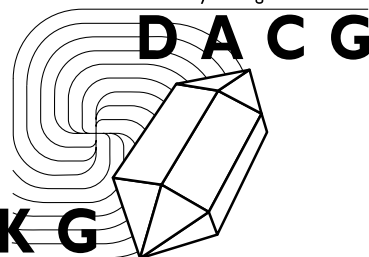


# FACET

dutch association for crystal growth



i n f o r m a t i e b l a d v a n d e

NVKG

nederlandse vereniging voor kristalgroei

oktober 2003

nummer 2

## FACET

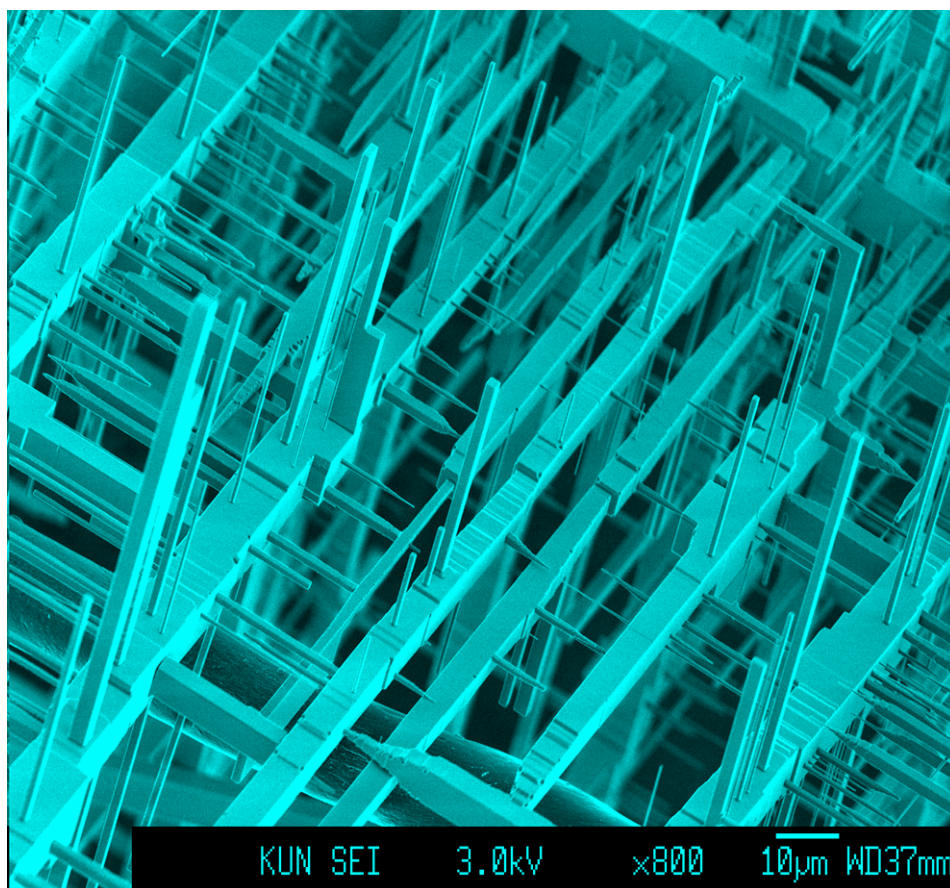
informatieblad van de NVKG  
sectie van de KNCV en de NNV

## redactie

J.W.M. Frenken

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## Bestuur NVKG

<a href="#">Dr ir HJM Kramer</a>	voorzitter
<a href="#">Prof dr JPJM van der Eerden</a>	secretaris
<a href="#">Dr R Geertman</a>	penningmeester
<a href="#">Prof dr JWM Frenken</a>	FACET
<a href="#">Prof dr E Vlieg</a>	lid
<a href="#">Dr RFP Grimbergen</a>	lid
<a href="#">Dr G Bögels</a>	lid

## Omslagfoto

Escher van keukenzout: Door via sublimatie en bij hoge oververzadiging te groeien, ontstaat een intrigerend netwerk van dendritische NaCl kristallen. Dit 3-dimensionale netwerk op micrometerschaal heeft een opvallende gelijkenis met sommige van de werken van M.C. Escher. De kristallen werden gegroeid door Wim Noorduyn en Sander Graswinckel op de afdeling Vaste Stof Chemie van Willem van Enckevort en Elias Vlieg aan de [Katolieke Universiteit Nijmegen](#).

## Redactioneel

Voor u ligt de tweede FACET van dit jaar. In deze FACET vindt u het programma en het aanmeldingsformulier voor de de NVKG-jaarvergadering en excursie, die georganiseerd wordt bij Fuji Photo Film B.V. te Tilburg, op 14 november 2003.

Zoals gebruikelijk doet de redactie op deze plaats een oproep naar input. 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.

[Joost Frenken](#)

## Elektronische FACET

Bij voorkeur sturen wij u de FACET op in de vorm van een PDF-file, die als attachment wordt toegevoegd aan een e-mail bericht. Voor de "digibeten" onder ons: een PDF-file kan probleemloos op *elke computer* worden gelezen. Hiervoor hebt u het programma Acrobat Reader nodig, dat *gratis* op uw computer wordt gezet vanaf de website van de firma Adobe: klik op het logo, of surf naar <http://www.adobe.com>.

Staat u nog niet op onze elektronische verzendlijst, geef uw e-mail adres dan a.u.b. even aan [ons](#) door!

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

## Algemene Ledenvergadering NVKG 2003 / Excursie Fuji

Datum: Vrijdag, 14 November 2003 (let op: nieuwe datum!)

Plaats: Fuji Photo Film B.V., Tilburg (zie routebeschrijving op volgende pagina)

### PROGRAMMA

9:30	ONVANGST en KOFFIE	
9:55	WELKOMSTWOORD	Dr. Yuzo Toda (Fuji)
10:10	<i>Introduction in photographic principles</i>	Dr. Jan Bouwstra (Fuji)
10:35	<i>Recent developments in silver halide crystal research</i>	Dr. Gertjan Bögels (Fuji)
11:00	<i>LEEM studies of self-assembly in the Pb/Cu(111) system</i>	Dr. Raoul van Gastel (UT)
12:00	LUNCH	
13:00	<i>STM at a gel-liquid interface</i>	Dr. Jan Gerritsen (KUN)
13:30	<i>Nucleation: simulation and experiments</i>	Dr. Joop ter Horst (TUD)
14:00	<i>Dyes used in photographic processes</i>	Drs. Edwin Aret (KUN)
14:30	ALGEMENE LEDENVERGADERING NVKG 2003	Dr.ir. Herman Kramer (TUD)
15:00	UITREIKING NVKG-KRISTALGROEIPRIJS 2003	Prof.dr. Elias Vlieg (KUN)
15:10	<i>Lezing Prijswinnaar NVKG-kristalgroeiprijs 2003</i>	
15:30	RONDLEIDING FUJI	Dr. Gertjan Bögels (Fuji)
16:30	BORREL en AFSLUITING	

### AANMELDINGSFORMULIER

Opsturen (bij voorkeur per email) aan: [Gebo@fuji-ef.nl](mailto:Gebo@fuji-ef.nl)

- Hierbij meld ik me aan voor de excursie naar Fuji Photo Film, 14 November 2003

Naam: \_\_\_\_\_

Instituut/Bedrijf: \_\_\_\_\_

Email/Tel: \_\_\_\_\_

- Ik wil deelnemen aan de lunch: Ja / Nee

- Ik heb de volgende onderwerpen voor de jaarvergadering \_\_\_\_\_

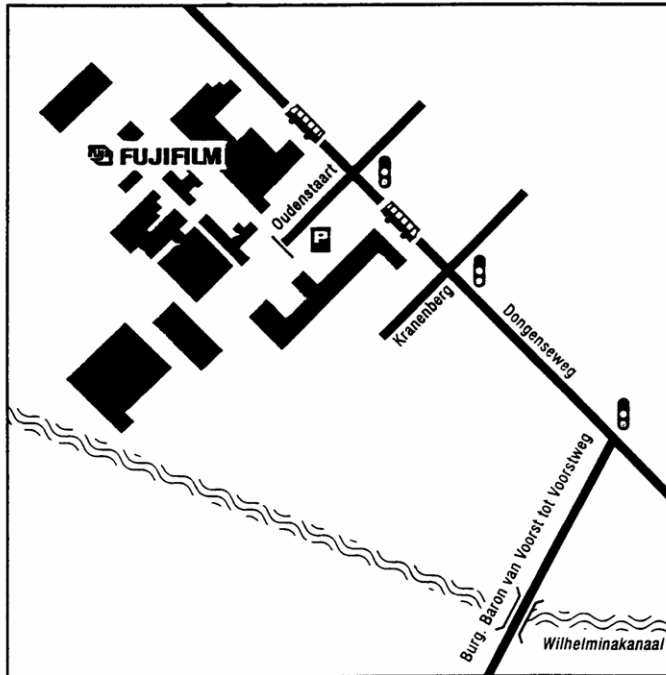
\_\_\_\_\_

Aan de deelname van de excursie en lunch zijn geen kosten verbonden. Wel is het noodzakelijk dat het aanmeldingsformulier tijdig wordt opgestuurd, i.v.m. de lunches.

Correspondentie: Dr. Gertjan Bögels  
Fuji Photo Film, Tilburg Research Laboratory-TD  
Postbus 90156, 5000 LJ Tilburg  
Tel: 013-5791329, Fax: 013-5791901, E-mail: [gebo@fuji-ef.nl](mailto:gebo@fuji-ef.nl)

Oudenstaart 1  
 Postbus 90156  
 5000 LJ Tilburg  
 Nederland

Telefoon +31 13 579 19 11  
 Telefax +31 13 570 11 15

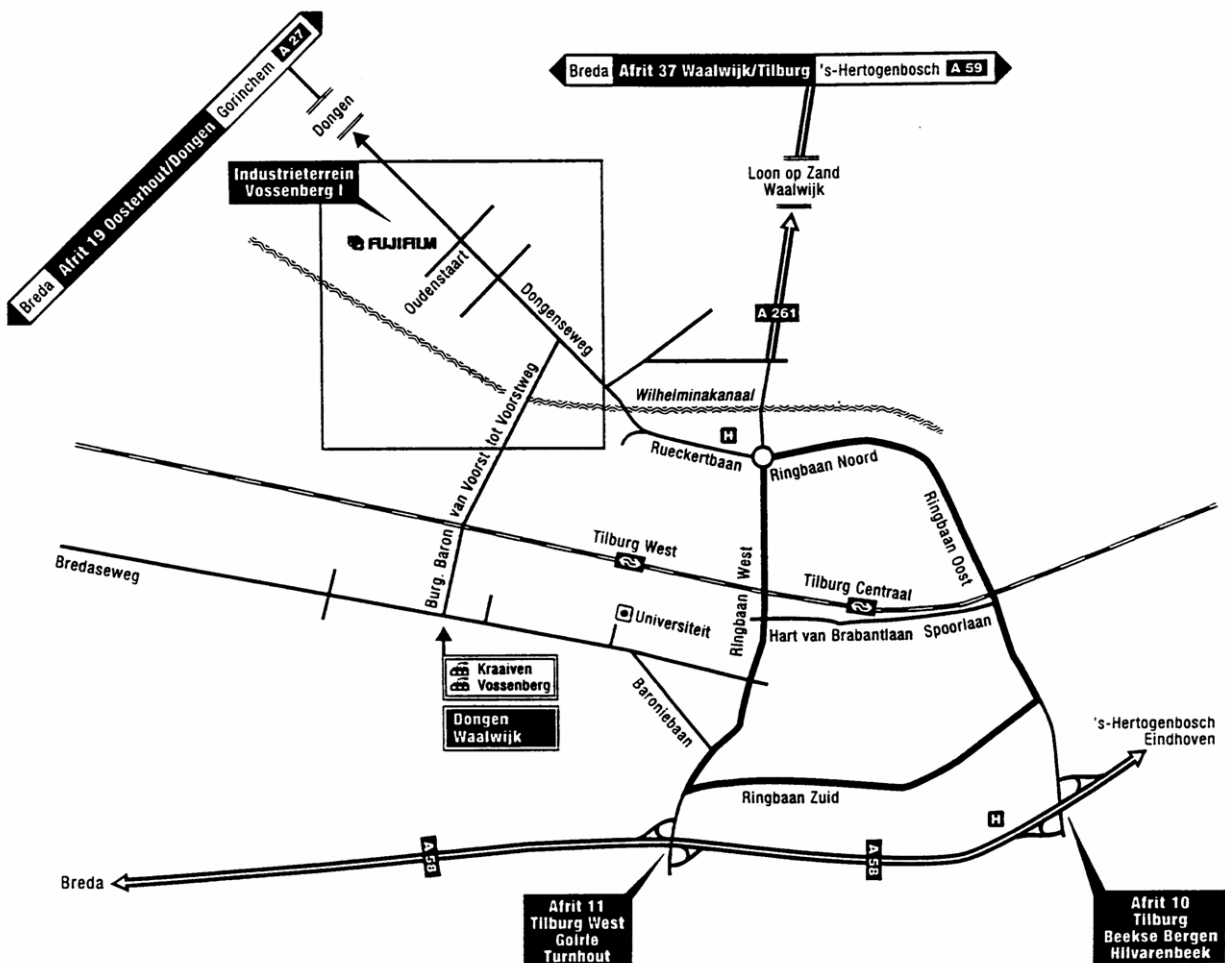


*Vanaf Centraal Station Tilburg*  
 Neem de interlokale busdienst,  
 lijn 127 richting Dongen.

*Vertrektijden van Tilburg CS*  
 Acht minuten over het hele uur  
 en acht minuten over het halve uur.

*Vertrektijden vanaf Fuji richting*  
*Centraal Station Tilburg*  
 Tien minuten over het hele uur en  
 tien minuten over het halve uur.

*Uitstaphalte*  
 Dongenseweg tegenover ingang  
 Fuji-terrein.



## **Agenda NVKG Jaarvergadering 2003: 14 november 2003, bij Fuji te Tilburg**

- Opening
- Notulen jaarvergadering 2002
- Mededelingen
- Jaarverslag 2002/2003

## **Notulen NVKG Jaarvergadering 2002: 8 november 2002 bij DSM te Geleen**

*Aanwezig:* 32 leden, waaronder 6 bestuursleden.

### **Opening**

De voorzitter opent de vergadering met een woord van dank aan DSM en aan gastheer en organisator Reinier Grimbergen in het bijzonder. Hij is blij dat de deelname zo groot is.

### **Notulen**

De notulen van de jaarvergadering 2001 worden ongewijzigd goedgekeurd.

### **Mededelingen**

Zoals beloofd bij de vorige vergadering, heeft Rob Geertman, geholpen door vele anderen, de ledenlijst verregaand opgeschoond. Er zijn nu 157 leden. De definitieve test is hoeveel leden de binnenkort te innen contributie zullen voldoen.

Het bestuur heeft besloten om, op het moment dat de international Organisation of Crystal Growth (IOCG) dat vraagt, een financiële bijdrage van maximaal € 450,- te geven. Met dit geld wil de IOCG een buffer creëren om nationale organisaties die de ICCG of ISSCG conferenties gaan organiseren een voorschot te kunnen geven, en om de kristalgroeprijzen die tijdens die conferenties worden uitgereikt te financieren.

De organisatie van ICCG IX/ISSCG XI (1995) is eindelijk afgesloten. De claim die NOVEM had gelegd is afgedaan. Cees Woensdregt, de voorzitter van de stichting die destijds namens de NVKG deze conferenties heeft georganiseerd, is bedankt voor zijn inzet en werk, en ontheven uit zijn functie. Elias Vlieg volgt hem op.

- FACET
  - Website
  - Financieel jaarverslag 2002/2003
  - Activiteiten komend jaar
  - Bestuurssamenstelling
  - Rondvraag
  - Sluiting
- 

### **Jaarverslag 2001/2002**

Het jaarverslag wordt ongewijzigd goedgekeurd.

### **FACET**

Dank zij inspanningen van Joost Frenken is er nu een mooi verenigingsblad. De elektronische verspreiding loopt goed. Iedereen wordt aangemoedigd kopij bij te dragen.

### **Website**

Ook deze is nu in goede vorm gebracht door Joost Frenken. Dit medium kan goed gebruikt worden om de informatie uitwisseling tussen de leden te bevorderen. Bijvoorbeeld informatie over elders door leden georganiseerde bijeenkomsten kan ingebracht worden.

### **Financieel jaarverslag 2001/2002**

Na een kleine correctie, in verband met omrekening van gulden naar euro, wordt dit goedgekeurd. Opgemerkt wordt dat de KNCV zich destijds bereid heeft verklaard om eens in de twee jaar de NVKG-kristalgroeprijzen te financieren. Rob Geertman zal hierover als penningmeester contact opnemen met de KNCV. De penningmeester wordt gedechargeerd. Rob Geertman en de kascommissie (Jan van Kessel en Jan Meijer) worden bedankt voor hun inspanningen.

### **Activiteiten komend jaar**

- Kristalgroepmarkt: vrijdag 13 juni 2003 te Utrecht.
- Najaarsvergadering: bij Fuji, Tilburg. Datum wordt nog bekend gemaakt.
- Andere activiteiten: Nog niet gepland door bestuur, initiatieven voor nationaal of internationaal georganiseerde activiteiten blijven mogelijk en worden door de vereniging aangemoedigd.

## Bestuurssamenstelling

Frank Heinrichsdorf heeft een nieuwe baan in Berlijn en heeft zich uit het bestuur teruggetrokken. De vergadering stemt in met het bestuursvoorstel om G.J. Bögels, werkzaam bij Fuji-Research in Tilburg, te benoemen als opvolger.

## Rondvraag

Niemand heeft iets voor de rondvraag.

## Jaarverslag van de Nederlandse Vereniging voor Kristalgroei (NVKG)

november 2002-november 2003

### Secretariaat

Prof. dr. J.P.J.M. van der Eerden  
Universiteit Utrecht  
Scheikunde, sectie Fysische Chemie van Grensvlakken  
Padualaan 8  
3584 CH Utrecht  
Tel: 030 - 2533125  
Fax: 030 - 2533946  
E-mail: [J.P.J.M.vanderEerden@chem.uu.nl](mailto:J.P.J.M.vanderEerden@chem.uu.nl)

### Ledenbestand

Het ledenaantal is momenteel 157.

### Bestuur

De taakverdeling binnen het bestuur was als volgt.

- |                               |              |
|-------------------------------|--------------|
| • Dr ir HJM Kramer            | Voorzitter   |
| • Prof dr JPJM van der Eerden | Secretaris   |
| • Dr R Geertman               | Penningmstr. |
| • Prof dr JWM Frenken         | FACET        |
| • Prof dr E Vlieg             | Lid          |
| • Dr RFP Grimbergen           | Lid          |
| • Dr G.J. Bögels              | Lid          |

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

### Verenigingsblad

Het verenigingsblad FACET is bedoeld om de communicatie binnen de kristallisatie-wetenschap in Nederland te bevorderen. Het blad bevat onder meer samenvattingen van relevante proefschriften, 'mooie' plaatjes uit kristalgroei-onderzoek en data van congressen en activiteiten die voor kristalgroei-ers interessant zijn. Initiatieven, besluiten en

## Sluiting

De voorzitter sluit de vergadering met een gelukwens aan de op dat moment nog onbekende winnaar van de NVKG-kristalgroeprijns 2003: Erik van Veenendaal.

plannen van de NVKG worden in de FACET gepubliceerd. Leden van de NVKG worden uitgenodigd kopij in te leveren.

De FACET wordt zoveel mogelijk elektronisch verspreid. In 2003 verschenen er twee edities van de FACET.

### Webpagina

Op de webpagina 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 [Joost Frenken](#) worden doorgegeven. De site heeft 'proefgedraaid' op: <http://www.physics.leidenuniv.nl/sections/cm/ip/NVKG>. Binnenkort wordt de site bereikbaar via <http://www.dacq.nl>

### Activiteiten 2002/2003

- *Jaarvergadering en excursie 2002*: Deze is gehouden op vrijdag 8 november 2002. Gastheer was DSM te Geleen, en de organisatie was in handen van Reinier Grimbergen. Vanuit DSM werd een inleiding gegeven over het belang van kristallisatieonderzoek voor DSM en de wijze waarop dit onderzoek is ingebed in het bedrijf. Diverse onderzoeksgroepen hebben hier onderdelen van hun werk gepresenteerd in het kader van het thema "Crystallization in Life Sciences".
- *Kristalgroeisymposium 2003*: Deze jaarlijkse bijeenkomst werd in 2003 op 13 juni georganiseerd in Utrecht, door Fiona Yarrow. De kristalgroeidag is vooral bedoeld om jonge onderzoekers kennis te laten nemen van elkaars werk. Na een inspirerende lezing van prof. Alfons van Blaaderen over

colloïdale kristallen presenteerden promovendi hun werk. De lezingen waren van een hoog wetenschappelijk niveau en de onderwerpen bestreken een breed spectrum van technologie tot theorie.

- *Jaarvergadering en excursie 2003*: Deze zal worden gehouden op vrijdag 14 november 2003 bij Fuji te Tilburg. De organisatie is in handen van Gert Jan Bögels. Dr. Jan Bouwstra zal een inleiding verzorgen over principes van de fotografie. Daarna zullen diverse onderzoeksgroepen werk presenteren. De kristalgroeprij 2003 zal uitgereikt worden en de winnaar zal een lezing

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### **Besluitenlijst NVKG-Bestuursvergadering 22 september 2003**

- Rob Geertman zal de overdracht van het voorzitterschap van de Stichting voor Kristalgroei aan Elias Vlieg regelen voor het einde van 2003.
- Bestuur en penningmeester besluiten de website <http://www.dacg.nl> in de lucht te brengen en up to date te houden.
- Contributie-inning zal voortaan door Rob Geertman per acceptgiro worden geregeld.
- Het bestuur besluit dat de (voorlopige) datum voor de Kristalgroeidag 2004 4 juni 2004 is.
- Elias Vlieg zal de kristalgroeprij expliciet onder de aandacht van Alfons van Blaaderen en Daan Frenkel brengen. N.B. Vastgesteld wordt nogmaals dat het voorgedragen

verzorgen. De dag zal worden afgesloten met een rondleiding en de uitreiking van een groepsfoto.

### **Kristalgroeprij 2003**

Deze zal tijdens de jaarvergadering 2003 worden uitgereikt aan een jonge onderzoeker voor hoogstaand wetenschappelijk onderzoek op het gebied van de kristalgroei. De selectiecommissie gaat daarbij uit van recente publicaties in de open literatuur en proefschriften.

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proefschrift niet uitsluitend over kristallisatie hoeft te gaan. Kwaliteit is het belangrijkste beoordelingscriterium.

- Herman en Joost denken na over een representatieve poster over de NVKG. Materiaal is grotendeels aanwezig bij Joost. De poster zou in het pdf-formaat verspreid kunnen worden en is dan overal afdrukbaar en bruikbaar.
  - Elias Vlieg gaat na hoe in België de kristalgroeiwedstrijd voor middelbare scholen is georganiseerd. Rob Geertman polst intern bij AKZO-Nobel of men daar steun aan zou willen geven.
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## RECENTE PROEFSCHRIFTEN

**Marianne Reedijk** Ordering at Solid-Liquid Interfaces

Gepromoveerd 13 januari 2003, KUN Nijmegen

Promotor Prof. Dr. E. Vlieg

The surface of a crystal is the place where the crystal interacts with its environment. Knowledge of the atomic structure of a solid-liquid interface is important to understand the different processes occurring at the surface, such as crystal growth. Both the structure at the solid side and on the liquid side of the interface deviate from the bulk structure. The crystal surface can show relaxations and even a reconstruction of the outermost surface layer. The liquid at the surface 'feels' the periodic potential of the crystal and can adopt some of its ordering. In this thesis two different kind of solid-liquid interfaces have been investigated, ionic crystals in water and molten metal monolayers on a germanium crystal.

The first two chapters describe the interface structure of KDP and KBC crystals in their growth environment. In chapter 2 we have used surface x-ray diffraction to determine the atomic structure of the liquid at the KDP/water interface using ultra-thin water layers. These ultra-thin layers were obtained using a specially developed 'environment cell' in which the relative humidity is 100% and the temperature can be controlled. The water layer thickness increases with increasing relative humidity and temperature (i.e. with increasing water vapor pressure).

The liquid structure at the interface shows two important features. First, at all conditions measured the crystal is covered with two ice-like layers of water molecules that are tightly bound to the surface and occupy well defined positions on the surface. Second, these ice-like layers are covered by a diffuse water layer in which the first layer of water molecules still shows some ordering. The highly ordered first two water layers were unexpected for this crystal in contact with its growth solution. These layers must arise from the strong interactions with the ionic surface and deserve further theoretical investigation.

Chapter 3 describes the surface structure of KBC crystals in an humid environment. Both the (001) and (00) faces are investigated. On both faces an etch-resistant layer develops, which is shown to be amorphous. The interface between the etch-resistant layer and the bulk KBC crystal is strongly influenced by the relative humidity. This indicates that water molecules can penetrate through this layer. The interface is atomically flat and shows no reconstructions. The crystal is terminated in an A termination, of which the outermost molecules are most sensitive to the relative humidity: at 40% RH

they show an expansion and at 100% they are compressed.

The measurements performed on the (00) face suggest a different atomic structure of this face, which gives some more insight in the hypomorphism found for the KBC crystals. Liquid metal monolayers on a Ge(111) surface are described in chapters 4, 6 and 5. In chapter 4 the Sn/Ge(111) system is discussed. At higher temperatures the Sn layer is molten.

The structure of the molten Sn-layer has been determined at different temperatures with SXRD experiments. Our analysis shows that the liquid Sn exists as a dynamic, 2D-layer with Sn atoms residing preferentially on sites imposed by the Ge(111) lattice. The structure of the liquid Sn layer gradually changes with temperature from more solid-like to more liquid-like. The most important change is the decrease of the percentage of Sn atoms near lattice sites at higher temperatures. The question arises whether this behavior changes if the liquid layer changes from 2-dimensional to 3-dimensional. Unfortunately, the Sn/Ge(111) system is not suitable to investigate this, because the Sn layer does not completely wet the Ge surface at higher coverage.

The Pb/Ge(111) system is investigated in the last two chapters. The structure of the low-temperature phase is discussed in chapter 5 while the nature of the melting transition is described in chapter 6. We have shown that at a nominal coverage of 4

3 ML two different  $v_3$  structures exist, the  $\beta$  and  $\beta'$  structure, which combine small structural differences with a large difference in transition temperature and melting behavior. The different melting behavior of the two phases can be explained by the bulk Pb atoms on the surface. On the  $\beta'$  surface, the excess Pb is distributed evenly on the surface in small islands. Each Ge(111) terrace is in direct contact with a bulk Pb island, and these islands act as a vacancy sink, inhibiting the  $\beta'$  structure from melting until the bulk melting point is reached. After cooling, the excess Pb is arranged in bigger islands that do not influence the melting behavior of the  $\beta$  phase. A microscopic technique (e.g. STM or LEEM) is necessary to confirm our hypothesis for the behavior of the excess Pb.

The critical exponents of the 2D phase transition of the  $\beta$  phase correspond to the values expected for mean field behavior. This indicates that the Pb atoms have long range interaction potentials.

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**S.X.M. Boerrigter** Modeling of Crystal Morphology: Growth Simulation on Facets in Arbitrary Orientations

Gepromoveerd 10 maart 2003, KUN Nijmegen  
Promotor Prof. Dr. P. Bennema  
Co-promotor Dr. H.L.M. Meekes

Many aspects of crystal morphology modeling are studied in this thesis. Most important of all, is the dependence of crystal growth on supersaturation-the driving force for crystallization, which not only influences the crystal morphology, but also polymorphism and nucleation.

It is shown that an unusual type of epitaxial growth can take place beyond a threshold supersaturation in the crystallization of a model steroid. The same compound shows pseudomorphism upon crystallization from the vapor phase.

Modeling studies show that the two structures are related polytypically.

The experimental morphology of gibbsite could be explained through the analysis of effective edge energies of two-dimensional nuclei on the crystal surfaces.

For this, the program MONTY is extremely useful. It uses the concept of the crystal graph, a description of the interactions between the growth units in the crystal. It allows Monte Carlo crystal growth simulations in any crystallographic direction.

The analyses on three fat morphologies support the idea that not the attachment energy is the relevant parameter for the growth rate of a crystal surface, but rather the edge energy of two-dimensional nuclei on the surfaces. Needle formation is explained by the systematic absences of barriers for 2D nucleation in all but a few crystallographic orientations. For paracetamol, growth simulations show that a supersaturation dependence can be reproduced quite convincingly using the experimentally determined growth mechanisms for the respective surfaces.

Finally, a hypothesis is studied that the morphology of the (sub-)critical nucleus resulting from a certain polymorphic structure must determine the effective barrier of formation of that nucleus, therefore determining the probability of formation of that polymorph. A model is derived and tested on a series of well-known polymorphic structures. It is shown that, indeed, a small majority of the compounds studied produce crystal structures with relatively high levels of isotropy.

**Ivan Buijnsters** Hot-filament chemical vapour deposition of diamond onto steel

Gepromoveerd 7 mei 2003, KUN Nijmegen  
Promotor Prof. Dr. J.J. ter Meulen  
Co-promotores Dr. W..J.P. van Enckevort en Dr. P. Shankar

*Summary and outlook*

*1. Introduction*

This thesis describes research on the deposition of polycrystalline diamond films onto steel substrates by means of the hot-filament chemical vapour deposition (HFCVD) method. Using this technique, thin layers consisting of randomly oriented diamond crystallites can easily be produced on substrate materials such as graphite, molybdenum, silicon and tungsten carbide [6, 2]. As steels are one of the most applied materials in today's industry, the use of steel substrate materials for the deposition of diamond coatings might find a wide application market. Till date, however, the direct deposition of diamond films onto steel substrate materials has been reported less frequently, because the diamond deposition process is complicated by a number of severe problems [7]. It has been

reported by Ong and Chang that the nucleation of diamond particles is extremely difficult due to the catalytic effect of iron on gas precursors, such as methane, to form graphitic soot. Moreover, the mismatch in thermal expansion coefficients of the grown diamond layers and the steel substrate will result in poor adhesion properties. In addition, the rapid diffusion of atomic carbon into the steel substrate reduces the amount of surface carbon species available for diamond growth. To solve these problems, several studies are reported on the application of interlayer systems or steel surface pretreatments [4, 8]. An overview of the different interlayer systems and pretreatment procedures reported so far is given in section 2.5.

As the number of different steels is extremely large, two types of steel, which are commonly used for various industrial applications, are

selected in the present work, i.e. AISI type 316 austenitic stainless steel and ferritic high-speed steel (toolbit, Quality-No. 1.3207). Three types of interlayer systems have been investigated, i.e. thin silicon layers (35-150 nm), about 2- $\mu$ m thick physical vapour deposited (PVD) CrN coatings and diffusion modified borided steels. The adhesion and corrosion pitting behaviour of the various diamond/ interlayer/steel systems have been examined by means of indentation/scratch adhesion testing and electrochemical polarization measurements, respectively. In the following paragraphs, the main outcomes of the work described in this thesis are summarized and discussed. In section 9.5, recommendations for future research are given.

### *2. Direct deposition of diamond onto steel*

Upon direct deposition, large amounts of graphitic soot are observed in the case of high-speed steel substrates, followed by the growth of diamond polycrystallites on top of a thick graphite layer. On the stainless steel the formation of a thick graphitic layer is not observed, as a composite structure of diamond and iron carbides is formed directly on the exposed surface. Based on cross-sectional analysis of the coated AISI type 316 stainless and high-speed steel substrates, it is seen that the in-diffusion of atomic carbon results in a highly different carburization process for both types of steel. At the surface of the austenitic stainless steel, a homogeneous iron carbide layer is formed, while a less uniform carbide case is observed for the high-speed steel. The difference in iron carbide formation and thus in the volume fraction of free iron at the exposed surfaces might explain the formation of large amounts of graphite in the case of the high-speed steel and that of diamond and iron carbides in the case of the stainless steel. As the growth of diamond directly onto steel substrate materials results in low quality and non-continuous diamond films, the use of interlayer systems to block the diffusion of both atomic carbon and iron are found necessary. In order to gain more understanding of the effect of a surface pretreatment on the nucleation and growth of diamond onto strongly carbide forming materials, a substrate pretreatment based on gas nitriding of pure chromium substrates is studied and described in Chapter 3 as well. It is well known that the use of pure chromium substrates generally results in the growth of

individual diamond grains only [5]. From the present work, it can be concluded that the gas nitriding pretreatment, which leads to the formation of a surface layer consisting of the more resistant CrN and Cr<sub>2</sub>N phases, favours the formation of continuous diamond films. In the case of steel substrates, the application of the gas nitriding pretreatment would result in the formation of iron nitrides. Therefore, an interlayer system consisting of a homogeneous PVD CrN coating is chosen and described in Chapter 4.

### *3. Use of interlayer systems*

Using PVD CrN interlayers and applying similar diamond growth conditions, continuous and adherent diamond films are obtained on the high-speed steel, whereas only individual crystallites are observed on the stainless steel due to partial delamination of the initially grown films. Micro-Raman spectroscopy measurements on the grown diamond layers show residual stress values of about 4 GPa for the high-speed steel and values of even 11-14 GPa are derived for the stainless steel, which explains the difference in adhesion. The results described in Chapter 4 clearly reveal different carburization of the CrN interlayer during the diamond CVD process for both types of steel. X-ray diffraction and EDAX analysis indicate the presence of mainly Cr<sub>7</sub>C<sub>3</sub> on the high-speed steel, whereas Cr<sub>3</sub>C<sub>2</sub> is the dominant carbide phase on the stainless steel. The present study also shows that the effect of the tool steel surface roughness on the nucleation and adhesion is very large. In Chapter 5 it is shown that Si interlayers of about 35 nm are efficient diffusion barriers for Fe but not for C during diamond growth onto steel. Despite the high diffusion rate of elemental Fe in the bulk Si phase [9], the diffusion of Fe from the steel matrix is most probably blocked by the formation of FeSiC phases at the surface. Because of the formed diffusion barrier, good quality diamond crystallites with a low fraction of graphite phases are deposited. However, the high carburization rate reduces the nucleation kinetics for diamond and a diamond/carbide composite structure is formed. The third type of interlayer system, which has been studied in the present work and which is described in Chapter 6, comprises a diffusion modified boride surface layer. By means of pack boriding, thick boride cases containing FeB and/or Fe<sub>2</sub>B phases are produced on both stainless and tool steel

substrates. These boride layers show a very high surface hardness (>3000 VHN), which gradually decreases on approaching the bulk. The presence of FeB at the surface results in very high thermal stresses and delamination of the diamond films on both types of steel. If only a Fe<sub>2</sub>B phase is present, continuous diamond films with low residual stresses are grown on both borided stainless and tool steel.

#### *4. Adhesion and corrosion resistance of diamond coated steel*

From the indentation and scratch adhesion tests, which are described in Chapter 7, critical load values for coating failure are obtained from the acoustic emission signals combined with surface analysis of the tested regions. The adhesion tests performed on diamond coated molybdenum and AISI type 316 stainless steel substrates with PVD CrN and boride interlayers show critical loads of 135, 100 and 69 N, respectively. A direct comparison made with the strongly adhering diamond layers on the molybdenum substrates indicates only a slightly inferior adhesion for the diamond coated stainless steel with the CrN interlayer. The scratch test performed on the diamond/borided steel system shows no significant coating failure up to 80 N. Applying both Rockwell C and steel ball indenters, kinetic friction coefficients in the range of 0.10-0.35 are derived. As the critical load values determined by both indentation and scratch adhesion tests are very sensitive to intrinsic and extrinsic factors such as indenter tip radius and testing environment, a direct comparison with other work is very difficult. In addition, the very few adhesion tests, which are described in literature, are performed on diamond coated tool steel and/or carbon steel substrates. Nevertheless, the present work shows that the use of boride and PVD CrN interlayers is highly promising for the growth of diamond films onto stainless steel substrates as well.

The corrosion resistance of the diamond coated tool steels with the three types of interlayer systems is evaluated by means of electrochemical polarization studies (Chapter 8). The corrosion resistance of blank tool steel in sodium chloride solutions is very low, but is significantly increased by the deposition of protective diamond layers. The present study shows that the effect of the applied interlayer systems on the shift of the corrosion potential is very strong. This can be explained by the

seeping of electrolyte solution through the diamond films via pores and junctions between the individual grains, thereby attacking the underlying interlayer system.

#### *5. Future work*

From the three types of interlayer systems studied in this work, the thin Si layers show minor results. It can be concluded that single Si interlayers are not very useful for the deposition of continuous diamond coatings on steels because of the inferior diffusion barrier properties for atomic iron and carbon. Despite the formation of good quality diamond crystallites, the production of continuous and well-adhering diamond films will be extremely difficult. Therefore, the use of Si interlayers for tribological applications of diamond coated steels can be ruled out and will not be studied in planned future work. The adhesion tests of the diamond coated stainless steels with the two other interlayer systems, which have been produced by pack boriding and CrN coating, show promising results. Optimization of these interlayers including layer thickness and chemical composition as well as the optimization of suitable substrate pretreatments is considered necessary in subsequent studies. As the thermal stresses acting on the grown diamond films are high and will have a negative effect on the tribological performance of the diamond coated steels, a detailed study of the effect of an increased CrN layer thickness on the accommodation of the thermal stresses will be rewarding. Also, the application of different PVD methods to produce these CrN interlayers might lead to still better accommodation of the residual stresses and/or adhesion of the grown diamond films. Similarly, the effect of the iron boride layer thickness on the accommodation of the thermal stresses needs to be investigated into more detail.

In Chapters 4 and 6 it has been shown that the substrate pretreatments prior to diamond growth have a strong effect on the nucleation and adhesion of the diamond layers. For example, a detailed study of the effect of applying different sand blasting and ultrasonic scratching procedures might further improve the nucleation and adhesion of the diamond films. In this respect, optimization of the diamond CVD process for each of the interlayer systems individually will also contribute to better results. The application of a two-step deposition process based on a relatively short nucleation step and a

subsequent growth step has been proven to be very efficient for the growth of high quality and good performance diamond films on various substrates [1, 3]. The introduction of a bias-enhanced nucleation (BEN) step has to be considered in future work as well, as the applied bias leads to ion bombardment of the steel substrate, thereby resulting in better nucleation kinetics and adhesion of the diamond coatings. Apart from the optimization of the substrate pretreatment and CVD process steps, additional work has to be done on the production and characterization of (ultra-) nanocrystalline diamond films. Using methane/argon as well as methane/hydrogen gas mixtures, fine-grained and high quality diamond films can be produced. Changing the gas mixture composition, the structure, composition and properties of the formed carbon films can easily be tuned. As nanocrystalline films show hardness values close to pure diamond, surface roughness values in the nanometer range and a thermal stability comparable to microcrystalline diamond films, these are very promising as protective coatings on steels as well. For the boride and PVD CrN interlayer systems, the fabrication of nanocrystalline diamond films and the characterization of the mechanical and electrochemical properties of these films will be explored in future work.

The indentation and scratch adhesion tests described in the present work indicate good adhesion of the diamond coatings on borided and CrN coated stainless steel. In future work, also the adhesion of diamond coatings on tool steel substrates has to be investigated. In order to evaluate the applicability of diamond coated steels with boride and CrN interlayers, the tribological properties such as the wear resistance and friction behaviour under sliding contact need to be studied. This can be done by applying the pin-on-disk tribometer and/or the rubber wheel test. In addition, the use of complex shaped steel substrates is the next, non-trivial step in evaluating the applicability of steel substrate materials for industrial purposes. The presence of convex and concave substrate shapes will have a strong effect on the adhesion of the grown diamond layers. The residual, thermal stresses acting on curved surfaces will

have components both parallel and perpendicular to the diamond layer, whereas the stresses acting on diamond films grown on flat substrates are considered biaxial. This will complicate the bonding properties of the diamond/interlayer/steel systems significantly. The present work has led to a better understanding of the use of various interlayer systems for the deposition of diamond onto steels. Though the diffusion modified boride and PVD CrN interlayers show highly promising results, the search for new interlayer systems has to be continued in the future. The most promising interlayers are based on diffusion modified systems, as these can accommodate the residual stresses more easily [10]. From the present work as well as from earlier studies [4, 8], it can be concluded that the application of Cr(-N) based interlayer systems results in superior adhesion of the grown diamond films and therefore in superior tribological properties of the diamond coated steels as well.

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**John Schermer** Flame Deposition of Diamond -a brilliant growth technique -  
Gepromoveerd 21 mei 2003, KUN Nijmegen  
Promotor Prof. Dr. P.K. Larsen  
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### *Background*

It seems unbelievable to produce high quality diamonds using barely more than a simple combustion torch, but the research outlined in this thesis shows that it is quite possible. The process by which the crystals are formed is known as chemical vapour deposition (CVD). After pioneering work in the former Soviet Union the world-wide interest for the production of diamond from a low pressure gas phase arose around 1982. Since then, research resulted in the development of different experimental methods to synthesize diamond.

In 1988 the first report about the flame deposition process was published. This intriguing method utilizes the simplest experimental set-up of all diamond CVD techniques. Deposition takes place in the reducing zone of a combustion flame and does not require a reactor vessel. After some practice in handling a commercially available acetylene-oxygen burner one can deposit diamond layers on, for example, molybdenum plates that are attached to a water cooled copper tube. In chapter 2, it is described how the process can be strongly improved by relatively small modifications in order to facilitate reproducible growth of the diamond layers.

The combustion of acetylene with oxygen produces the energy needed to drive the deposition process, while a small excess of acetylene over oxygen provides the carbon atoms which under the right circumstances will crystallize into diamond. From every million carbon atoms added to the flame, maximally about ten end up in the diamond layer. Virtually all others are, after an initial conversion to CO, finally removed as CO<sub>2</sub> gas. This relatively low carbon efficiency of the flame method is explained by the fact that the acetylene provides both the raw materials and the necessary energy for the deposition of the diamonds.

### *1. Polycrystalline layers*

This thesis consists of two parts. In Part I, which comprises chapters 3 up to 6, the deposition of polycrystalline diamond layers on molybdenum

substrates is studied. These layers consist of randomly oriented, microscopically small diamond crystallites (typically 1-100 μm in diameter) in a matrix of different nanocrystalline and amorphous hydrocarbon phases, known as diamond-like carbon (DLC). The diamond crystallites are bounded by planar faces or facets in different directions. If the CVD process takes place at the right temperature and with the right gas phase composition, a nice continuous film of closely interconnected diamond grains is formed. In part I the optimization of the flame deposition process with respect to homogeneity, deposition rate and purity of the diamond layers is described. For this purpose the layers are examined using several microscopic and spectroscopic techniques. The experimentally found results are explained very well using a model of the time dependent development of the gas phase composition following the primary combustion of the source gases at the flame front as outlined in chapter 2.

It is demonstrated that the radial variation in growth rate and morphology of the diamond deposits is primarily correlated to the diffusion of nitrogen from the ambient air into the flame and the shape of the dark boundary layer in the gas phase above the growing surface. The study described in chapter 5 demonstrates that it is possible to eliminate the influence of nitrogen in the central area of the diamond deposits by the use of the right deposition conditions and an acetylene gas purification procedure. It is also demonstrated that the presence of nitrogen does not necessarily have a negative effect on the quality of the diamond layers. By the controlled addition of small nitrogen concentrations to the flame, layers can be produced in which the diamond grains are oriented in such a way that the upper surface of the deposits predominantly consists of {001} facets parallel to the substrate. These so-called <001> textured diamond layers can be of significantly higher quality (smoother surface finish and less crystallographic defects) than layers with randomly oriented crystallites. Based on the experimental results a model is derived in

chapter 6 that describes the mechanism behind the development of the textured layers.

## *II. Single crystals*

Part II of this thesis consists of the chapters 7 up to 10. In this part the homoepitaxial growth of single crystal diamond layers is studied. These are diamond layers, which are deposited on millimetre sized natural diamond crystal plates. In the carbon rich flame the natural diamond seed crystals grow in thickness generating macroscopic diamonds that are easily to handle during examination. Analyses of these single crystals exclusively yield information on the diamond material properties, while the results obtained from polycrystalline layers are always biased by the presence of DLC between the diamond grains.

The quality of the diamonds appears to be strongly dependent on the particular ordering of the carbon atoms at the crystal surface on which deposition takes place. In this respect a distinction is made between stable/flat and unstable/rough faces. All crystallographic directions in which signs of surface stabilization were found on flame deposited diamonds can be described by Miller indices  $\langle hhk \rangle h \square k$ . The surfaces in all other directions are unstable. During deposition on these unstable faces, like for example  $\{110\}$ , the roughness of the surface strongly increases, which finally leads to the formation of microfacets. This growth mechanism results in a reduced material quality due to the incorporation of impurities and formation of cracks.

From the theoretical description of the diamond lattice given in chapter 9, it is deduced that the atoms at the surface of the stable faces are ordered in such a way that a certain percentage of them mutually can form additional bondings. In general, this surface reconstruction is obtained by direct dimer bonds. However, as a consequence of the high CO concentration in the gas phase during flame deposition, in this particular process the additional bonds might also be formed by so-called  $>C=O$  bridges. In both cases a connected net of carbon atoms is formed directly at the surface of the growing layer, so there is only a low probability that impurities like nitrogen are incorporated into the diamond lattice. The research further indicates that crystallographic imperfections, such as cracks and twins, easily develop if growth takes place on the stable  $\{111\}$  faces. Summarizing all results it is concluded that the best quality diamonds are grown on seed crystals having a  $\{001\}$  surface. Using several spectroscopic techniques it is demonstrated that, if grown under optimized conditions, the quality of these

crystals equals or exceeds that of the best natural diamonds. Taking into account the simplicity of the deposition system, this surprisingly good quality might be related to the previously mentioned high CO concentration in the gas phase.

An important advantage of flame deposition over most other diamond CVD techniques is that a small increase of the oxygen flow creates a gas phase composition in which diamond can be etched. In chapter 10 it is described how this property is used to etch away possible imperfections at the edges of the seed crystals prior to the deposition process. In this way the crystallographic defects, which usually develop at the edges of the single crystal diamond layers, are eliminated. On the basis of this result it is demonstrated that the flame technique is perfectly suited to overgrow a (001) mosaic structure of several seed crystals by one single crystal diamond layer.

## *Utilization*

Compared to other diamond CVD methods, a 10 to 100 times higher growth rate is obtained over a maximum deposition area of about 1 cm in diameter by using the standard flame deposition process. However, for most industrial applications of diamond as described in chapter 1, a large deposition area is of more importance than a high growth rate. Attempts reported in literature to increase the deposition area covered using the flame method by a more efficient utilization of the carbon atoms while maintaining the high deposition rate and quality, proved not successful. In this respect also the use of turbulent burners as described in chapter 4 of this thesis did not lead to an improvement. Since upscaling towards larger deposition areas is already accomplished by the use of other diamond CVD methods, the best way to utilize flame deposition is for those applications in which the specific advantages of this fascinating technique are maximally exploited.

1) Brilliant growth technique. The combination of high growth rate and quality and a small deposition area indicates that the flame deposition technique is excellently suited for homoepitaxial growth of high purity single crystal diamonds. It should be realized that the required natural or high pressure synthesized seed crystals are only available in smaller sizes. If necessary, the surface might be enlarged by the application of mosaic growth.

2) Model and demonstration system. The results as described in this thesis show that the flame deposition technique is a perfect model system for the investigation of the diamond crystal growth mechanisms. The high growth

rate and simple experimental equipment make the method also very suited for training of students and demonstration purposes.

3) Portable growth technique. Unlike other methods, no reactor vessel is required for the

flame deposition process. Therefore, it is possible to develop a mobile set-up by which large structures can be coated with a diamond film on the spot.

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