte tour langs de R&D faciliteiten en laboratoria van Synthon, werd de dag ontspannen afgesloten met een borrel. Onder het genot van een hapje en een drankje passeerden de onderwerpen van de lezingen nogmaals de revue en werden nieuwe plannen voor toekomstige onderzoek en samenwerkingen gesmeed!

European Activities on Crystal Growth Berlin meeting (20-21 October 2010)

A meeting was organized by and at the IKZ in Berlin to discuss crystal growth activities in Europe. Representatives from many European countries were present. Eastern Europe has a long tradition in crystal growth and provided many participants; Ukraine in particular has many large institutions, e.g. the Institute for Single Crystals with 250 people!

One topic was participation of the crystal growth community in framework programmes of the EU. FP7 is already well under way, so FP8 is what we need to prepare for. This will have three major sectors: Science for Science, Science for Competitiveness and Science for Society. The first is expected to be smaller than before, for the second the support of large industries is needed and the third deals with the 'grand challenges'. Crystal growth as theme seems unlikely to be successful; it needs to be part of a larger programme together with applications (e.g energy). Early lobbying is required.

Everyone was in favour of restarting the series of European Conferences on Crystal Growth (ECCG). Following earlier ones in Zurich (1976), Lancaster (1979) and Budapest (1991), ECCG-4 will be held in Glasgow in 2012, probably June 17-20. Expected number of participants: 300-500. This should be a three-annual conference. The three-year period means that there is a sequence of the IUCr Congres (next in 2011), ECCG (next in 2012) and ICCG (next in 2013). Bids for ECCG-5 in 2015 have already been put forward. Most likely, there will further be a slot on a specific crystal growth topic every year at the E-MRS meeting.

Various groups have been active in the area of education. The Spanish community is particularly successful, organizing two schools in Granada and a Master in Seville every year. A combinations of several German and French institutions will start a ''European Master on Crystal Growth" that will take a full two years to complete and that contains a heavy theoretical part plus an internship.

The European activities may result in a formal European organisation, but initially an informal federation is proposed. All international crystal growth activities (meetings and schools) should be reported to the IOCG, so that the IOCG website will help to avoid collisions between meetings.

Elias Vlieg, Nijmegen (as Dutch representative and vice-president of the IOCG)

Recente proefschriften

Dr. Tim Bohnen
"Hydride vapour phase epitacy growth of GaN, InGaN, ScN, and ScAlN"
Promotor: prof. dr. E. Vlieg
Co-promotor: dr. P.R. Hageman
Verdedigd op 1-6-2010

Summary

Currently gallium nitride (GaN) is used to make Blu-ray DVD players, blue, and white LEDs. GaN's 3.4 eV bandgap enables it to emit light in the blue and UV. However, GaN also possesses a tremendous potential for additional high power and high frequency devices, such as amplifiers for radar systems and cellular base stations. Unfortunately, GaN, such as it is currently grown on foreign substrates for e.g. LEDs, contains to many crystalline defects to be a suitable medium for these high power applications. These de-fects originate from the mismatch between GaN and substrate. Though numerous substrates, such as sapphire, silicon, or silicon carbide are available, no substrate, except GaN itself, is suited for the production of high power GaN devices.

In order to grow such GaN devices on GaN, one needs to have a high quality GaN crystal. Several techniques currently compete to produce these native GaN substrates. Among them is 'hydride vapor phase epitaxy' (HVPE), which is the sole bulk GaN growth method, capable of growing GaN on foreign substrates. Chapter 4 describes how the introduction of a low temperature GaN layer helps eliminate defects during the high temperature GaN film growth. Heating the low temperature nanocrystalline layer to the growth temperature changes its morphology into a .m-sized island structure. When these islands coalesce during the subsequent overgrowth phase, small voids are formed in between neighboring islands. These socalled pinhole defects allow the GaN, that is grown above them from the sidefaces of the islands, to relax. This relaxation drastically reduces the number of defects in the GaN film.

The higher growth rates of HVPE with respect to the other bulk GaN growth method is another advantage of the HVPE method. In chapter 5, we demonstrate that the substitution of HCl by Cl2 increases this growth rate even further by a factor 5. Additionally, the use of Cl2 reduces the parasitic deposition of GaN around the gallium precursor inlet. This allows for the growth of thicker wafers in a single growth experiment, namely 1.2 mm when using Cl_2 in contrast to 300 .m by HCl-based HVPE.

Not only the thickness but also the diameter of GaN wafers needs to be scaled up in order to reduce the price of GaN-based devices. Chapter 6 discusses a set of rules, based on the conservation of dimensionless numbers, which allow one to transfer a working process from a smaller reactor to a larger one. The processes in both reactors will then be similar, as we have demonstrated by computer simulations.

Another method of growing high quality GaN lies in the application of buffer layers between the GaN and the foreign substrate. One example is the low temperature GaN layer discussed in chapter 4. Scandium nitride (ScN) would be much better suited as a buffer layer, as the ScN (1 1 1) plane fits almost perfectly on the common GaN (0 0 0 1) plane. To this end, and since ScN itself possesses many interesting properties, we grew thin ScN (1 1 1) films on 6H-SiC. These results are discussed in chapter 7.

Against all expectations, nanowires appeared on the grown ScN films. These nanowires appeared to consist of a scandium aluminum nitride (ScAlN) alloy. In chapter 8, the details regarding the formation of these nanowires are explained. Apparently, the scandium metal was capable of etching its alumina holder, resulting in the release of aluminum into the gas phase. This aluminum then deposited on top of the ScN films, where it began to cluster into small metal droplets. These droplets were then able to act as catalysts for the nanowire growth. Between them ScN and AlN cover most of the visible spectrum. Therefore the optical properties of these nanowires were investigated. The results are described in chapter 9. In contrast to ScAlN, InGaN covers the entire visible spectrum. This opens up potentially interesting possibilities for optical applications, such as III-nitrides based LEDs en lasers of any chosen color. Hence, we have attempted the growth of InGaN by HVPE, as is written in chapter 10. Both HCl and Cl_2-based HVPE were applied to produce gaseous indium and gallium precursors. The growth rates in

the case of HCl were disappointingly low. For the use of Cl_2, the growth rates were higher. The indium content, however, was low. This was due to the formation of an indium chloride layer on top of the indium metal. This layer prevented further contact between the Cl_2 and indium and indium was released into the gas phase solely through the slow evaporation of this indium chloride layer.

In summary, this dissertation describes several novel methods to create larger, better, and cheaper GaN crystals via hydride vapor phase epitaxy. This should reduce the costs of GaN-based technology, such as Blu-ray. In addition, some fundamental insight into the growth of HVPE GaN on sapphire was obtained. This will help us reduce and control the number of defects in the GaN crystal. Finally, the HVPE method was adapted to create different III nitrides, such as ScN, ScAlN, and InGaN. These novel III nitrides will play an important role in the next generation of III nitride-based electronics and other applications.

Dr. Hina Ashraf
"Development of HVPE process for bulk-like growth of GaN"
Promotor: prof. dr. E. Vlieg
Co-promotor: dr. P.R. Hageman
Verdedigd op 6-7-2010

Summary

Crystal growth resembles to baking a pizza. The issues in a crystal growth of GaN can be understood by taking an analogy of baking a pizza. You want to make a pizza with your favorite toppings and cheese. However, if the base of the pizza or the baking conditions (baking time, oven temperature, etc) are not right, the pizza will not be eatable despite the fact you opt for the best toppings. The same is true for GaN. It posses the ideal properties for optical and electronic devices, however, non-availability of good substrates (on which it has to be grown) and diffcult optimization of the growth methods result into GaN material with a high defect density, which is not desirable for the opto-electronic devices.

This thesis describes the growth and characterization of GaN. GaN is one of the wide band gap III-Nitride semiconductors. As said earlier, it is highly suitable for modern electronic and opto-electronic applications due to its excellent intrinsic properties. Most of the GaN based applications are deposited on foreign substrates. This is because of the limited availability of GaN native substrates.

Sapphire is one of the best choices as a foreign substrate for GaN growth despite its large lattice and thermal mismatch with GaN. Its easy availability at reasonable prices and its ability of withstanding extreme growth conditions are the main reasons for picking sapphire as a substrate for GaN epitaxy. On the other hand, the quest for GaN substrates demands growth techniques capable of growing GaN at high speeds. HVPE has emerged as a growth technique, which is capable of growing bulk-like GaN of high quality at high deposition rates. The duo of HVPE as a growth method and sapphire as a substrate was the first one to be employed for GaN growth and still is one of the best developed combinations in this regard.

The growth of GaN on sapphire, though, carries disadvantages which lead to the formation of cracks and a high bowing of the GaN epi-layers and sapphire. Additionally, the lattice mismatch between sapphire and GaN leads to a high dislocation density which prevents the realization of high power devices. The goal of this work was to deal with these issues, while growing thick GaN epi-layers on sapphire substrates by HVPE.

In the first phase of this work, the growth process was develop in a newly built, horizontal HVPE reactor. Theoretical modeling of the reactor, already performed at the department, greatly helped in optimizing the process experimentally. The experimental optimization resulted in the growth of thick layers (300 µm) on sapphire and MOCVD-templates. The MOCVD-templates consists of thin GaN layers (~ 2 µm) grown on sapphire substrates by MOCVD. Structural and optical characterization studies showed that the layers grown on both types of substrates possessed high quality. One of the main achievements of this work was that the successful optimization resulted in a reduction of the dislocation density in HVPE epi-layers, a dislocation density of 10^8 cm^{-2} was obtained in comparison to the dislocation density of 10^9 cm^{-2} in the starting MOCVD-templates. The average order of dislocation density was 10^7 c cm^{-2} in case of the GaN layers grown directly on sapphire. The reproducibility of the process was high in terms of producing crack-free, specular layers with a smooth surface morphology, especially for growth on sapphire substrates. In case of growth on MOCVD-templates, the overgrown HVPE layers suffered from a different degree of cracking due to the varying values of the strain in the MOCVD-templates. The results are discussed in detail in chapter 3.

High power UV-lasers have wide range of medical and opto-electronic applications demanding for effcient and long life time UV-lasers. The efficiency of laser structures is directly related to the quality of material, they are based on. GaN-based UV-laser performance is highly effected by (threading) dislocations. These defects effect the lasing effciency and shortens the life time of lasers.

As discussed earlier, the growth on sapphire substrates using optimal conditions resulted in material with a dislocation density in the order of 10^7 cm^{-2}. This defect density in GaN is acceptable for applications like light emitting diodes (LEDs), however, high power lasers require a maximum defect density of 10^5 cm^{-2}. Hence, one of the goals of this work was to introduce techniques in our optimized process that work towards a further reduction of the dislocation density in the grown GaN epitaxial layers.

In a first approach (which is discussed in detail in chapter 4 of this thesis), we treated MOCVD and HVPE-grown samples with defect selective etchants, resulting in the formation of V-shaped pits on dislocations. These V-shaped pits have three distinct sizes corresponding to the three different types of dislocations present in GaN. The largest pits are formed on the screw-type dislocations, while the middle and the smallest-sized pits correspond to the mixed and edge dislocations, respectively. In this work, samples were etched, resulting in deep pits, and overgrown with a 20 µm thick HVPE layer. SEM and DICM studies revealed that the, screw-type dislocation related, pits were mostly overgrown without filling in the pits with GaN because of the large inclination angles of the walls (~ 60°) and depth of 1.6 µm. In some cases, edge/mixed dislocations in the vicinity of the large pits formed on screw-type dislocation were also overgrown without filling in. The overgrowth, without filling-in, of the defect-related pits prevented the propagation of dislocations in the overgrown layers and resulted in a 50% local reduction of the dislocation density. The method was particularly succesful in MOCVD samples because of its high density of screw-type defects present in contrast to HVPE-grown GaN.

The second approach used in order to reduce the number of dislocations in the HVPE-grown layers was that a SiN_x treatment was introduced at different stages of the growth process. As a result of this SiN_x treatment, a nano-porous SiN_x layer is formed, which promotes selective nucleation in the initial stages of the process. Selective nucleation results in a low generation of dislocation type defects. SEM studies of the etched layers with a thickness 60 µm revealed that the SiN_x treatment worked best when introduced after deposition of the GaN nucleation layer on sapphire. The dislocation density in epi-layers grown with the optimal SiN_x treatment resulted in a reduction of the dislocation density from 10^7 cm^{-2} to 10^6 cm^{-2}. High quality GaN epi-layers were grown with this method as depicted by the SEM, TEM, and PL study, see chapter 5 for detailed results.

There is no better substrate for GaN epitaxy than the native GaN substrate. This is a well understood fact. HPNSG (high pressure nitrogen solution growth) and ammonothermal are the main bulk-growth methods. The ammonothermal method emerged as the most effective method and production of 1.5 inch wafers is recently reported. However, there are still difficulties in producing large-sized GaN boules with this method. The other approach is the production of quasi-bulk or free-standing GaN substrates by first growing on foreign substrates and later getting rid of the substrate by laser lift off method, spontaneous separation, etc.

We also worked towards the realization of a GaN substrate in this project work. We used thermal expansion coefficient mismatch between GaN and sapphire to our advantage. Thicker GaN layer (0.6 to 1.2 mm) were grown which were impervious to the thermal strain generated during the cooling of sample to room temperature and hence, resulted in a spontaneous separation of free-standing GaN with cracking of sapphire. HCl and Cl_2-based HVPE processes were employed to study the spontaneous separation mechanism.

In the HCl-based HVPE process, the GaN-templates, which were 300 µm thick GaN layers deposited directly on sapphire, were overgrown. The overgrown layers were up to 600 µm in thickness. These overgrown layers spontaneously separated itself from the substrate due to built up of high thermal strain during cooling of samples to room temperature. The spontaneous separation was observed in large pieces, but separation of a full 2 inch wafer was not realized. This implies that the thickness of the overgrown layer was not sufficient enough to withstand the thermal strain. Growth of layers thicker than 600 µm was hindered by parasitic deposition. A study of the properties of free-standing GaN revealed that they had a low dislocation density and excellent optical and structural properties. The FS-GaN had only a small amount of residual strain which was homogeneously distributed in axial as well as in planar direction. The interesting aspect of this study was that the spontaneous separation took place in the GaN layer and not from the sapphire substrate, as usually believed. A detailed study of the spontaneous separation mechanism and properties of free-standing GaN is presented in chapter 6.

The spontaneous mechanism was studied using a Cl_2-based HVPE process as well (see chapter 7). High deposition rates , i.e. 4x of the HCl-based HVPE process, and a reduced rate of parasitic deposition allowed to grow for longer time in the Cl_2-based process. Hence, layers of thickness 0.8- to 1.2 mm were overgrown on the GaN-templates (300 µm thick GaN layers deposited directly on sapphire). These thicker layers were separated in one piece as whole 2 inch wafers during cooling down. These free-standing layers had a smooth morphology with an occasional appearance of pits. The structural quality was high as depicted by XRD rocking curve scans. Sharp, narrow peaks, and nominally present yellow luminescence in PL spectra confirmed the excellent optical quality of the spontaneously separated complete 2 inch GaN wafers.

The effect of GaN substrates on the quality of HVPE-grown GaN layers was also studied (see chapter 8). Bulk-GaN substrates were prepared by one of the bulk growth methods and supplied by a commercial vendor. XRD, µ-Raman spectroscopy, etching and DICM techniques were employed for this purpose. The dislocation density in these layers was in the same order as in the substrates, i.e., 10^4 cm^{-2}. In some cases, the defects appeared as a result of surface finishing steps in substrates, which contributed to an increase of dislocation density upto 10^6 cm^{-2}. Narrow FWHM of XRD rocking curves depicted an excellent structural quality of the overgrown HVPE layers. Both the HVPE layers and substrates had the same amount of strain illustrating that HVPE itself does not introduce more defects. Carrier concentration in the substrates was in the order of 10^{19} cm^{-3} which reduced to 10^{17} cm^{-3} in the subsequently overgrown layers. This implies that HVPE process is capable of producing layers of high purity and does not introduce further impurities in the growing layers.