Ordered Dewetting and Self-Organization of Microdroplets on Surfaces

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(Received July 8, 2004)

The formation of ordered dewetted patterns of organic materials on substrates is described. The driving force for dewetting is the interfacial tension between substrate and organic solution. The observed regular order of the formed microdroplets, or “microdomes” can be explained by so-called dissipative structures, a concept developed by Ilya Prigogine. The apparent violation of the second law of thermodynamics (which should prohibit formation of ordered structures from isotropic solution) can be explained by the overall increase of the entropy by the evaporating solvent. The role of the substrate in the formation of ordered dewetted microstructures will be discussed briefly. In the second part of this paper examples for the application of dewetted microstructures in the field of photonics will be given. Special emphasis will be made not only for polymeric but also for low molar mass compounds.

1. Introduction

1.1 Dewetting

Dewetting is one of the processes that can occur at a solid-liquid or liquid-liquid interface. Generally, dewetting describes the rupture of a thin liquid film on the substrate (either a liquid itself, or a solid) and the formation of droplets. The opposite process—spreading of a liquid on a substrate—is called wetting. The factor determining the wetting and dewetting is the so-called spreading coefficient $S$

$$S = \delta_s - \delta_f - \delta_{SF}$$  \hspace{1cm}(1)$$

where $\delta_s$ and $\delta_f$ are the surface free energies of the substrate and film, respectively, and $\delta_{SF}$ is the interfacial energy between film and substrate.\(^1\) When $S > 0$, the surface is considered wettable, and if $S < 0$, dewetting occurs.

Wetting and dewetting are important processes for many applications, including adhesion, lubrication, painting, printing, and protective coating. For most applications, dewetting is an unwanted process, because it destroys the applied thin film.

In most dewetting studies a thin polymer film is spun onto a substrate. Even in the case of $S < 0$ the film does not dewet immediately if it is in a metastable state, e. g., if the temperature is below the glass transition temperature of the polymer. Annealing such a metastable film above its glass transition temperature increases the mobility of the polymer chains and dewetting takes place.

When starting from a continuous film, an irregular pattern of droplets is formed. The droplet size and droplet spacing may vary over several orders of magnitude, since the dewetting starts from randomly formed holes in the film.\(^3\)–\(^5\) There is no spatial correlation between the dry patches that develop. These dry patches grow and the material is accumulated in the rim surrounding the growing hole. In the case where the initially homogeneous film is thin (in the range of 100 nm), a polygon network of connected strings of material is formed,\(^9\) like a Voronoi pattern of polygons.\(^10\) These strings then can break up into droplets, a process which is known as the Rayleigh-Taylor instability.\(^11\) At other film thicknesses, other complicated patterns of droplets on the substrate can be observed,\(^12\) which stem from a fingering instability of the growing rim around the dry patch.

1.2 Dewetting on patterned surfaces

For many applications in fields ranging from biology to photonics and electronics, surface patterning is essential. The production of high-performance devices with micrometer features is usually based on li-
thography techniques, where a designed and pre-
formed pattern is transferred onto a substrate, either
by photolithography, contact printing,13) or ink-jet
printing, just to mention the most common tech-
niques. The problem with these approaches is the size
limitation (in case of ink-jet printing the smallest
structures are in the range of several ten µm), and the
material restrictions (for photolithography com-
ounds have to be susceptible to actinic light). Thus
one approach to overcome these difficulties is the
dewetting of a thin film on a prepatterned surface.
Since the wetting parameter S depends on the interfa-
cial energies it is possible to have selective wetting
and dewetting on patterned surfaces where each of
the two different surface areas have different surface
energy.14–16) Typically, a hydrophilic/hydrophobic pattern is
prepared on a flat substrate by photolithogra-
phy or micro-contact printing. The wetting/dewet-
ting material (usually a polymer) is applied by spin
coating, dip coating, or ink-jet printing. The selective
dewetting takes place either during the application of
the material while still in the liquid state, or later in
an annealing step, where the polymer is heated above
glass transition temperature. A related technology
uses the confinement in small channels to produce a
selective dewetting pattern on non-prestructured sub-
strates. Here, a thin spin coated polymer film is al-
lowed to dewet while in contact with a microcontact
printing mold.17)

1.3 Dewetting on nonstructured substrates by
self-organization

The last example in the previous paragraph does
not involve patterning of the substrate. Still, because
it needs a micro-contact printing mold, I still consider
this as an example of reproducing a lithographically
designed pattern by dewetting.

In the next paragraphs I want to introduce ordered
patterns produced by dewetting, but without the help
of any predesigned and fabricated molds or masks.

This method relies on the self-organization of
molecules. Organic molecules are known to assemble
into larger aggregates, like micelles, monolayers, bi-
layer membranes, etc. This self-assembly is induced
by intermolecular interactions, like van der Waals
forces, the hydrophobic effect, electrostatic interac-
tion or hydrogen bonding. Thus structure formation
is driven by the chemical potential and is a process
towards thermodynamic equilibrium.

Self-organization, on the other hand, is the forma-
tion of molecular aggregates far away from thermo-
dynamic equilibrium. It may involve the same inter-
molecular interactions as for self-assembly, but in or-
der to sustain its structure, a self-organized system
needs the flow of energy and continuous entropy pro-
duction.

In the above examples of dewetting on non-
structures substrates, the ruptured thin polymer film
is non-volatile. Mass transport only takes place
within the plane of the film. Hence there is little pos-
sibility of entropy increase, since all material is con-
0

limited in a thin film, or in droplets on the substrate.18)

1.4 Convection and fingering instabilities

The situation is different when a solution is cast
onto a substrate. Such a ternary system (substrate,
solvent and solute) gives rise to interesting phenom-
ena. When a volatile solvent is cast, immediate
evaporation of the solvent occurs. Thus the surface of
the solution cools down, due to the heat of evapora-
tion, and convection cells may appear19) due to the
density-difference-driven downwelling of the cooler
parts of the solution. This is the so-called Rayleigh-
Bénard convection.20) In addition, concentration fluc-
tuations of the solute influence the local surface ten-
sion, which also leads to convection, which was first
correctly described by Marangoni in 1865. He reex-
amined the results of Thompson, the first to describe
convective motion in aqueous ethanol solutions.21)
Both, temperature and concentration gradient driven
convection can occur at the same time, and complex
patterns can evolve, with hexagonal convection cells
in the center of an evaporation solution droplet and
horizontal convection rolls at the edges. The com-
bined effects of temperature and concentration gra-
dients are most pronounced at the edge of the evaporat-
ing solution, at the three-phase-line (the contact line
between substrate, solution and air). A fingering in-
stability can develop at this edge, similar to the “tears
of wine” at the edge of water/ethanol solutions.22)
The size distribution of these fingers can be astonish-
ingly narrow along the three-phase-line. In 2001 Ho-
soi and Bush published a detailed summary of the
history of the research into convection and proposed
a mathematical model for the development of con-
vection cells and tears or wine.23) They also describe
the migration and merging of fingers along the three-
phase-line. The movement of smaller fingers towards
larger ones and subsequent merging of neighboring
fingers was described experimentally in 1999. It was
found that, after an induction period, an array of
similar sized and spaced fingers can be formed (see
also Fig. 1 and explanation below).22, 24) Even though
the fingers are in a highly non-equilibrium state (with
Examples of micronsized polymer "domes"

1.5 Droplet formation

Most of the research on convection and fingering instabilities was done on solutions that have a very large, or "infinite" reservoir. That means that the three-phase-line is more or less stationary. The whole situation changes when instead of a large volume of solution, a small droplet of solution is used. The evaporation of the solute then leads to a decrease in volume, and the diameter of the droplet decreases. Thus there is a movement of the three-phase-line perpendicular to its extension. This recession can be non-continuous, that is the speed of the receding is oscillatory in a stick-slip-like motion, and the polymer is deposited in stripes parallel to the three-phase-line.\(^\text{19}\) The other possibility is a smooth recession. Since the fingers contain a high polymer concentration, they are more viscous than the rest of the solution, and tend to recede slower over the substrate. Hence the fingers elongate, become instable, and break up into droplets, similar to the Rayleigh-Taylor instability of free liquid jets.\(^\text{25, 26}\) Often one can find that the fingering distance along the three-phase-line is similar to the distance of the droplets formed by the break-up of the finger. In this case, a regular 2-dimensional pattern of micronsized polymer droplets can be formed.

This pattern formation seems to violate the second law of thermodynamics, since a non-structured, homogeneous solution on a non-structured substrate leads to an ordered array of micrometer-sized polymer droplets. This is one example of an order-from-disorder phenomenon that was called "dissipative structure formation" by Prigogine and Nicolis.\(^\text{27}\) The driving force is the dissipation of energy and thus the increase of entropy surrounding the ordered structure. In the case of polymer solutions, the heat of evaporation of the solvent and the increase in entropy of the evaporated solvent molecules is the driving force. Thus, the overall system has indeed increased its entropy, even though a part of it—the polymer on the substrate—became ordered.

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2. Examples of micronsized polymer "domes"

Dewetting is a general physical phenomenon and depends only on the wettability of the substrate by the polymer. Thus many different polymers can form dewetted structures, such as polystyrene (Figs. 2 and 3), poly-ion-complexes (Fig. 1), DNA, conducting polymers, dendrimers, and others.

The main factors that determine the size of the domes are polymer concentration and the receding speed of the three-phase-line. The higher the concentration and the lower the speed, the larger the domes become. The velocity of the three-phase-line depends of course on the casting volume, diameter of the solution droplet and the evaporation speed of the solvent. Thus temperature and volatility of the solvent are crucial, too. Figure 4 shows a drawing of a casting apparatus used to prepare large areas (up to several cm\(^2\)) of dewetted polymer microdomes. A teflon spacer around a glass rod controls the width of an air gap between rod and substrate. The polymer solution is placed between the glass rod and the substrate and capillary force leads to the formation of a straight three-phase-line across the substrate. The glass rod is rolled over the substrate and thus controls the evaporation speed of the solution and the receding speed of the three-phase-line. If necessary, the substrate can be heated from below.

The domes prepared by this method can have a diameter between 200 nm and several micrometers. The size distributions of the domes depend on the formation of a regular fingering instability, which can be distorted by surface roughness. Thus smooth substrate, like mica and etched silicon wafers (roughness < 1 nm) give rise to samples with a very narrow dome-size distribution and inter-dome spacing. Rougher substrates, such as indium tin oxide (ITO)
Organic dyes in polymer matrices

or float glass (roughness approx. 10 nm) leads to a
pinning of the three-phase-line at surface inhomoge-
neities and samples with broader dome size distribu-
tions are obtained (Fig. 5).

The height of the dome depends on the diameter
and the contact angle of the polymer with the sub-
strate. It was confirmed by atomic force microscopy
and electron microscopy that the domes have the
shape of a spherical cap. For polystyrene the contact
angle is typically 5°, so that the height of the dome is
approximately 5% of its diameter. The volume of a
dome can be calculated as follows:

\[ V = \frac{1}{2}Ah + \frac{1}{6}\pi h^3 \]  (2)

V is the volume, A the surface area and h the
height of the polymer dome. A dome with a diameter
of one micrometer has a volume of less than 1 atto li-
ter and each dome contains only a small number of
molecules. In the following, I give several examples
where the aggregation state of organic molecules can
be controlled by using such microdomes.

3. Organic dyes in polymer matrices

3.1 Cyanine dyes and their J-aggregates

Cyanine dyes are one example for a class of or-
ganic compounds where the aggregation state of the
dye can be controlled by dewetting.

The so-called J-aggregates of cyanine dyes are
known since the 1930 s. Jelly\(^{32}\) and Scheibe\(^{33}\)
independently discovered that ionic dyes of the cyanine
type form aggregates in aqueous solution. They have
a characteristic very narrow and red-shifted elec-
tronic absorption peak, compared to the molecularly
dispersed state. The fluorescence quantum yield of J-
aggregates is very high, and thus J-aggregates show a

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![Fig. 2. Optical micrograph of an evaporating polystyrene solu-
tion.](image1)

![Fig. 3. Atomic force microscope image of a dewetted polysty-
rene sample on freshly cleaved muscovite mica. The height of the domes is approximately 15 nm.](image2)

![Fig. 4. Schematic drawing of the rollar apparatus used for dewetting of larger samples (up to 2 cm × 7 cm).](image3)
bright fluorescence with a short lifetime of the excited state. All these qualities, sharp absorption peak, short lifetime and efficient energy transfer, makes the J-aggregates ideal light sensitizers, e.g. in color photographic films. Hence there has been a strong and long-standing interest in the control of their photophysical properties. Both from quantum mechanical calculations as well as experimentally, it became clear that the excited state in an aggregate is not confined to a single molecule, but extends over several tens of molecules and thus the size of a J-aggregate determines the photophysical properties.

Besides in solution, J-aggregates also form on mica surfaces, in polymer matrix films, where fiber-like super-aggregates with a length of several 100 µm are formed. Even though the spectral properties can be determined, the fibrous structure does not allow the measurement of a single J-aggregate. By using dewetted polystyrene films with a micrometer-sized dome structure, it should be possible to produce J-aggregates with a more defined size, since the formation of the J-aggregates is limited to the volume of a single dome. Casting mixed dye polymer solutions onto substrates leads to dewetting and the formation of micron sized polymer domes with a dye content between 0.1 and 15 wt%.

Fluorescence microscopy proved that the cyanine is incorporated into the polymer domes, since the area in between the domes does not fluoresce. The domes have a small size distribution and are regularly spaced (Fig. 6).

It can be seen that each dome contains a countable number of J-aggregates, and thus their number and interactions can easily be controlled by the dye concentration and the dome size. Lower concentration and smaller domes, respectively, lead to a smaller number of aggregates per dome. Thus it became possible to produce single J-aggregates which are isolated from each other in a well-defined environment. This effect can only be seen in non-homogeneous, microstructured samples, like the dewetted domes.

The fluorescence spectra of single domes show a size effect in which larger domes show red-shifted fluorescence peaks. Thus this implies that larger domes contain J-aggregates with, on average, a larger number of cyanine molecules per J-aggregate. Thus
the physical confinement leads to a control of the fluorescent behavior.\textsuperscript{40)}

### 3.2 Crystalline dyes for non-linear optics

Non-linear effects, like second harmonic generation of light, require the non-centrosymmetric arrangement of dipolar compounds. One way to achieve this goal is the synthesis of organic dyes with a strong permanent dipole moment and a non-centrosymmetric crystal structure. But in addition to these requirements on the molecular level, also problems of film formation have to be solved. Compounds with a strong dipole moment have a strong crystallization tendency, and thus inferior film-forming properties. Co-casting a dye and a polymer solution leads to the dewetting and dome formation of the polymer, while the dye is incorporated in the polymer dome. Crystallization takes place after dome formation. Figure 7 shows an optical micrograph of a dome with incorporated dye nanocrystals. A dendritic crystal can be seen, which has apparently started from a crystal seed in the center of the dome. Since all the dye molecules are inside the polymer dome, the crystal can only grow inside the dome, the crystal size and morphology can be controlled by the dome size and dye concentration.

![Fig. 7. Optical micrograph of a crystalline dye in a polystyrene microdome.](image)

4. Dewetting of low molar mass compounds and crystallization control

Since dewetting does not depend on the molecular structure of the solute, many different compounds can be used. But it is crucial that no crystallization occurs during the dewetting. Compounds that crystallize during the solvent evaporation will form crystals in solution. Convection will transport these crystals to the solution edge and deposit them at random places. These adsorbed crystals then act as pinning sites for the receding three-phase-line and severely disrupt the ordered dewetting. Thus it is necessary to have compounds, which do not crystallize spontaneously. This seems to be a severe restriction, given that most organic low molar mass compounds are known to crystallize. But because of the fast evaporation rate, many compounds form a supercooled amorphous state, which is metastable at temperatures below the bulk melting point.

Annealing such an amorphous dome sample at room temperature leads to polycrystalline domes. Another amorphous sample was annealed at 50°C and single crystals were formed.\textsuperscript{41)}

Since the speed of crystal growth depends on the degree of undercooling, the crystallization of the domes in the room temperature sample occurs immediately after the formation of a crystallization seed in each dome. Rapid crystallization facilitates the formation of defects and thus the formation of polycrystals. Keeping the sample at higher temperature decreases the speed of crystal growth, and thus allows the formation of small, micronsized single-crystalline domes.

Increasing the annealing temperature of an amorphous sample to 80°C leads to the formation of crystal fibers. This shows that, at annealing temperatures of up to 50°C, the integrity of the domes is preserved and each dome crystallize independently, but at temperatures 50 K below the bulk melting point of 130°C, the morphology of the sample changes drastically.

Extremely long fibers with a length of up to 1 cm can be formed upon keeping the sample of another dye at room temperature. A decreased density of domes in the vicinity of the fibers can be seen. Thus a mass transport between the amorphous domes and the crystals have to take place. This can be explained by an incomplete dewetting, where the sample consists of a thin continuous film with partially dewetted domes on top. The formation of a crystallization seed preferably occurs in the domes and not in the film, since most of the material is concentrated in the domes. The large mobility of the molecules at room temperature, which is just 50 K below the bulk melt-
Organic light emitting diodes by dewetting point of 74°C, leads to crystallization of the dome. Molecules from the surrounding continuous film can diffuse to the crystal and the crystal can grow further. If the crystal has a face with a preferred growth direction parallel to the surface, a crystal needle can develop. Since the thin continuous film is thus more and more depleted, molecules from neighboring domes diffuse into the film in order to maintain the equilibrium film thickness and hence provide more material for further crystal growth.

Figure 8 shows an electron microscope picture of a single crystal of tetraphenylbenzidine formed by dewetting with subsequent annealing.

5. Organic light emitting diodes by dewetting

Since dewetting leads to the formation of micron-sized droplets of photofunctional materials, one possible application is in the field of organic light emitting diodes (OLEDs).

Most commonly used techniques for patterning are ink jet printing,42,43 or evaporation through a shadow mask. Besides the obvious need of patterning for full color displays, also monochrome devices can profit from patterned electroluminescent layers. Crystallization of the material in the layers can lead to dendritic crystal growth, which destroys the device.44 Micro-patterning the material will restrict the possibility of growth and confine the defect to a small area without the possibility to destroy the whole device.

Figure 9 shows the optical micrograph and the luminescence image of the same area of a device containing dewetted microdomes of tolyl, phenyl-diaminobiphenyl (TPD), a hole transport material. Compared with the patterns prepared on mica, the
two-dimensional order of the TPD domes is much less, which can be explained by the larger surface roughness of the PEDOT/PSS coated ITO electrode. But since the microdomes have a density of ca $10^6 \text{ mm}^{-2}$, individual domes cannot be seen with the naked eye. The slightly different dome sizes and spacings average out, and a homogeneous electroluminescence is observed by the naked eye. The TPD domes have a diameter of 0.5 to 2 $\mu$m and are fairly homogeneously in size and inter-dome spacing. By comparison of the transmission image with the EL image we can conclude that all microstructured dots emit light.\textsuperscript{45}

6. Conclusion

Dewetting is a process in which a thin film ruptures on a substrate or a receding edge of a liquid develops a fingering instability. This process is governed by the interfacial energies of the substrate and the coated material. By using dilute solutions, ordered dewetting can lead to samples in which micrometer-sized droplets, or “domes” are formed. Depending on the casting conditions, samples with narrow dome size distribution and dome distances can be prepared. Polymeric as well as low molar mass compounds can be used and the limited diffusion of molecules within the microdomes can be applied to control the aggregation state of organic compounds in the microdomes. In this paper, several examples of organic dyes were presented and the controlled formation of cyanine J-aggregates and dye crystals was reported.

Acknowledgments

I want to thank Prof. M. Shimomura for his support and valuable discussions, especially concerning early experiments and the elucidation of the dewetting mechanism. I also thank N. Maruyama, R. Chiba, M. Watanabe, K. Okamoto, S. Kurimura, J. Sato, K. Kaga, H. Kagayama, T. Ishighe, T. Wada, S. Arakaki, H. Oyamada, Prof. T. Imai, and Prof. C. Adachi for experimental support. This work was financially supported by JST (PRESTO) and MEXT (Research in Priority Areas).

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