Controlled Fabrication of Molecular Nano-Dot Patterns

Stephan Rath, Helmut Port
3. Physikalisches Institut, Universität Stuttgart, D-70550 Stuttgart, Germany
E-mail: s.rath@physik.uni-stuttgart.de

Abstract. Our empirical method to fabricate molecular dots from thin organic films by dewetting, is further developed and quantified. The films are deposited at UHV conditions on helium-cooled substrates. Controlled annealing to room temperature transforms the films into homogeneous distributions of isolated dots. To achieve regular and closely packed patterns of nano-dots we applied the dewetting process on topographically structured substrates as templates. The dots are characterized and accessed by scanning microscopies.

1. Introduction
Previously, we set-up a fabrication method for molecular dots that involves thermally induced nanostructuring of originally extended flat amorphous molecular films; these are evaporated in the UHV at low temperatures. In [1] the empirically found similarity of the structure formation with the dewetting of highly viscous liquids on non-wettable substrate was reported. Further extensive measurements on the same molecular system (phenyl-thiophenefulgide, Ph-T-F, on quartz glass substrate) reveal a dewetting behaviour (see Fig. 1) directly comparable with polymer melts, in particular with polystyrene (PS) at low molecular weight [2][3]. The analogous model description provides a quantitative analysis and determination of relevant process parameters. In this way control on the dot formation is achieved. Moreover, by applying the dewetting method in combination with (lithographically) structured substrates, well-ordered dots arranged in regular, for instance hexagonal, lattices can be prepared. Patterns of nano-dots with variable sizes and lateral distances have been produced.

Figure 1 Formation of molecular dots by dewetting from thin evaporated films
2. Experimental
The samples used in this work have been prepared via UHV vapor deposition onto chemically and plasma cleaned quartz glass substrates at 10K, in a nominal thickness range of \( d_{\text{nom}} \) between 2 and 22nm. Temperature-controlled annealing to room temperature (295K) equally is performed on flat or pre-structured substrates. The resulting irregular or regular dot patterns, respectively, are covering surface areas on up to several \( 10\,\text{mm}^2 \) scale.

The pre-structure in the glass substrates was made by electron beam lithography (x-lith GmbH, Ulm), in different surface morphologies.

Optical in-situ micrographs have been recorded online while dewetting, using a cooled CCD camera and dark field mode [1]. AFM images have been taken ex-situ in a commercial AFM (MFP-3D by Asylum Research).

![Figure 2](image)

**Figure 2**: Characteristics of dewetting, schematic, see text: a) Effective interface potential b) Thickness fluctuations, c) Young’s equation.

3. Dewetting of thin molecular films and dot formation
The dewetting behavior of a thin (fluid/polymer) film commonly is characterized by the effective interface potential \( \phi(h) \), fig.2, where \( h \) is the distance of the liquid-vapor interface from the substrate (see for instance [3][4][5]). \( \phi(h) \) measures the free energy of a thin layer of thickness \( h \) on top the substrate. It results from two contributions, a short-range repulsive one and long-range van der Waals attraction. The stable and unstable cases of a two-component system, film/substrate material, are discriminated by the sign of the Hamaker constant, \( A<0 \) and \( A>0 \), respectively (Fig.2). The value of \( A \) parameterizes the strength of the long range interaction.

For \( A>0 \) the film becomes unstable, thermally induced surface fluctuations develop and a particular one \( \lambda_s \), in narrow frequency range is increasing fastest such that its amplitude reaches the film thickness \( h \). There-upon the film breaks-up and as a first stage of dewetting dry holes are formed. The number of early created holes characteristically decreases with the film thickness, fig.3a, and due to its correlation with \( \lambda_s(h) = [-8\pi^2 \sigma / \Phi^*(h)]^{0.5} \sim h^2 \) the average hole distance \( d_{\text{hole}} \) increases with \( h^2 \), fig.3b. These findings are typical for the so-called spinodal dewetting stage, but not enough for its proof. For to get the clear-cut attribution a clarifying Minkowsky analysis [2][6] of the data is in progress.

From ellipsometry measurements the Hamaker constant of our system is determined: \( A=2.6 \times 10^{-20} \pm 1.5 \times 10^{-20} \text{J} \), thus verifying the unstable case, see above.
In analogy to the polymer PS further two stages of the dewetting process are distinguished. In the second stage the holes increase in size and develop a rim at velocities depending on the film thickness. The fluid-like behavior (Newtonian fluid) of our film material becomes apparent in the particular shape of the rim, fig.4. The tail of the rim towards the hole is determined by the wetting angle $\theta$ according to Young’s equation, fig.2c. For our system $\theta$ amounts to about 30 degrees.

The rim shape versus the film exhibits oscillatory behavior. From this oscillatory decay the viscosity of our system (Ph-T-F on quartzglass) $\eta = 10^6 \ldots 10^7$ Pa s is obtained [7], a comparable value as for PS films at 100 °C.

During time in stage two, for thinner films the holes continuously grow until they meet whereas in thicker films they develop fingering intermediate structures (fig. 1b in [1]) before they meet. In fig.4 (right) the time dependence of the hole diameter is plotted. It is close to the $t^{2/3}$ dependence, which for the polymer case [8] is taken as characteristic for slipping movement of the rim.

In the third stage of dewetting, the coalescing rims of the holes as well as the fingering structures decay in discrete segments as a consequence of Rayleigh instabilities. These promote the subsequent growth of dots in irregular distributions on the substrate surface.
Generated dots
On flat substrates, the molecular dots are always spatially random and have a broader size and height distribution (Fig. 5). The spherical dot shape, however, is maintained for different sizes.
On long time scales, between several days and weeks, within the distribution of dots coarsening occurs, i.e. larger dots grow at the expense of smaller ones thus reducing the overall dot density. This presumably diffusion type of process is made possible like in PS [9][10] by a wetting layer of the order of 1nm (corresponding to $h_{\text{eq}}$ in fig. 1) as determined from small angle X-ray diffraction measurements.

![Figure 5 a) Irregular dot pattern on flat substrates; b) dot shapes for different dot sizes; c) height distribution of dots in a).](image)

4. Control on regular pattern formation
The fabrication of regular dot patterns is achieved via dewetting on periodically structured substrates. The dots preferentially grow in holes, for instance, fig. 6. And the ordered dots manifest a much better size homogeneity than those on flat surface. They reveal a high long-term stability, which results from pinning effects [11] as verified on different substrate patterns. No coarsening effects are observed. On the other hand, dewetting and dot growth are affected by the geometrical profiles, size and depth of the pits in the structured substrate. Therefore, the individual interdependences governing the growth conditions of specific patterns require very detailed studies. Various types of substructures and different molecule/substrate combinations are investigated.

At present, little is known in general about topographically structured substrates and the influence on dewetting. Recent model calculations of PS [12] are limited to one-dimensional groove patterns and not applicable in this case.

In conclusion, by quantitative analysis of the dewetting behavior of thin organic molecular films, control on the dewetting process towards formation of molecular dots is achieved. In combination with structured substrates fabrication of regular nano-dot patterns is demonstrated. These are well suited for various applications in nano-photonics and molecular electronics.
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