Patterned Substrates Guide Defect Growth in Colloidal Crystals
(see p. 5A)
About the Cover:
Cover illustration by Jan Hilhorst. Colloidal self-assembly has shown promise for the cheap and fast production of photonic materials. One drawback is the lack of control over the inclusion of defects in such crystals, which has to be done through post-processing or multiple growth steps. This cover image (left) shows a naturally occurring growth defect that leads to the formation of intrinsic stacking faults in sedimentary colloidal crystals. By mimicking this defect in growth templates prepared by electron beam and focused ion beam lithography (middle and right), stacking faults can be grown in a single step at predetermined positions and with predetermined growth directions. Properly chosen templates can thus create stacking fault intergrowth structures at a specific height in a crystal. These can be interesting candidates for optical propagation channels as well as fundamental studies of defect behavior. For more information, see “Defect Engineering in Sedimentary Colloidal Photonic Crystals” by Jan Hilhorst, D. A. Matthijs de Winter, Joost R. Wolters, Jan Andries Post, and Andrei V. Petukhov on pages 10011-10018.
Defect Engineering in Sedimentary Colloidal Photonic Crystals

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ABSTRACT: In this paper, lithographic methods are successfully employed to create growth templates for colloidal self-assembly, enabling the inclusion of crystallographic defects at predetermined positions. It is shown that through smart template design stacking faults can be grown predictably into face centered cubic structures. More interestingly, by precise guiding of the stacking faults hollow intergrowth channels can be grown at predetermined lateral and vertical positions. The mechanisms involved in defect growth are promising for extension of this technique to more complex crystal structures, such as the diamond structure, as well as to more complex faults, including corners and t-junctions.

INTRODUCTION

Colloids are promising materials for the cheap and fast production of photonic devices through self-assembly.1−5 However, several hurdles remain to be taken before applications can be realized. First, a robust method for synthesizing three-dimensional structures with a full photonic band gap has to be found. Second, the disorder that is intrinsic to self-assembled systems has to be reduced to a minimum, to prevent the closure of the band gap. Third, control over the incorporation of defects at desired positions has to be achieved to be able to add functionality for the realization of more complex applications.

For the first hurdle, the synthesis of structures with a full band gap, several methods have been proposed. Both the face centered cubic (fcc) and hexagonal close packed (hcp) structures, that can be formed from spherical colloids with isotropic interactions, do possess a full band gap if the crystal structure is inverted.6,7 This means that the voids in the colloidal crystal are filled up with a high refractive index material and the colloids are etched out.2,7 Syntheses routes to pure hcp and fcc crystals have been proposed and high quality crystals of both structures have been obtained experimentally.9−11 However, the band gap of the resulting structures is very sensitive to disorder and is unsuitable for practical purposes.12,13 A structure that is more promising for generating a robust full photonic band gap is the diamond structure.14,15 This structure does not form from single component dispersions of colloids with isotropic interactions; yet, several pathways to synthesize it have been proposed.15−18 Still, none of the proposed pathways for self-assembled systems have been realized experimentally, and if the diamond structure can be grown in this way, the second hurdle has to be taken: growing the crystal with a sufficiently small concentration of defects. Self-assembled colloidal structures are very susceptible to disorder.19−21 The weak interparticle interactions cause colloidal crystals to have more defects than their atomic counterparts. For example, the equilibrium concentration of vacancies lies at around 10−4 per unit cell for colloids close to melting,22 while for copper at room temperature it is around 10−22,23 Experimentally, vacancy concentrations up to 1% have been reported for colloidal crystals, due to crystal growth kinetics.24 The same comparison can be made for stacking faults. For atomic crystals, the model system for studying stacking faults has always been cobalt, which can have up to ~10% stacking disorder in a preferred hcp structure.25,26 For colloidal crystals, 50% of stacking disorder is an exception,20,21,27−29 although thermodynamically the crystals should be fully fcc.30 As both vacancy and stacking fault concentrations in experiments are typically higher than expected on the basis of free energy calculations, kinetics play an important role in the formation of colloidal crystals. It has been demonstrated that reducing crystal growth speed indeed reduces the amount of stacking disorder.31 One way to increase the degree of perfection in colloidal crystals is therefore to grow crystals slowly. Still, some degree of stacking disorder remains in such crystals. Another method to reduce such disorder is the use of growth templates.10 By promoting the growth of specific crystal planes that are unique to a single crystal structure (for example the fcc {100} plane or the hcp {1100} plane), crystals free of stacking faults can be grown,9,10,32 although the ideal crystal structure may be a little distorted through a nonideal spacing of the template structure. This can, for example, deform the fcc structure to a face centered tetragonal one with a small deviation from perfect fcc.33 Nonetheless, we will discuss the crystals in this study as fcc and hcp crystals, as their structures are close to the ideal ones.

The template growth procedure may be extended to force the growth of so-called Laves phases onto a binary colloid mixture16 or to guide the growth of a faultless diamond structure in dispersions of patchy particles.18 This way, the first...
two conditions for the formation of high quality self-assembled photonic crystals may be fulfilled at the same time, namely, the reduction of disorder to acceptable levels, as well as the growth of structures with a full photonic band gap.

Finally, if high-quality crystals can be grown by templating, their functionality may be improved by growing faults at selected positions, creating optical propagation channels. One way to introduce defects in a regular way is by confining the crystal within a regular, well-defined space. This can result in exotic crystal structures with regularly spaced stacking faults or changes in crystal orientation depending on gap spacing.34−36 A precise, controlled way of including defects is through crystal postprocessing using two-photon polymerization.37 With this method, defects like propagation channels can be “written” in any desired shape.

In this paper we present a way to include defects at precisely defined positions in colloidal face-centered cubic crystals through template growth, without any postprocessing steps. Figure 1a shows a mechanism that was proposed recently38 for the growth of slanted intrinsic stacking faults in sedimentary colloidal crystals. These consist of two \{111\} planes with hcp structure growing upward through the crystal under a 70.5° angle with the horizontal,38−40 as shown in the bottom part of Figure 1a. Nucleation of such defects is suspected to occur when two half-planes grow toward each other, leaving a defect line in between. Sedimenting particles fall into the defect and start the growth of a slanted fault there. (b,c) Structures of the templates used in this paper. (d,e) Experimental realizations of the structures shown in (b) and (c).

In this paper it is shown that by mimicking this type of line defect in crystal growth templates, defects can indeed be grown into crystals with a high quality fcc structure. More strikingly, we show that this can be done in crystals with horizontally oriented hexagonal planes, that are normally degenerate with respect to preferred crystal structure. In addition, templates for incorporating more advanced fault structures into fcc crystals are investigated. These templates involve the fcc \{100\} plane to lift the stacking degeneracy that exists on hexagonal \{111\} planes. In addition, height steps are included in the templates to guide the direction of growth of the faults. The analogy between the fcc and diamond structures makes the same methods applicable to a wider range of structures and could potentially lead to a growth method fulfilling all three criteria for growing high quality photonic crystals.

**EXPERIMENTAL SECTION**

**Electron Beam Lithography.** Substrates used for E-beam lithography consisted of glass microscope coverslips of 22 mm in diameter, coated with a layer of Indium Tin Oxide (ITO) with a resistivity of 100 Ω-sq−1 (Diamond Coatings Ltd.). The substrates were cleaned by ultrasonication in a beaker containing isopropanol (Acros, “pure”), after which a layer of 950 kDa PMMA was spincoated onto the ITO-side from an 8 wt % solution in anisole (solution obtained from Microchem). A Delta 10 spincoater was used at 5000 rpm (ramp 1 s) for 60 s, after which the resist was baked on a 180 °C hot plate for 60 s, producing a 400−500-nm-thick resist layer.

Lithography was performed in a Raith E-Line setup with an acceleration voltage of 20 kV and an electron dose varying from 1.8 to 10.8 μC/cm².
RESULTS AND DISCUSSION

Template Optimization. Figure 1b,c shows schematics of templates of the various kinds used in this study. Figure 1d,e contains images of the experimental realizations of these templates. Figure 1d is a confocal image obtained by removing excitation filters from the confocal microscope to get signal from scattered laser light. This template was created with electron beam (E-beam) lithography. Figure 1e is a scanning electron microscopy (SEM) image recorded in the focused ion beam (FIB)-SEM instrument just after creating the template. Results on the incorporation of defects will be presented later. First, the properties of the templates and the results of the writing process will be discussed.

The template shown in Figure 1b is one of the templates used for testing of the nucleation hypothesis shown in Figure 1a. These will be labeled hexagonal templates throughout this paper. The defect in this image is wider than the mismatch created by growing a B and a C layer toward each other, as in Figure 1a. Such templates were used as well, but in this case, a wider defect of 1.35d was created to accommodate a larger height difference for sedimenting particles, as illustrated in the bottom part of Figure 1a. This larger height difference was chosen to exactly match the height step of 0.12 kgT to 0.19 kgT per particle.

To prevent influences of stacking disorder on defect growth, experiments were also performed on nondegenerate fcc \{100\} planes. Like on the hexagonal templates, defects can in principle be grown on a flat \{100\} plane if a structure representing a 2D intersection of a \{100\} plane and an intrinsic stacking fault is included in the template. As in the hexagonal templates, the symmetry of such a flat template excludes control over the growth direction of a stacking fault. To gain more control over the direction of defect growth, templates with a height step were created, shown in Figure 1c and e. This height step, combined with the positioning of the holes, replicates the exact configuration of an intrinsic stacking fault as it exists in an fcc crystal. In the configuration illustrated in Figure 1c, with a lower region between two faults, the two formed stacking faults grow toward each other and react upon meeting. Such templates were created using an FIB, as this enables milling of a substrate to introduce the required height step in a template.

FIB-milling is a more versatile technique than E-beam lithography in the sense that structures can be produced in any type of material without prior treatment. This makes the creation of height steps more straightforward, accurate, and reproducible than with E-beam lithography. However, the typical milling time for a single template is approximately 5 min. With a setting up time of 20 min. With a typical milling time of 20 min. The E-beam setup produces approximately 60–90 templates per hour and is therefore more suited for exploring parameter space. A technique that has not been explored here, but has good potential for structures with micrometer sized features, is soft-lithography. This is not as customizable as E-beam or FIB lithography, but could be interesting for cheap mass-production of templates.

Resulting Crystal Structures. Hexagonal Templates. Crystal growth on hexagonal templates did not produce slanted...
faults on every attempt. A major factor determining final crystal quality is the hole spacing distance in the templates. For this reason, most substrates contained many similar templates, with varying spacing. Typically, templates with a spacing of 1.05d–1.06d were found to yield the best results, where d is the average particle diameter. When the lattice spacing was chosen correctly, either the defects were closed in the first few layers above the template or slanted faults were formed that persisted for many layers, depending on the exact growth conditions and on chance. For polymethyl methacrylate (PMMA) particles of 600 nm radius in cis-decahydronaphthalene (cis-decalin), persisting defects were formed in approximately 50% of the crystals, but the success rate can be improved by introducing a height step in the templates as described later for the FIB templates. Examples of successful defect incorporation on hexagonal templates are given in Figure 2. Figure 2a shows a confocal slice through the first layer of particles on a template. The defect line is indicated by the arrow. Although the slice was taken through the first layer of particles, a row of particles can be seen in the defect, indicating that these particles have sedimented below the level of the second layer, as assumed in the nucleation model in Figure 1a. A cross-section of the same crystal along the plane orthogonal to the defect is shown in Figure 2b. The direction of gravity in this picture is indicated by the arrow to the left. The arrow in the middle of the image points to the row of particles that have sedimented into the templates.
defect. These are clearly positioned below the other particles in the second layer.

When the structure higher in the crystal is investigated, the fcc structure is apparent from the rows of particles in ABC stacking. This is highlighted by the solid white line. The kink in this line is where the slanted stacking fault is grown into the structure. This is clarified in Figure 2c, that contains a Ballview image made of the detected particle coordinates from a 3D confocal data set of the same crystal. The view is the same as in Figure 2b, but now, green particles have been detected as fcc and red particles as hcp. Here, the top part of the crystal can be seen to be fully fcc, with the slanted stacking fault running through it in red. These images are representative of the structures containing such faults on these templates: good quality fcc crystals with slanted stacking faults originating from the substrate. This indicates that a small disturbance, like a defect line, can be enough to lift the degeneracy of the hexagonal plane and force fcc growth. The nucleation mechanism, however, does not correspond to the mechanism shown in Figure 1a. The bottom layers in Figure 2b do not form an fcc structure from the start, as indicated by the dashed lines. This can also be seen in Figure 2c, where the bottom layers have no determined crystal structure. In most crystals formed on hexagonal templates, this was a recurring problem. The first layer follows the template structure perfectly, but the second and third layers are often much less crystalline. Still, the height step introduced at the template often produced a slanted stacking fault higher in the crystal.

Another example of a crystal grown on a hexagonal template is shown in Figure 2d,e. Again, the arrow indicates a particle lying in the defect line and the white line indicates the fcc structure with slanted stacking fault. Here, the second layer was also less crystalline than the first layer on the template, but the crystal structure close to the substrate was more defined than in Figure 2a–c. This data set was therefore used to identify the mechanism of propagation of the fault and the height step through the less-ordered region. Figure 2f displays the mechanism as it was proposed together with the structure observed in Figure 2d. In the first mechanism, the left hcp layer originates from the defect line, while in the second mechanism the right hcp layer originates there. This has a strong effect on the crystal structure: while the right side of the crystal remains identical for both mechanisms, the left side is twinned in the measured case. Similar undesired stacking disorder in the first few layers was observed in all measurements and differed from crystal to crystal. We attribute this to the stacking degeneracy of the fcc {111} planes, which is intrinsic to the hard sphere system. Polydispersity may also play a role, although at 2.5% polydispersity, the effects are expected to be marginal. Crystal quality may be improved by slowing down crystal growth by either lowering the particle concentration or using smaller particles. We found, however, that smaller particles produced faults less frequently at the desired position, as their smaller gravitational energy gain upon sinking into the defect line reduced the possibility of growing faults. The same was true for density matched particles in TTC, which resulted in much more random crystals and hardly any slanted stacking faults. Lowering the particle concentration was impractical, as typical particle concentrations were already at 0.34 v% and lowering the concentration would lead to too thin crystals.

The difference between various crystal grown onto the same substrate indicates that the mechanism is clearly not universal, but the transmission of the height step, as shown in Figure 2f, is universal and does create slanted stacking faults higher in the crystal. The disorder in the first layers, however, may result in the growth of different types of slanted stacking faults. In addition to intrinsic stacking faults, extrinsic ones have also been observed, as well as two layers of hcp separated by two fcc layers (shown in Figure 2g and h, respectively).

Focused Ion Beam {100} Templates. To solve the problem of unwanted stacking disorder and to gain control over the growth direction of the defects, {100} templates with height steps were fabricated. By milling away parts of a substrate and patterning the milled region as shown in Figure 1c,e, a structure corresponding to an intrinsic stacking fault can be created in the template. By including two of such height steps in a mirrored configuration, a pair of stacking faults can be grown toward each other, resulting in a line where the two faults meet, at a specific height in the crystal. This is not possible on a {111} plane, where stacking faults can only grow toward each other with 60° angles between them, as shown in Figure 3.

Figure 3. Schematic of the orientation of slanted stacking faults and therefore the orientation of fcc {111} planes on templates of {111} and {100} planes.

Results of crystal growth on a {100} template are shown in Figure 4. Figure 4a shows the first layer grown on a FIB-template. The template is located in the center part of the image, where the particles have assembled into a square configuration. This region is lighter than the remainder of the image, as the particles have sedimented into the template, resulting in a slightly different focal plane than the surrounding crystals. In the template area, an even brighter bar can be seen. This is the bar that has been etched away to allow part of the crystal to have a well-defined height difference with the rest of the structure, to produce stacking faults. A side view of the same crystal is shown in Figure 4b. Despite the small size of the templates, no grain boundary effects were observed. The only effect was a gradual shrinking of the grain with height, resulting in a pyramidal shape of the grains. A resulting grain boundary can be seen in the top left of Figure 4b.

The arrow to the left indicates the direction of gravity and therefore points toward the template. From the template, two intrinsic stacking faults grow upward, at the position of the kinks in the solid white line. Halfway through the image, these faults meet and interact to form a channel through the crystal. Above that, the stacking faults continue to grow upward. The
of $10^{-3} k_BT$ per particle,\textsuperscript{30} result in a total energy of $\sim 10 k_BT$ for the full stair-rod configuration. Here, the stacking fault energy of $\sim 0.5 k_BT$ makes up a minor part of the dislocation energy.

Contrary to the stair-rod configuration, the crossing fault configuration does not contain a dislocation, as a Burgers circuit\textsuperscript{23} drawn around the defect closes perfectly, meaning that there is no net elastic deformation of the lattice around the line defect. The energy of this configuration consists of the stacking fault energy of the four stacking faults bordering the defect, and the energy needed to create the channel through the crystal. As the stacking fault contribution for a fault extending 250 particle diameters into the crystal was calculated to be $\sim 10^3 k_BT$ per stacking fault in an atomic crystal, a configuration containing four stacking faults has a much higher energy than a stair-rod configuration, even without the penalty of creating the gap in the defect line. This additional term is mainly made up of the energy required to break the bonds between the particles indicated by the arrows in Figure 4c. Per particle length of defect, two interparticle bonds are broken, which for typical atomic fcc crystals have bond strengths on the order of $10^5 k_BT$ per bond,\textsuperscript{48} adding only marginally to the total defect energy.

In the colloidal case, the four stacking faults extending 250 particle diameters contribute $\sim 1 k_BT$ to the defect energy. The energy required for creating the additional 0.16 $d^3$ of volume in the defect, assuming a crystallization pressure of 11.7 $k_BT d^{-3}$,\textsuperscript{48} is $\sim 1.9 k_BT$. Contrary to the atomic case, the energy of this configuration is smaller than for the stair-rod configuration, mainly attributable to the low stacking fault energy in colloidal crystals.

The dislocation energies for both atomic and colloidal crystals are displayed in Figure 5 as a function of crystal size. A sedimentary colloidal crystal is usually smaller than 250 particle diameters, but it can be seen here that the crossing faults configuration is more stable than the stair-rod configuration over the whole range of crystal sizes. For atomic crystals it is exactly the opposite.

This shows that the crossing faults defect is possibly unique to colloidal crystals, although they may exist in atomic crystals as metastable structures resulting from reactions between two stair-rod dislocations. This has to be taken into account if defects are to be grown into more complex colloidal structures, as the energy balance may shift from one dislocation type to another, depending on the interparticle interactions. In addition, more complex crystal structures can harbor additional types of defects that may come into play.
Contrary to the flat templates, the templates containing a height step produced the same stacking faults in each experiment. Stacking faults reproducibly grew into the same direction and crossed each other at the same height above the template. On most templates, some slanted faults still nucleated at other positions as a result of the presence of vacancies or due to a lattice mismatch, but on templates with a lattice constant of 1.06d, the resulting structures were almost defect-free. The resulting structures hold promise for the selective incorporation of defects in otherwise defect-free colloidal photonic crystals. By infiltrating the fcc structure with a high refractive index material and etching out the colloids, crystals with a full photonic band gap can be obtained. The intergrowth channels in the crossing fault structure can then function as propagation channels for light. As mentioned in the introduction, one of the drawbacks of inverted fcc photonic crystals is their sensitivity to other types of disorder, that readily close their band gap. A solution for this problem in self-assembled colloidal systems is the use of templates that have been predicted to stabilize the Laves phases in binary mixtures of colloids. The different components of these binary crystal structures are separately arranged on a diamond and a pyrochlore lattice, each of which possesses a larger and more robust band gap than the inverted fcc structure. Although the diamond and pyrochlore structures are more complex than the fcc structure, they also show a large degree of similarity. This includes their susceptibility to stacking disorder and formation of dislocations. As the growth of such structures has been predicted to occur only if induced by templates, these same templates can be modified to produce defects at desired positions, analogous to the templates used here.

Another promising direction where templates may be employed to incorporate faults is the use of patchy particles. Patchy particles constitute one of the most promising directions for creating self-assembled structures with, for example, the diamond structure. Through preferred oriented attachment, patchy particles are able to generate non-close-packed structures that have more favorable optical properties than the close-packed structures that can be formed by purely repulsive colloids. Again, templates may be employed to guide the particles into the desired structure.

**SUMMARY AND CONCLUSIONS**

Results on the selective incorporation of slanted intrinsic stacking faults in sedimentary colloidal crystals are presented. Crystal were grown on flat hexagonal and square templates containing 2D projections of slanted faults, as well as on square templates with height steps mimicking ideal stacking fault configurations. On all of these templates, stacking faults were grown at the desired positions, albeit with varying degrees of success. On the hexagonal templates, faults were formed in approximately 50% of the crystals.

Square {100} templates were produced to improve the nucleation of faults at the desired position, as unwanted stacking disorder parallel to the substrate is absent in such structures. These templates, including platforms of different height to guide the growth direction of the faults, were produced using ion beam lithography. These mimicked the ideal structure of intrinsic stacking faults and reproducibly produced fcc crystals of good crystallinity with stacking faults with the right position and direction. Intergrowth of two such stacking faults resulted in small channels through the crystal at well-defined positions.

The results presented in this study hold promise for fundamental studies of crystal defects as well as the generation of functional photonic crystals.

The crossing faults defect discussed are but one example of various defects that occur in colloidal crystals. Many of these share characteristics with atomic crystals, while others, like the crossing faults defect, may be completely new.

With respect to photonic crystals, the fcc structure might be useful, as it can have a full photonic band gap if the crystal is inverted, but the results obtained here can also be viewed as a model for more complex structures. Among these are the sodium chloride structure, the binary Laves phases, and structures built from patchy particles. All of these structures share their susceptibility to stacking disorder with the fcc structure and can therefore be modified using a similar approach with proper template engineering.

To fully explore the potential of the structures presented here, efforts to characterize the optical properties of such structures have to be made. The presence of a hollow channel may provide propagation channels through a photonic crystal, but the stacking faults bordering the defect may also cause losses. Therefore, both calculations as well as experiments have to be performed in future work.

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**Author Contributions**

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**Notes**

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