

## MANIPULATING COLLOIDAL CRYSTALLIZATION FOR PHOTONIC APPLICATIONS: FROM SELF-ORGANIZATION TO DO-IT-YOURSELF ORGANIZATION

ALFONS VAN BLAADEREN,<sup>1,2</sup> KRASSIMIR P. VELIKOV,<sup>1</sup> JACOB P. HOOGENBOOM,<sup>1,2</sup> DIRK L. J. VOSSEN,<sup>1,2</sup> ANAND YETHIRAJ,<sup>1,2</sup> ROEL DULLENS,<sup>1</sup> TEUN VAN DILLEN,<sup>2</sup> ALBERT POLMAN<sup>2</sup>

<sup>1</sup>*Condensed Matter Dept., Debye Inst., Utrecht University, P. O. Box 80000, 3508 TA Utrecht, The Netherlands*

<sup>2</sup>*FOM Inst. for Atomic and Molecular Physics, P.O. Box 41883, 1009 DB Amsterdam, The Netherlands*  
*A.vanBlaaderen@phys.uu.nl*

### INTRODUCTION

Photonic crystals are regular three-dimensional (3D) structures with which the propagation and spontaneous emission of photons can be manipulated in new ways if the feature sizes are roughly half the wavelength and the coupling with the electromagnetic radiation is sufficiently strong. 'Early' speculation on these new possibilities can be found in the Refs.<sup>1-4</sup> A more recent overview can be found in Ref.<sup>5</sup> and, of course, the other chapters in this book. A useful analogy to guide thinking about the properties and the applications of photonic crystals is the propagation of electrons in a semiconductor in comparison to the propagation of photons scattered by a regular 3D dielectric material. An example is the possibility of opening up a region of energy, a photonic band gap, for which the propagation of photons is forbidden, in analogy to the electronic band gap present in semiconductors. However, there are also important differences; for instance, the scattering of photons cannot be described well by scalar wave equations because the polarization of light cannot be neglected. Most theoretical and experimental work for visible light applications have until now focused on pure dielectric structures, interestingly, recent calculations have shown that metallo-dielectric structures should also be considered as having very interesting photonic properties in the visible, including, if one neglects absorption, a complete band gap.<sup>6-8</sup> And even with absorption taken into account, it seems that for relatively thin photonic crystals most of the interesting optical properties remain.<sup>8</sup>

Because the feature sizes of photonic crystals need to be about half the wavelength of the electromagnetic radiation of interest, the actual realization of such structures for near-infrared and visible light is quite a challenge. In this paper we want to give an overview of

the methods we are currently investigating to achieve well-defined 3D structures with submicron feature sizes by the manipulation of the self-organization of colloidal particles. We will focus here primarily on colloidal crystals for which the inter-particle spacing is close to the particle's size, so the structures can be dried. This will allow for a large dielectric contrast and also for the possibility to use the colloidal crystals as templates to make so-called 'inverse' structures. This last process, recently reviewed in Ref.<sup>9</sup>, is not part of the present paper, but it requires the same high quality crystals needed for photonic crystals made directly from (metallo-)dielectric spheres. It is the present understanding that only inverse structures of the colloidal crystal lattices can be easily made (like face centered cubic, FCC) will have a complete band gap. However, the density-of-states can also be modulated quite strongly in photonic crystals of high-index-core-shell systems. Moreover, binary structures or other complex structures like 3D quasicrystals have hardly been investigated and by removing one of the sphere sizes, by heating or dissolving them, relatively low filling fractions can be obtained. In the case of metallo-dielectric spheres the situation is reversed and the 'reverse' structures do not have a complete band gap, while many crystalline symmetries of spherical particles in liquids have a complete band gap.<sup>6-8</sup>

Before going into specific examples of the manipulation of colloidal crystallization, we will first explain what we mean by the two terms: *colloidal* and *self-organization*. An important aspect in the definition of what should be called a colloid or colloidal particle is the fact that these particles, which can consist of macromolecules or other subunits, undergo so-called Brownian motion. This erratic motion is the direct result of the not completely averaged-out collisional effects of solvent molecules constantly hitting the particle. Brownian motion ensures that a concentrated colloidal dispersion in which many particles interact with each other can find a thermodynamically well-defined equilibrium state. If certain criteria are met, such as the concentration of particles and a high monodispersity (narrow width in the size distribution), these systems will spontaneously form regular 3D structures or colloidal crystals completely analogous to molecular crystals.<sup>10,11</sup> This kind of (mostly first-order) phase transition can be described by statistical mechanics and we will use the possibility of such calculations as our definition of 'pure' self-organization (SO). A self-organizing system thus organizes itself in a state of lowest free energy. Therefore, shaking a box with ball bearings, even though the balls under the right frequency and amplitude might arrange themselves on a lattice, is not considered self-organization.<sup>12</sup> On the other end of the extreme, one has 'do-it-yourself-organization' (DYO) where control over the kind of structures that can be made is highest, but where no minimizing principle guides the organization of matter. Most methods used in making integrated circuits, like lithography, are DYO and in most cases 3D structures need to be built up in a layer-by-layer fashion. Although DYO methods offer great control, they are generally slow, costly, and not easy to extend to many unit cells in three dimensions because errors tend to accumulate. On the other hand, pure SO leads relatively easily to larger 3D structures, but control over, e.g., crystal symmetry and orientation is harder to achieve.

After a brief experimental section, we first will describe the kind of colloidal model particles we are using, with reference to the literature on how these can be made and characterized. Subsequently, we will give typical examples of how colloidal crystallization can be manipulated. Manipulation is possible by playing with the boundary conditions, like crystallization against a corrugated wall or between two confining walls, by using strong electric fields both at low frequencies and optical frequencies, by a flow field and, even further away from equilibrium, by controlled drying. Finally, we will show how high-energy heavy ion-irradiation can be used to deform inorganic photonic crystals in a controlled way.

## EXPERIMENTAL

As this paper is intended to give an 'educational' oversight of the projects being pursued to manipulate colloidal crystallization, the experimental section is relatively short and intended to give an idea on how the experiments were performed. For details we will refer as much as possible to literature.

The seeded growth of fluorescent silica *core-shell* colloids and the particle characterization by many different techniques (e.g., scanning and transmission electron microscopy SEM, TEM and light scattering) is described in Refs.<sup>13-15</sup> Very monodisperse silica seed particles can be made by performing silica growth in a microemulsion.<sup>16</sup> Recently, the fluorescent core colloidal model system properties have been extended by the development of a polymethylmethacrylate (PMMA) shell layer that can both be density and index matched.<sup>17</sup> Other core-shell systems with nanocrystalline and metal cores are briefly described in Refs.<sup>15,18</sup> and references cited in that paper.

The fluorescently dyed PMMA templates used in the *colloidal epitaxy* studies were made by electron beam lithography.<sup>19</sup> We also used particle templates made by optical tweezers (see below).

The effects of *electric fields of low frequencies* were also studied using confocal microscopy on matched fluorescent core-shell colloids. The colloids were imaged through transparent tinindiumoxide electrodes, more experimental details are given in Ref.<sup>20</sup> The effects of a *flow field* on the structures generated in these electro-rheological fluids were studied similarly as described by Amos et al.<sup>21</sup>

Multiple time-shared *optical tweezers* were constructed as described by Visscher<sup>22</sup> using opto acoustic modulators to manipulate a 1064 nm cw laser beam. The set-up constructed by us can be combined with confocal microscopy (Leica TCS). The positively charged cover glasses were made as described in Ref.<sup>23</sup> using a silane coupling agent (3-aminopropyltriethoxysilane).

*Controlled drying* experiments were performed as given in Ref.<sup>24</sup> using silica spheres dispersed in ethanol.

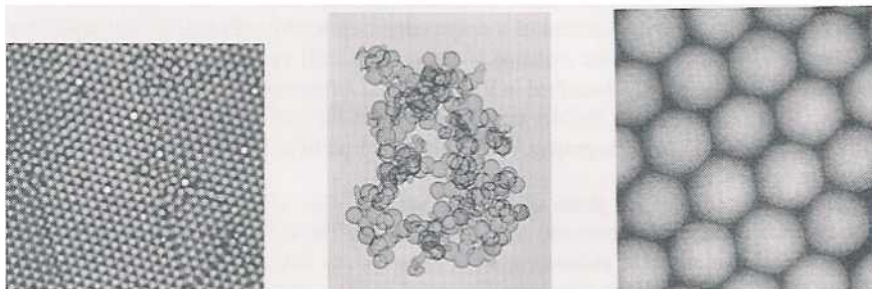
*Deformation by ion* ( $\text{Xe}^{4+}$ , 4 MeV) *irradiation* with fluences about  $10^{14}$  ions/cm<sup>2</sup> is described in Ref.<sup>25</sup>

## RESULTS AND DISCUSSION

### Core Shell Colloids

The colloidal particles used all have a core-shell geometry, with cores of metal (silver, gold), a nano-crystal (e.g., ZnS or CdS), or a high index dielectric material (e.g., ZnS). The shells used are made of silica or polymethylmethacrylate (PMMA) and both can be covalently labeled with organic dyes. The advantage of using a core-shell approach is the increase in flexibility in tuning both the optical properties and the interaction potential between the colloidal particles. For instance, in the case of a high index core and a lower index shell, like ZnS covered with silica, the high index filling fraction can be optimized even when the spheres are touching and at the same time the strong Van der Waals forces that would be present between pure ZnS particles can be reduced significantly.<sup>10</sup> Further, the core-shell approach allows a quite natural way of random doping of the photonic crystals. An example is shown in Fig. 1 where a fluorescence scanning confocal microscopy picture is shown of a solid solution of 10% larger fluoresceine labeled silica spheres on the lattice positions of a crystal of rhodamine labeled spheres (diameter 950

nm). Although this particular example is not so interesting for photonic applications, it does illustrate a general procedure in which photonic crystals can be 'doped' in a random way by using core-shell systems. For instance, in the case of the synthesis of 'air-sphere' or 'inverted' photonic crystals where a colloidal crystal is used as template and the particles are removed after deposition of other material by oxidation and heat or by dissolving them, high dielectric material can be positioned on lattice positions (which would normally be air) by using high-index core-shell particles. Also, in the reverse situation where one would like to dope a photonic crystal of (metallo)dielectric spheres with a 'hole' (low dielectric material), one could, for instance, use a latex sphere as dopant and later burn it away, or one could make use of hollow particles as shown in Fig. 2.<sup>15,18</sup>



*Figure 1.* Confocal micrograph of a solid solution of fluoresceine labeled particles (white) on a crystalline lattice of rhodamine labeled spheres (bar 2  $\mu\text{m}$ )

*Figure 2.* TEM picture of hollow silica spheres (radius 60 nm) created after dissolution of the ZnS cores.

*Figure 3.* TEM picture of silica spheres made by seeded growth where the initial seeds were grown in a microemulsion. Radius: 35 nm, relative width of the size distribution: 2 %.

### Manipulating Colloidal Crystallization: Colloidal Epitaxy

The ability to manipulate the boundaries of the container in which crystallization takes place is a powerful way to steer the crystallization process. The reason for the increased possibilities compared to the atomic world is directly related to the size of colloids. Because colloids are so much larger than atoms, truly 'atomically' smooth walls can be made easily. If the container walls are only several particle diameters away, then this distance determines the crystal structure that will optimally fit. At high volume fractions of particles the most important contribution to the free energy is the packing efficiency. Not only can the orientation of the crystals be induced, but also new structures, like buckling phases, have been found.<sup>26</sup>

Furthermore, making corrugations on container walls that are of the size of the colloidal building blocks is also possible. We made use of such structured walls to manipulate colloidal crystallization in ways which are very similar to epitaxial crystal growth. By having the spheres slowly fall down through sedimentation on the template and by heterogeneous nucleation at the wall, large crystals could be made. We have grown large, pure face centered cubic (FCC) crystals from particles that interacted with an almost hard-sphere potential both on non-close-packed (100) and (110) crystal faces. These crystals could be grown mm's thick (several thousand layers).<sup>19</sup>

Here we show the first results obtained by growing hard-sphere like colloidal crystals onto a template with the (110) crystal face of a hexagonally-close-packed (HCP) crystal (Fig. 4). The HCP colloidal crystal structure is meta-stable compared to FCC crystals for particles with a hard-sphere potential and becomes even more unfavorable in free energy

for softer potentials. The free-energy difference between an FCC and HCP stacking for hard-sphere-like potentials is quite small though (on the order of  $\sim 10^{-4} kT/\text{particle}$ ).<sup>27</sup> However, as far as we know, a pure HCP crystal has not yet been observed. These results not only open up the use of HCP colloidal crystals for photonic applications, but will also allow a systematic study of the effects of stacking errors. Hard-sphere crystals have the tendency not to crystallize in the thermodynamically most stable FCC form, but instead with a random stacking sequence of close packed layers (*ABC* stacking is FCC, while *ABA* is HCP). In the same way as this has been done with the HCP templating, it is also possible to grow any desired stacking sequence!

Electrostatic repulsion on flat walls can also be used to influence colloidal crystallization. Recently, 2D templates made with regions of opposite surface charge were shown to direct 2D colloidal crystal formation.<sup>28</sup> Also non-close-packed structures could be formed additionally using capillary forces in a similar way as described in the section on controlled drying.

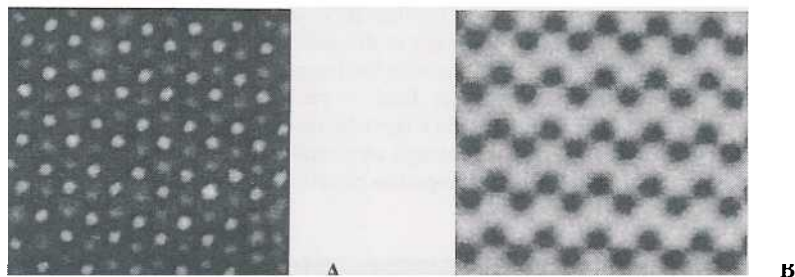


Figure 4. Confocal micrographs of the first colloidal HCP crystal. a) (Dyed) PMMA template with holes in the symmetry of the (110) HCP plane. b) 8 th (and vaguely 7th) layer of the HCP crystal above the template. Sphere diameter  $1.4 \mu\text{m}$  fluorescent core diameter  $385 \text{ nm}$ .

### Manipulating Colloidal Crystallization: Electric Fields, Low Frequencies

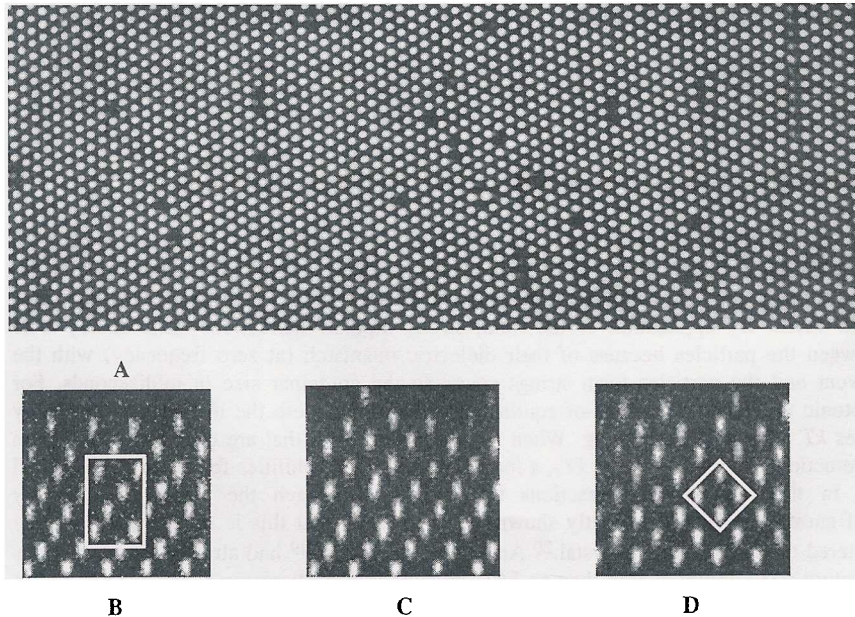
Colloidal particles dispersed in a solvent with low conductivity and subjected to a relatively high electric field ( $\sim 1 \text{ V}/\mu\text{m}$ ) are called electro-rheological fluids because the application of the field can turn the low viscosity dispersion, reversibly, into a solid with a yield stress. By application of the field, strong dipolar interactions (tens of  $kT$ ) arise between the particles because of their dielectric mismatch (at zero frequency) with the solvent and the particles form strings spanning the container size in milliseconds. For photonic applications, far out-of-equilibrium structures where the interactions are many times  $kT$  are not so interesting. When structures can form that are closer to equilibrium (interactions only a few times  $kT$ ), a lot of interesting possibilities for control are opened up. In this regime of interactions the system can reach the lowest free energy configuration. We have recently shown experimentally that this is (most likely) a body centered tetragonal (BCT) crystal.<sup>20</sup> An energy calculation<sup>29</sup> had already shown that this structure has a lower energy than an FCC crystal, and, furthermore, it has been found in computer simulations.<sup>30</sup> However, a full free energy calculation, including entropy, has not been done. In addition we found an interesting metastable sheet-like configuration that formed from the strings of particles and that slowly turned into the BCT crystals (see also the figures in the section on flow).<sup>20</sup>

In the same work we have also shown that if the initial charge stabilized dispersion is made concentrated enough that an FCC colloidal crystal is formed, it can be switched through a martensitic crystal transition from FCC into BCT. Moreover, without a field the

FCC crystal remains oriented with its (100) face parallel with the transparent electrode surface. For the photonic crystals made from metallo-dielectric spheres, this ability to switch between two different colloidal crystal structures is quite interesting (see the contribution of Moroz), even though a milliseconds switching speed is relatively slow.

Here we want to report on what happens when the electric field is not applied along the direction of gravity as described in Ref.<sup>20</sup>, but instead in the plane perpendicular to gravity. In this case the transparent electrodes were replaced by two metal wires with a thickness of 50  $\mu\text{m}$  a few mm apart. Now the electric field is in a plane perpendicular to gravity and the electric field can be used to ‘anneal’ the crystals that have already formed or can also influence crystallization when it takes place. In this geometry single crystals of several mm could be grown. Figure 5a shows a close packed plane of a single crystal imaged with a confocal microscope, where the electric field direction is in the imaging plane approximately from top to bottom. We chose to show a relatively defect rich plane, as in this case, the electric field direction becomes obvious from the alignment of these defects in the field.

In Figs. 5b-d the same electric field configuration with the electric field in the plane perpendicular with gravity was used. Except in this case a relatively thin colloidal crystal was imaged under different field strengths with the image plane parallel to gravity and the electric field perpendicular to the image field. It can be seen in Figs. 5b-d that the transition from FCC to BCT takes place in a layer-by-layer fashion. Clearly, the additional ability to tune the particle interactions through an electric field provides for extra degrees of freedom to switch or tailor photonic properties of colloidal crystals.



*Figure 5.* Confocal micrograph of: **a)** close-packed plane of a single BCT crystal created by application of an electric field ( $\sim 0.5 \text{ V}/\mu\text{m}$ ) directed from top to bottom and the direction of gravity perpendicular to the ( $x$ - $y$ ) imaging plane. **b-d)** micrographs ( $x$ - $z$  plane) taken at three different electric field strengths (field direction perpendicular to the imaging plane, gravity from top to bottom), showing the layer-by-layer transition from FCC to BCT crystal symmetry ( $0.08 \text{ V}/\mu\text{m}$ ,  $0.1 \text{ V}/\mu\text{m}$  and  $0.08 \text{ V}/\mu\text{m}$  resp.). Colloid diameter  $1 \mu\text{m}$ , fluorescent core nm  $400 \text{ nm}$ .



### Manipulating Colloidal Crystallization: Electric Fields, Optical Frequencies

If particles with a refractive index higher than the suspending liquid are placed in an inhomogeneous light field, they will experience forces pushing them toward the highest field strength. Simply focusing a laser beam of several mW with a high numerical aperture microscope objective is sufficient to trap colloidal particles (silica, latex) with sizes of several hundred nm to several  $\mu\text{m}$  in water. After the pioneering work of Ashkin<sup>31,32</sup> these optical tweezers or optical traps have become an important manipulation and force measuring tool in (micro) biology.<sup>22</sup> Recently, optical traps have also been used to measure interaction potentials between colloids and to create a 2D potential field to induce 2D colloidal crystallization.<sup>33,34</sup>

Here we show in Fig. 6a that a time shared optical trap created with opto acoustic modulators can easily place 50 particles on any desired 2D pattern. We plan to use this ability to induce and manipulate 3D crystallization with high index core-shell colloids that can be trapped in a sea of matched fluorescent core-shell colloids that can be imaged with confocal microscopy. Another example of the use of optical tweezers is shown in Fig. 6b where silica spheres have been attached one by one onto a substrate with opposite surface charge. We are extending this method of pure DYO to 3D structures and have already successfully grown 3D crystals by using the 2D structures as templates for colloidal epitaxy.

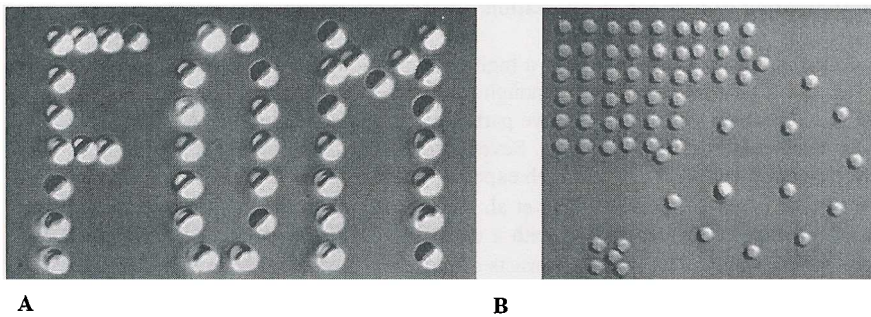


Figure 6. Video microscopy picture of: a) the letters FOM formed in water using  $1.4 \mu\text{m}$  diameter silica colloids and time-shared pairs of optical tweezers, distance from the cover glass  $\sim 5 \mu\text{m}$ , b) the same colloids that were placed one by one on a glass cover glass with opposite surface charge.

### Manipulating Colloidal Crystallization: Flow Fields

Although colloidal crystals have such small elastic moduli –one of the reasons for the term 'soft condensed matter'- that they are easily melted by a flow field, they can also be manipulated in less destructive ways by flow. As recent experiments on PMMA hard-sphere colloidal model particles have shown, mm size single (twinned) FCC colloidal crystals could be obtained relatively easily by applying a simple shear field.<sup>21</sup> As far as we know, shear has not yet been used to make crystals for photonic applications. We plan to investigate the effects of a simple shear between two parallel glass plates in real space using a confocal microscope. The shear cell we are designing will have the ability to move both the top and bottom plate, so that the plane of zero velocity, where imaging is easy, can be moved through the sample volume. Initial experiments without a controlled shear cell, but just moving two glass plates with a spacer between two fingers already shows the organizing effects of flow on the structures that form under the influence of an electric

field of low frequency (1 MHz). The metastable sheets that were described as precursors to the BCT crystals in Ref.<sup>20</sup> and above, are seen in Fig. 7a to be aligned by the flow. The regularity is probably due to the initial density of the colloids, however electric field induced interactions cannot be ruled out yet. After two hours the sheets started to turn into crystals but some of the initial shear induced orientation was still visible (Fig. 7b).

Not only will it be easy to combine shear alignment of colloidal crystallization with electric fields, there are also unexplored ways to use it in conjunction with templates and binary crystallization.

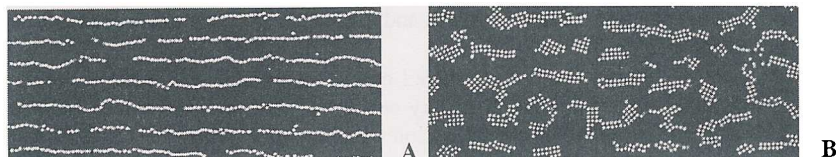


Figure 7. Confocal micrographs showing structures formed in an electric field ( $0.5 \text{ V}/\mu\text{m}$ ) after application of a simple shear one minute after application of the field. Both the shear and electric field were perpendicular to the imaging plane. a) sheets formed after several minutes. b) start of BCT crystal formation after two hours. Colloid diameter  $1 \mu\text{m}$ , fluorescent core  $\text{nm } 400$ .

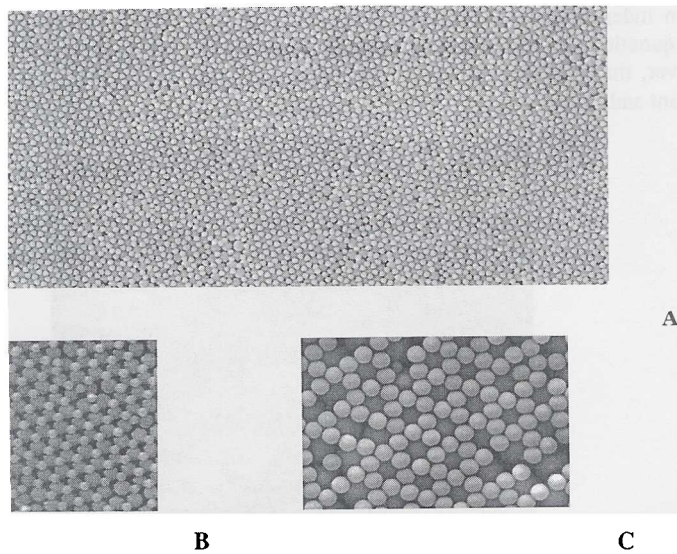
### Manipulating Colloidal Crystallization: Controlled Drying

If colloidal particles are present in a high concentration in a thin liquid layer wetting the surface of a substrate that is thin enough for particles to stick through, the line tension at the liquid particle interface can drive particles together and cause close packed structures to be formed after complete drying. Several groups have explored this way of covering a substrate with colloidal crystals both experimentally and theoretically. A recent review of the subject is given in Ref.<sup>35</sup> Jiang et al. recently demonstrated that cm wide areas could be covered by controlled drying with a constant number of colloidal crystal layers in a very simple way.<sup>24</sup> The method consists of putting a (glass) substrate vertically in a slow drying suspension of a certain volume fraction. If drying of the solvent is slow enough for it to be the limiting process, the number of layers is only a function of the volume fraction (and a constant related to the particle radius and solvent properties). Fifty layers have been deposited in one try and several depositions can be performed after each other. Unfortunately, this method does not work for particles so heavy that the settling rate is larger than the reclining meniscus. For silica this is a radius of about 200 nm. We did explore the method for particles with a significantly smaller particle polydispersity (see the section on the core-shell colloids) than explored in Ref.<sup>24</sup> and found mm size single crystals and cm size regions with constant number of spheres (results not shown here). Moreover, the templates used for the colloidal epitaxy procedure surprisingly are also able to manipulate this kind of colloidal crystal deposition (for some initial results see Ref.<sup>15</sup>).

Here, however, we want to focus on the possibilities this method has to produce structures that cannot be formed (easily) by using bulk crystallization. This is because this method is a lot closer to DY0 than it is to SO. Although it is likely that Brownian motion is still important to have the particles find a local 'best' packing arrangement, controlled drying is certainly not a reversible equilibrium method. However, the DY0 aspect opens up a lot of ways to tune the structures. One obvious possibility is to build up the photonic crystals in a layer-by-layer fashion where some of the particles in the layers (or some layers) have different properties than other particles (or layers). For instance, the method works also for the deposition of just one single layer and it is not difficult, if particles of exactly the same size are used, to build up a close packed crystal consisting of alternating layers of silica and latex spheres. In Fig. 8a it is shown that after depositing a layer of



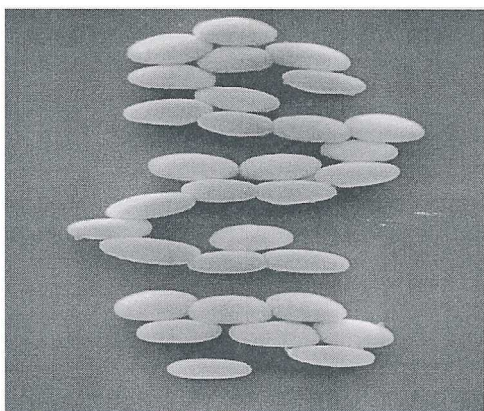
silica spheres with a radius of 202 nm, it is possible to deposit a layer of smaller spheres (size ratio 0.60) in the hexagonal pattern of holes left by the larger spheres. These are first results that have not yet been optimized, but they do demonstrate that an  $AB_2$  crystal that is also known to be formed in bulk colloidal crystallization<sup>36</sup> at this size ratio (0.60) can be built up in a layer by layer fashion. The third layer of larger spheres will be stacked *right on top of the first layer, etc.* What was not expected was that for a *slightly different* size ratio (0.49) structures like shown in Fig. 8b and Fig. 8c formed. If these structures, here only consisting of two layers are thought to repeat themselves in 3D this would lead to crystals of the form  $AB_1$  and  $AB_3$ , respectively. Both these crystals would not form in bulk binary crystallization. Although not expected, the formation of the  $AB_3$  packing arrangement for the size ratio 0.49 can be understood. Just for this size ratio the arrangement depicted in Fig. 8c leads to the smaller spheres just touching. The arrangement leading to  $AB$  crystals, Fig. 8b, is even more amazing. It is clear that it formed when the concentration of spheres was below the value that leads to the configuration depicted in Fig. 8a. However, it was unexpected that the small spheres would not occupy the hexagonal holes randomly but instead formed a regular pattern where the smaller spheres were never touching. The explanation for the forces organizing the small spheres has to be that the spheres minimize the surface tension of the drying film while going into the holes. Research is ongoing to determine the optimal growth conditions for the structures shown in the Fig. 8 and to see if they can indeed be extended in 3D. As these are only the first trials, it is likely that other surprises will show up at other size ratios and by a more systematic investigation using templates.



*Figure 8.* SEM pictures of: **a)** two layers of particles with size ratio 0.60 (larger sphere radius 202 nm) deposited by a controlled-drying process layer-by-layer. The two layers form the start of an  $AB_2$  crystal.  
**b-c)** two layers with size ratio 0.49 (larger sphere radius 202 nm). The start of an  $AB_1$  crystal (**b**) and of an  $AB_3$  crystal (**c**).

### Manipulating Colloidal Crystallization: Deformation by Ion Irradiation

Once final inorganic photonic structures using colloids have been made, be it direct by using colloids or 'inverse' structures by using crystals as templates, it would be convenient if there was a method for optical fine-tuning. For relatively thin ( $< 10$  micron) photonic crystals, high energy ion beams of heavy atoms provide for such a method. We recently discovered that such beams of heavy atoms can linearly deform particles perpendicular to the direction of the ion's path, if the energy of the beam is large enough to go through the inorganic colloidal particle and most of its energy is delivered through electronic stopping.<sup>25</sup> In this way, single inorganic amorphous or polycrystalline colloidal spheres can be turned into oblate ellipsoids (Fig. 9) or by multiple irradiations from different directions into more complex shapes.<sup>25</sup> When the particles are part of a colloidal crystal, however, the deformation process becomes more complicated because the stress build-up induced by the deformation is anisotropic. This results in a deformation of the particles that depends on the relative orientation of the ion beam with respect to the colloidal crystal orientation. In order to demonstrate the possibilities, we deformed ZnS-core (radius 84 nm) silica-shell (total radius 130 nm), particles in a thin colloidal crystal consisting of 5 layers (Fig. 10). These core-shell particles were optimized to have the widest stop gap.<sup>18,37</sup> Because the crystal is relatively thin, the stop gap is not very deep and it is superimposed on a background scattering caused by defects. The fringes are due to interference between the quite flat top and bottom crystalline planes. It is clear, however, that a significant shift of 41 nm occurred in the position of the stop gap. At this time we cannot predict this shift, because it is caused both by a deformation of the particle shape *and* a change in the crystal symmetry and lattice constants, both of which are not yet known independently. Work is in progress to simulate the deformation process so that more quantitative predictions can be made. From the first results presented here, it is clear, however, that high energy ion irradiation does allow for fine tuning of both the lattice constant and/or the symmetry of inorganic thin ( $< 10$   $\mu\text{m}$ ) colloidal crystals.



*Figure 9.* SEM picture of core-shell ZnS-silica (core 333 nm, total radius 350 nm) particles deformed into an oblate ellipsoidal shape by ion irradiation. Ion beam in plane (top-bottom) with respect to the image plane.

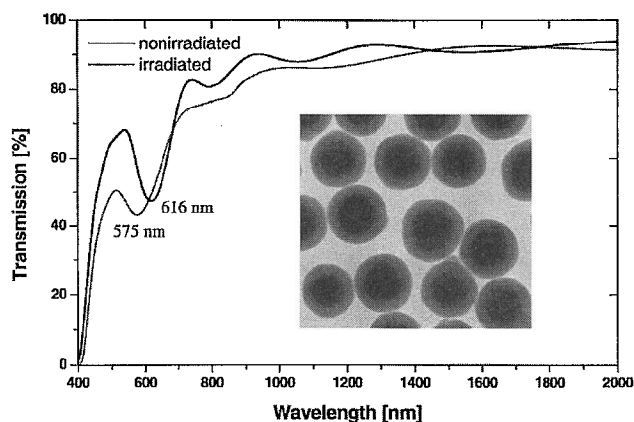


Figure 10. Transmission spectra taken of ZnS-silica core-shell colloidal crystal deformed by ion irradiation (Inset ZnS core radius 84 nm total radius 130 nm; before irradiation). The crystals were 5 layers thick and formed by controlled drying. The shift in the transmission minimum is 41 nm.

## CONCLUSIONS

Shortly after the discovery of the first transistor there were researchers who wanted to stop research on the subject of semiconductors as everybody in the field was getting different results. Photonic crystal research has only just made its first 'semi conductor' for light, a structure with a (possible) complete band gap in the near infrared using silica colloidal crystals as templates.<sup>38</sup> It seems certainly a daunting, if not impossible, task to meet the purity and low defect levels that were required in the semi conductor industry to achieve reproducible results. For instance, this would mean the growth of a colloidal crystal the size of a km with only one dislocation in it! It is quite clear though, that such extreme levels of control will not be necessary to achieve interesting photonic applications. Certainly, an optical transistor, which would likely require very regular crystals on the one hand and great control over defects and doping on the other, is still some time away. However, we hope to have shown in this contribution that although the ways to explore colloidal crystallization and colloidal crystals for manipulating photons have only just started, it is already clear that the potential for the level of control is high. The most promising methods to arrive at useful photonic structures are a mix of pure 'self-organization' and pure 'do-it-yourself' organization. Also, most of the methods of which examples are shown can be combined to achieve new effects and several interesting directions to manipulate the properties of colloidal photonic crystals have not even been explored yet, like, the use of the anisotropic refractive index of liquid crystals to switch the photonic properties. If, as we believe, the pace of progress keeps its present fast rate, the first applications for visible and near infrared light, including possibilities for new physics, will arrive soon.

## Acknowledgements

Ad Legendijk and Willem Vos (University of Amsterdam) are thanked for discussions. We are grateful to Anja K. van Langen-Suurling and Hans Romijn (DIMES, Delft) for

making the (master) templates for colloidal epitaxy. Marileen Dogterom, Cendrine Faivre and Astrid van der Horst (FOM Inst. AMOLF, Amsterdam) are thanked for setting up the optical tweezers. This work is part of the research program of the 'Stichting voor Fundamenteel onderzoek der Materie (FOM)', which is financially supported by the 'Nederlandse organization voor Wetenschappelijk Onderzoek (NWO)'.

## REFERENCES

1. V. P. Bykov, Spontaneous emission from a medium with a band spectrum, *Sov. J. Quantum Electron.* **4**, 861 (1975).
2. S. John, Strong localization of photons in certain disordered dielectric superlattices, *Phys. Rev. Lett.* **58**, 2486 (1987).
3. E. Yablonovitch, Inhibited spontaneous emission in solid-state physics and electronics, *Phys. Rev. Lett.* **58**, 2059 (1987).
4. J. D. Joannopoulos, R. D. Meade, and J. N. Winn. *Photonic Crystals* ed., Princeton Univ. Press, Princeton, (1995).
5. T.F. Krauss and R.M. Delarue, Photonic Crystals in the Optical Regime - Past, Present and Future, *Progress in Quantum Electronics* **23**, 51 (1999).
6. A. Moroz, Three-dimensional complete photonic-band-gap structures in the visible, *Phys. Rev. Lett.* **83**, 5274 (1999).
7. A. Moroz, Photonic crystals of coated metallic spheres, *Europhys. Lett.* **50**, 466 (2000).
8. W. Y. Zhang, X. Y. Lei, Z. L. Wang *et al.*, Robust photonic band gap from tunable scatterers, *Phys. Rev. Lett.* **84**, 2853 (2000).
9. O. D. Velev and E. W. Kaler, Structured porous materials via colloidal crystal templating: From inorganic oxides to metals, *Adv. Mater.* **12**, 531 (2000).
10. W.B. Russel, D.A. Saville, and W.R. Schowalter. *Colloidal Dispersions* ed., Cambridge University Press, Cambridge, (1995).
11. T. Palberg, Colloidal crystallization dynamics, *Curr. Opin. Colloid Interface Sci.* **2**, 607 (1997).
12. O. Poulliquen, M. Nicolas, and P. D. Weidman, Crystallization of non-Brownian spheres under horizontal shaking, *Phys. Rev. Lett.* **79**, 3640 (1997).
13. A. van Blaaderen and A. Vrij, Synthesis and Characterization of Colloidal Dispersions of Fluorescent, Monodisperse Silica Spheres, *Langmuir* **8**, 2921 (1992).
14. N. A. M. Verhaegh and A. van Blaaderen, Dispersions of Rhodamine-Labeled Silica Spheres - Synthesis, Characterization, and Fluorescence Confocal Scanning Laser Microscopy, *Langmuir* **10**, 1427 (1994).
15. A. van Blaaderen, From the dc Broglie to visible wavelengths: Manipulating electrons and photons with colloids, *MRS Bull.* **23**, 39 (1998).
16. F. J. Arriagada and K. Osseasare, Synthesis of Nanometer-Sized Silica By Controlled Hydrolysis in Reverse Micellar Systems, in: *Colloid Chemistry of Silica*, Amer. Chemical Soc., Washington, Vol. 234, (1994).
17. W. K. Kegel and A. van Blaaderen, Direct observation of dynamical heterogeneities in colloidal hard-sphere suspensions, *Science* **287**, 290 (2000).
18. K.P. Velikov and A. van Blaaderen, ZnS-core silica-shell colloids for photonic applications, *Submitted* (2000).
19. A. van Blaaderen, R. Ruel, and P. Wiltzius, Template-directed colloidal crystallization *Nature* **385**, 321 (1997).
20. U. Dassanayake, S. Fraden, and A. van Blaaderen, Structure of electrorheological fluids, *J. Chem. Phys.* **112**, 3851 (2000).

21. R. M. Amos, J. G. Rarity, P. R. Tapster *et al.*, Fabrication of large-area face-centered-cubic hard-sphere colloidal crystals by shear alignment, *Phys. Rev. E* **61**, 2929 (2000).
22. K. Visscher and S. M. Block, Versatile Optical Traps with Feedback Control, in: *Methods in Enzymology*, R B Vallee, ed Academic Press, San Diego, Vol. 298, (1997).
23. D. L. J. Vossen, T. van Dillen, M. J. A. de Dood, T. Zijlstra, E. van der Drift, A. Polman, A. van Blaaderen, Novel method for solution growth of thin silica films from tetraethoxysilane, *Adv. Materials* **12**, 1434 (2000).
24. P. Jiang, J. F. Bertone, K. S. Hwang *et al.*, Single-crystal colloidal multilayers of controlled thickness, *Chem. Mat.* **11**, 2132 (1999).
25. E. Snoeks, A. van Blaaderen, T. van Dillen *et al.*, Colloidal ellipsoids with continuously variable shape, *Adv. Materials*, **12**, 1511 (2000).
26. S. Nesper, C. Bechinger, P. Leiderer *et al.*, Finite-size effects on the closest packing of hard spheres, *Phys. Rev. Lett.* **79**, 2348 (1997).
27. S. Pronk and D. Frenkel, Can stacking faults in hard-sphere crystals anneal out spontaneously?, *J. Chem. Phys.* **110**, 4589 (1999).
28. J. Aizenberg, P. V. Braun, and P. Wiltzius, Patterned colloidal deposition controlled by electrostatic and capillary forces, *Phys. Rev. Lett.* **84**, 2997 (2000).
29. R. Tao and J. M. Sun, 3-Dimensional Structure of Induced Electrorheological Solid, *Phys. Rev. Lett.* **67**, 398 (1991).
30. R. Tao and Q. Jiang, Simulation of Structure Formation in an Electrorheological Fluid, *Phys. Rev. Lett.* **73**, 205 (1994).
31. A. Ashkin, Acceleration and trapping of particles by radiation pressure, *Phys. Rev. Lett.* **24**, 156 (1970).
32. A Ashkin and J M Dziedzic, Optical levitation by radiation pressure, *Phys. Rev. Lett.* **19**, 283 (1971).
33. D G Grier, Optical tweezers in colloid and interface science, *Curr. Opin. Colloid Interface Sci.* **2**, 264 (1997).
34. E. R. Dufresne and D. G. Grier, Optical tweezer arrays and optical substrates created with diffractive optics, *Rev. Scient. Instr.* **69**, 1974 (1998).
35. F. Burmeister, W. Badowsky, T. Braun *et al.*, Colloid monolayer lithography-A flexible approach for nanostructuring of surfaces, *Appl. Surf. Sci.* **145**, 461 (1999).
36. P. Bartlett, R. H. Ottewill, and P. N. Pusey, Freezing of Binary-Mixtures of Colloidal Hard-Spheres *J. Chem. Phys.* **93**, 1299 (1990).
37. A. Moroz and C. Sommers, Photonic band gaps of three-dimensional face-centred cubic lattices, *J. Phys.-Condes. Matter* **11**, 997 (1999).
38. A. Blanco, E. Chomski, S. Grachtchak *et al.*, Large-scale synthesis of a silicon photonic crystal with a complete three-dimensional bandgap near 1.5 micrometres *Nature* **405**, 437 (2000).