

PHOTONIQUE MOLECULAIRE :
MATÉRIAUX, PHYSIQUE ET COMPOSANTS
MOLECULAR PHOTONICS: MATERIALS, PHYSICS AND DEVICES

Organic thin film crystal growth for nonlinear optics: present methods and exploratory developments

Sabine Manetta^a, Marcel Ehrensperger^a, Christian Bosshard^{a,b*}, Peter Günter^a

^a Nonlinear Optics Laboratory, Institute of Quantum Electronics, ETH Hönggerberg, CH-8093 Zürich, Switzerland

^b CSEM Alpnach, Untere Gründlistrasse 1, CH-6055 Alpnach Dorf, Switzerland

Accepted 1 March 2002

Note presented by Guy Laval.

Abstract We discuss different methods to grow organic single crystalline thin films from solution. Specifically, we address exploratory developments and apply them on the highly nonlinear material DAST (4'-dimethylamino-N-methyl-4-stilbazolium tosylate) in a DAST/methanol system. We describe the nucleation and growth thermodynamics in solution using a solubility diagram and its Ostwald–Meiers metastable region. The important experimental parameters for bidimensional growth are discussed and first promising results are presented. *To cite this article:* S. Manetta et al., C. R. Physique 3 (2002) 449–462. © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

organic single crystals / thin film / growth methods / DAST

1. Introduction

Materials with large nonlinear optical and electro-optic active properties are very important for photonic applications. If well designed organic materials may be much superior to their inorganic counterparts due to the combination of excellent nonlinearities and almost purely electronic origin of the effects [1,2]. As an example organics are of prime interest for high-speed electro-optic modulators [2,3].

There are two important classes of organic materials: doped polymers and crystals. Polymers are potentially cheap and especially easy to process in thin films. Although excellent progress has been achieved recently [4], their inherent active nonlinear optical properties are limited by the maximum chromophore concentration, by their spatial distribution and by the orientational relaxation in the film. On the other hand, organic crystals have superior nonlinear optical properties, but they are difficult to process, especially in thin films. In this work, we concentrate on crystalline films and present several methods to grow organic thin films with special focus on the organic salt DAST (4'-dimethylamino-N-methyl-4-stilbazolium tosylate), one of the best organic materials for second-order nonlinear optics (see Table 1 and Fig. 2) [5–11].

* Correspondence and reprints.

E-mail address: christian.bosshard@csem.ch (C. Bosshard).

Table 1. Organic crystal growth methods

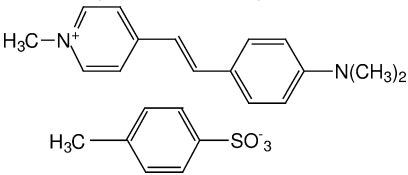
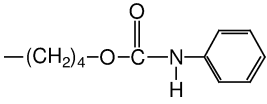
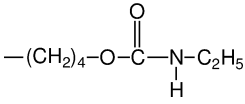
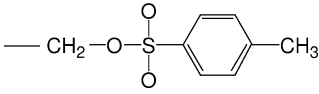
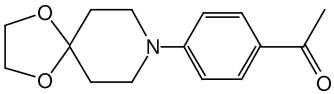
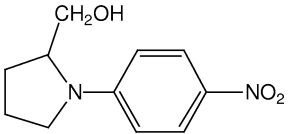
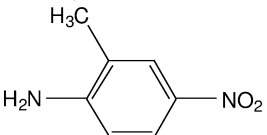
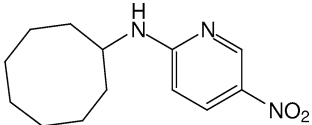
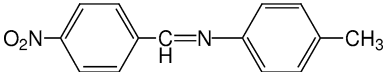
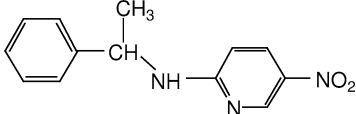
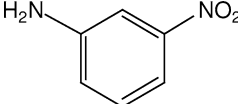
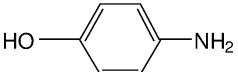
Materials from the melt (M) and/or solution (S)	Thickness (μm)	Single crystal area	Ref.
<i>Cut and polish</i>			
DAST 4'-dimethylamino-N-methyl-4-stilbazolium tosylate	S	20–25	$3 \times 7 \text{ mm}^2$ before polishing [19]
			
<i>Etching, bleaching, and dragging</i>			
DAST	S	2–3	Waveguide, width of $4 \mu\text{m}$ [27–29]
<i>Shear method, from the melt or highly concentrated solution</i>			
Polydiacetylenes, different monomers used:			[34]
TCDU 5,7-dodecadiyne-1,12-diol bis(phenylurethane), side group:	M	0.4–2	1 cm^2
			
ETCD 5,7-dodecadiyne-1,12-diol bis(ethylurethane), side group:	M	0.4–2	1 cm^2
			
pTS 2,4-hexadiyne-1,6-diol bis(p-toluenesulfonate), side group:	S	1	50 mm^2
			
APDA 8-(4'-acetylphenyl)-1,4-dioxo-8-azaspiro [4,5] decane	M	5	Not given [35]
			
DAST	S	3	Not given [26]
NPP N-(4-nitrophenyl)-(L)-prolinol	S	3	1 cm^2 [36]
			

Table 1. (Continued)

Materials from the melt (M) and/or solution (S)	Thickness (μm)	Single crystal area	Ref.
<i>2D-Bridgman–Stockbarger or from a supercooled melt between 2 plates</i>			
MNA 2-methyl-4-nitroaniline 	M	5–10	2–3 mm in length and width [37]
COANP 2-cyclooctylamino-5-nitropyridine 	M	8.7	0.5–1 cm ² [16,38]
NMBA 4-nitro-4'-methylbenzylidene aniline 	M	3–30	1–2 cm ² with cleavage lines due to thermal expansion [21]
MBANP (-)-2-(a-methylbenzylamino)-5-nitropyridine 	M		
mNA 3-nitroaniline or metanitroaniline 	M		
ABP 4-aminobenzophenol 	M	Not given	8 × 15 mm ² [23]
MNA	M	0.95	1 cm ² [22]
COANP	M	5–20	a few mm long [39]
<i>Zone refining/recrystallization and inverted bell technique</i>			
mNA	M	2	5 × 15 mm ² [40]
MNA	M	~ 1	cm × cm [24]
<i>Isothermal solvent evaporation from solution, between two plates</i>			
ABP	S	Not given	Not given [23]

Molecular engineering for the optimization of microscopic optical properties and crystal engineering for non-centrosymmetric packing are the preliminary steps to growth engineering and integration of the material to the final device. These are all decisive steps to reach any prototypical application. We here concentrate on the growth engineering since the two first steps have been successfully carried on until now, providing excellent nonlinear optical efficient materials for potential integration [2].

Thin organic monocrystals may be grown from the melt, solution or vapor phase. Examples of crystals grown from a liquid mother phase are listed in Table 1. The different growth methods will be described and discussed afterwards. The best-known vapor method is the molecular beam epitaxy [12,13], or organic molecular beam deposition [14]. The electrospray technique is another vapour growth method [15]. Of course, this technique is adapted to thin films in the case of molecules surviving vacuum conditions, which is critical for π -extended molecular crystals. Another method relying on self-assembly is the Langmuir–Blodgett technique ([16,17] and references therein). Langmuir–Blodgett films and molecular beam deposition are not discussed further in the present paper.

Because the growth units have to be carried through the mobile mother phase to the growing crystal, the growth ability of a given crystal from the liquid phase usually increases with increasing equilibrium concentration of the mobile phase (100% for a melt). Materials that can be molten may be dissolved as well. The contrary is not true, since thermal stability is additionally required for melts. This is a typical problem for nonlinear optical chromophores. Indeed, their molecular hyperpolarizability is commonly increased by elongating the molecule in particular with double bonds. This elongation, however, often leads to a decrease of the decomposition temperature.

In the following, we will discuss briefly some theoretical aspects of 2D crystal growth. We then provide an overview of already existing growth methods and present several exploratory methods to grow organic crystalline thin films from solutions containing less than 5% of solute. These are namely, the 2D ΔT -, the travelling cell-, the capillary-, the undercooled flow cell-, and the molecular solution epitaxial methods. We use them for solutions but they may as well be applied to the melt. Finally, we summarize the results and provide an outlook for future work.

2. Crystal growth theory for 2D organic materials from the liquid phase

Crystallization is nothing more than a phase transformation requiring an activation energy. From a thermodynamical point of view, much may be explained with the help of a schematic solubility phase diagram (Fig. 1).

The metastable or Ostwald–Meiers region (see, e.g., [18]) is limited by a nucleus dissolution curve and a stable nucleus formation curve. It is not straightforward to determine if nuclei are present or not in a system (concentration c , temperature T) found in this area. If there are no nuclei, then the solution is supersaturated, and has probably been quenched from a pure solution. If nuclei are found and kept under constant conditions (c , T), they will grow. After nucleation, undercooling must be produced to a lesser

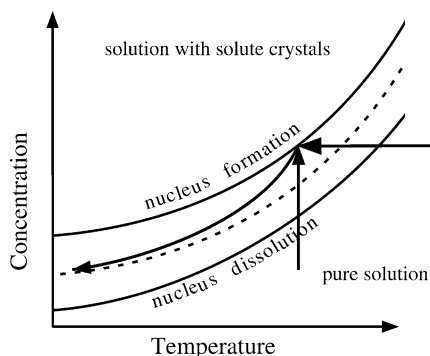


Figure 1. Schematic solubility curve with macroscopic nucleation and growth paths.

extent, since the 3D surface formation is not to be overcome again. This is why one should differentiate the nucleation conditions from the growth conditions in the experiments.

There are two basically different paths to undercool the system. They are represented with the two arrows in Fig. 1. An horizontal displacement of a pair of coordinates stands in practice for a slow-cooling experiment. A vertical displacement illustrates a slow-evaporation experiment. At the microscopic level, these two processes often play complementary roles. As an example, a crystal growing due to external heat flux is surrounded by concentration gradients, and an isothermal crystal growing under constitutional undercooling releases latent heat while solidifying. Constitutional undercooling describes the event that the liquid temperature within the boundary layer is higher than the actual temperature imposed by the environment.

Concretely, isothermal methods provide some general benefits to growth such as the easy temperature control and the constant growth rates during the whole experiment. Therefore, the homogeneity of the final crystal and its quality are improved.

A third practical growth method is based on transport processes. If external chemicals intervene, the solubility phase diagram is actually shifted since the whole system composition is changing. If solute transport occurs by convection (for example) within a closed system, the process is comparable to solvent evaporation.

To summarize this section, there are basically three ways to obtain supersaturation: slow cooling, solvent evaporation, and transport techniques.

General expressions for the growth rates are given by Elwell and Scheel [18]. Important parameters in these expressions are among others the growth temperature T , the temperature difference ΔT , the cooling rate dT/dt , the temperature gradient dT/dx and the speed through the temperature gradient w (if required), the change in solubility per degree dn_e/dT , and σ the relative supersaturation. Typical values would be $T = 30\text{--}40\text{ }^\circ\text{C}$, $\Delta T = 2\text{--}10\text{ }^\circ\text{C}$, $dT/dt = 1\text{--}5\text{ }^\circ\text{C/day}$, $dT/dx = 1\text{--}5\text{ }^\circ\text{C/cm}$, $dn_e/dT = 0.02\text{--}1.2\text{ (g/100g)/}^\circ\text{C}$, $\sigma = 0.1\text{--}2\%$. Usual linear growth rates are in the range of 2 mm/month to 3 mm/day.

3. Growth methods for 2D organic crystals from a liquid phase

In the following we present established growth methods of thin crystalline films. The advantages of mechanical methods such as cutting and polishing or etching of bulk crystals are that one can arbitrarily select the crystallographic orientation of the thin film, as well as its initial bulk quality. If all conditions (solvent, pressure, oil, atmosphere) to be used to polish the organic crystal are known, it is easy to obtain a high-quality surface finish. Still, the major drawback is that organic crystals are brittle and cracks will form during polishing in the ultimate slimming step since the mechanical shear strength will proportionally decrease with the thickness. In the case of DAST, the thinnest obtained samples were around 20 μm , as shown in Table 1 [19].

A light drawback of this method is that the thin film, even if it would reach a thickness for applications (typically 1–2 μm), would have to be somehow integrated to the device. It would be safer to grow and integrate the thin film at the same time. By etching the sample, one might obtain thinner films previously integrated, but the surface finish would be affected.

There is much published work on 2D organic crystal growth using a melt shear or a solution shear method (Table 1). This is an elegant, efficient and impressive method, leading to 1 μm thin and 1 cm^2 large single crystals.

The different steps of the method are as follows. First, the melt or solution is placed in between two substrates (for example using capillary force) and is kept under constant pressure. Then one substrate is slid with respect to the other, orienting the melt or solute molecules. Supersaturation is reached through subsequent slow cooling (for both cases) or evaporation (for the solution case) and the molecules are forced to crystallize. Precise descriptions of the technique and principles can be found in [20].

This method is particularly suited for large molecules and especially from the melt, since the molecular diffusion required for the growth from solution limits the final crystal area and polycrystallinity would be favored. The drawback is that there is no certainty of the alignment of the molecules, hence of the crystallization (instead of an amorphous phase formation), especially in the case of low solubility systems.

2D Bridgman–Stockbarger method was used for example in [21] for mNA and NMBA grown from the melt. Since the Bridgman growth method consists of moving a closed system through a temperature gradient, the material is beforehand encapsulated, usually in a tube. The adaptation to 2D growth is quite simple. As an example two glass substrates pressed together may be placed in a common Bridgman tube. The resulting thickness depends on the growth space geometry and other details of the set-up such as the external applied pressure. Thicknesses were shown to vary between 3 and 30 μm .

The main advantage of the method is that the growth rate is controllable and consequently the quality and single crystallinity of the film as well. As an example Ko et al. [22] forced crystallization to occur by using a grooved substrate.

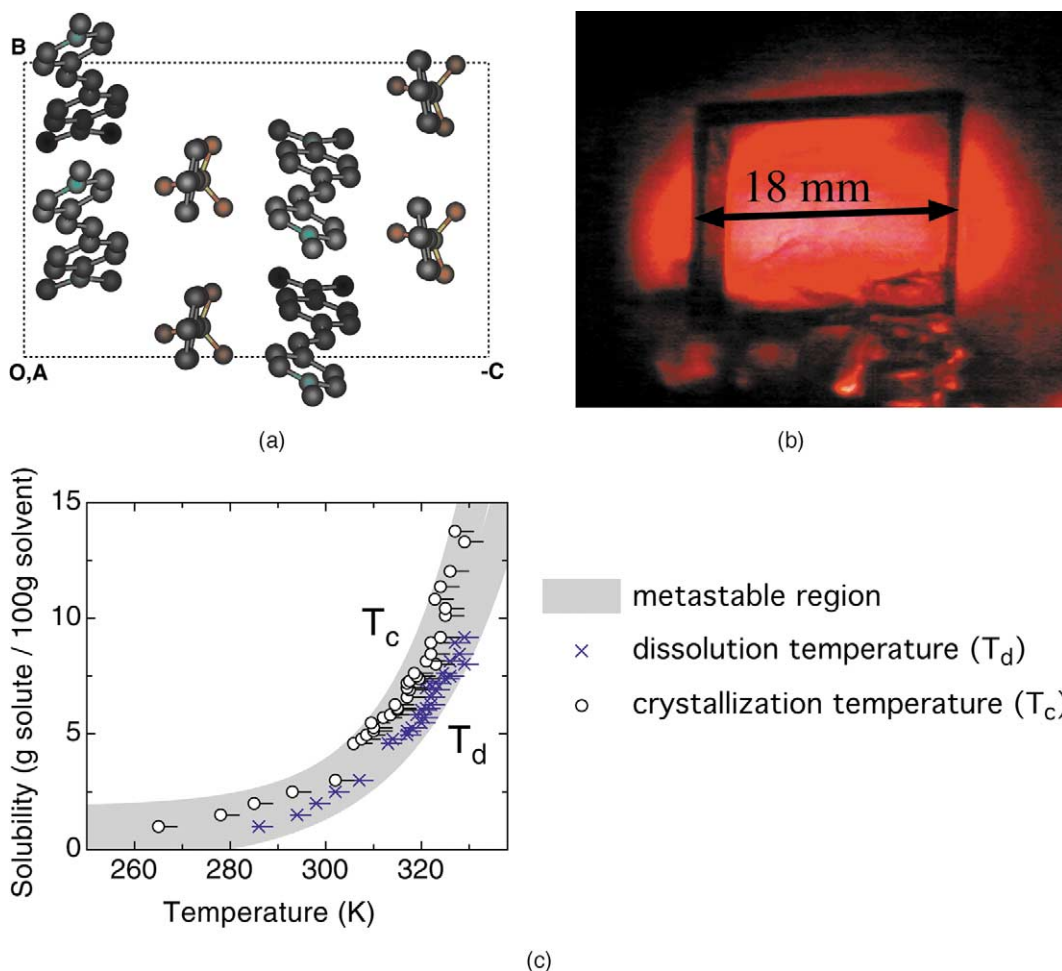


Figure 2. (a) Crystal structure of DAST (see Table 1 for molecular structure), (b) bulk DAST growing in solution, (c) solubility curve and metastable region of DAST in methanol. The dissolution temperatures were measured by slowly heating up a clearly saturated solution, while crystallization temperatures were measured by slow cooling down the same pure solution.

The clear drawback is the fact that this method is adapted to thermally stable materials, which is not necessarily the case of molecules with delocalized π -electrons. Another basic problem in the 2D Bridgman–Stockbarger growth is the inevitable thermal back-dilatation leading to crack formation during the cooling of the film down to room temperature. In fact the substrates should have the same dilatation coefficients as the organic material (a technically quite challenging problem).

An elegant way to avoid back-dilatation is to carry out the process at the same temperature, i.e. a vertical path in the solubility diagram (Fig. 2). This is obtained through 2D isothermal solvent evaporation from solution as presented in [23] for ABP crystals grown from the DMF solution. In this case the saturated solution was fed in between two substrates by capillary action. This method avoids the huge restriction of using melttable organics. At the same time, cracks through back-dilatation are not dangerous anymore.

Zone refining and inverted bell techniques are presented by Gauvin and Zyss [24]. Once a solid organic thin film has been grown, it is common to observe polycrystallinity. This occurs even more often in 2D growth than in 3D growth, since the specific container area is higher so that heterogeneous nucleation is more likely, decreasing the critical nucleus formation free energy. Still, there is a remedy against polycrystallinity: the so-called inverted bell technique, which consists of recrystallization of the thin crystals surrounding an arbitrary selected single crystal seed of good quality and morphology. Recrystallization in this case begins with the selective radial re-melting of all undesired neighbour crystals, followed with a globally radial re-adsorption of the molecules on the growing surfaces, this under a minimum temperature gradient to hinder the aperiodical adsorption of the molecule on ‘wrong’ sites or the ‘wrong’ way. This is the reason why a careful control of the temperature profile is an absolute requirement for this technique.

The inverted bell technique is a clever and efficient method that has been adapted to 2D growth from usual purification methods [25] or recrystallization in general. Of course it only applies to thermally stable materials.

Finally, it should be mentioned that much effort has been devoted to the preparation of thin films and waveguides of DAST by various methods with promising results [19,26–29].

4. Exploratory methods for 2D organic crystal growth from the solution

4.1. General remarks

We present here our own exploratory growth methods. As mentioned earlier, we focus on the growth of the highly nonlinear organic salt DAST (see Table 1 and Fig. 2). We will only discuss the DAST/methanol system in all experiments described below.

DAST may only be grown from solution (i.e. methanol) since it decomposes below its melting point ($T_m = 256$ °C). Bulk DAST crystals are usually grown by slow cooling of a saturated solution (not supersaturated). The morphology varies between c-plates and chunky prisms, depending on the growth conditions. Care must be taken to keep the atmosphere water-free because a centrosymmetric hydrated second phase preferentially grows in a humid environment [30].

In Fig. 3 the three different cells with bidimensional growth cavities that we used for our experiments are shown. In cell 1, the spacing is obtained by welding together two quartz substrates pressed against each other with a 20 μm thin molybden leaf, removed just before a complete sealing is achieved. This method led to spacings larger than 20 μm , and one usually obtains a spacing up to 40 μm .

The spacing of cell 2 is defined by a pre-etching step, with the advantages that the surface is extremely flat and the thickness under control. Here again, the actual space is not limited by the etched depth but it depends on the welding step, too. Estimated total spacing for a 4 μm etched channel is 10 μm .

In cell 3 the spacing could be varied between 1 and 10 μm (or even more). Moreover, surface treatment (structure and/or material) is an additional important parameter. When required, teflon caps can be used to hermetically seal the cells.

The temperature gradient throughout the cell walls determines the temperature gradient in the solution, and thus the growth rates. Therefore a better control on the growth rates is achieved for cell walls as thin as

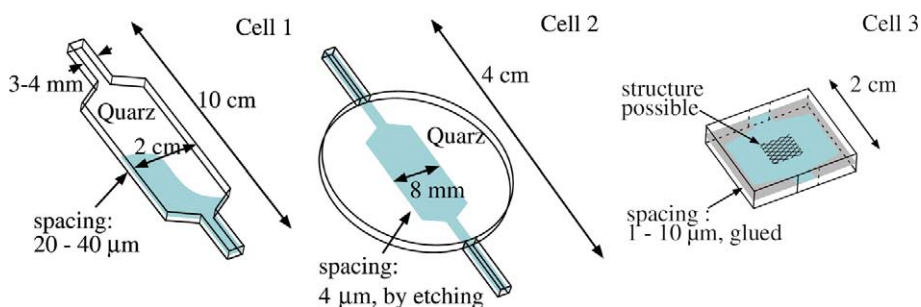


Figure 3. Growth cells used in the different experiments.

possible. Moreover, the cell material should be a bad heat conductor (to allow a steep temperature gradient if required). This is why it is of prime importance that the temperature and temperature gradients surrounding the growth cell are efficiently transferred (close contact).

4.2. Two-dimensional ΔT method

A thin hermetic cell (types 1 or 2 in Fig. 3) is placed in an oven at temperature T_1 . Its lowest extremity is placed in an aluminium holder at T_2 with $\Delta T = T_2 - T_1 > 0$. The cell is filled with the solution. Excess solute is present at the bottom of the cell. In our experiment $T_1 = 36^\circ\text{C}$ and $T_2 = 42^\circ\text{C}$. A picture for clearer view of the set-up is given in Fig. 4.

The principle is the same as for bulk ΔT growth, see, for example, [31]. The excess material found at the bottom of the cell dissolves and the solution at T_2 is constantly supersaturated. The hot saturated solution flows upwards to the cooler region of the cell maintained at T_1 . So, supersaturation at the top of the cell is reached by solute transport in a temperature gradient by thermal convection. Heterogeneous spontaneous nucleation occurs due to the sudden supercooling imposed by the up-streaming solution. After nucleation, growth conditions are totally constant since (i) the stationary convection regime provides a constant supersaturation around the growing seed and (ii) the growth temperature T_1 is fixed.

The ΔT -induced growth occurs through transport. The higher the $\Delta T/T^2$ ratio, the faster the crystals will grow [18]. On the other hand, a slow growth rate increases the crystal quality. Hence a small ratio is

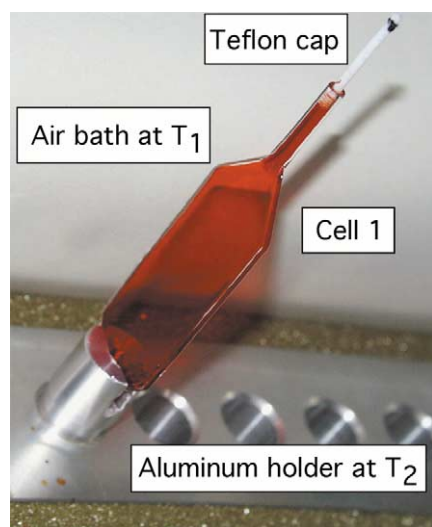


Figure 4. Picture of the 2D ΔT set-up. Cell 1 is filled with a DAST/methanol solution. The aluminium holder is maintained at $T_2 = 42^\circ\text{C}$ and the air is kept at $T_1 = 36^\circ\text{C}$.

preferred and temperature control is thus essential in this method, since it is the only control we have on the growth cell, assuming starting purity is at its maximum. The growth rate is well proportional to the equilibrium concentration which depends exponentially on the temperature in the temperature domain of interest (solubility diagram, Fig. 2(c)). Hence we have to optimize ΔT for a fixed growth temperature.

Our experimental results can be summarized as follows. Although this method is very successful for bulk growth, so-called 2D crystals were obtained already in the bidimensional cavity but only at the bottom of the cell. The reason for this type of short-distance growth is probably linked to the cell's geometry. It has a high heat capacitance compared to the solution transported throughout the film by convection. The temperature gradient is therefore local and steep, causing nucleation near the Al/air interface, before the material streams upwards. This is why we suggest an even smaller temperature difference or a different cell geometry would help to increase the chance of nucleation at the bottom of the cell.

4.3. Travelling cell method

The set-up for the travelling cell growth experiment is as follows. Cells of types 1 and 3 were used. First, the material is filled inside the two cell's ends. Then the solvent is added. Possible air bubbles are removed by heating up the system and closing it when the solution is at its hottest, following the solution's shrinkage due to thermal back-dilatation by moving the teflon caps at the same time. The whole system is kept at a constant temperature (36 °C in our case). The cell is fixed on a motorized holder. It moves down at a low speed of 0.1 to 0.5 cm/day through a well-isolated local heater.

The principle is the same as in purification processes by solution zone passages [25,32], or recrystallization in metals. The two differences between the travelling cell and the one used for purification are that the heating element is fixed in the travelling cell's set-up, and that the cavity is two-dimensional. Growth is driven by slow cooling transport processes as well as transport processes.

Undercooling of the solution is the driving force, its effect is first nucleation through a motion at constant concentration across the crystallization boundary of the metastable area in the solubility graph (Fig. 2(c)). Note that convection within the cell may help growth through additional material supply, which may add some solutal undercooling to the thermal undercooling.

Both the thermal gradient and the temperature difference should be minimized to provoke slow growth rates. The easiest way to reduce the nucleation rate is to slow down the speed of the cell. Care must be taken since nucleation might even not occur at all. In this case two travelling steps are recommended. First, the cell will cross the heater rapidly (3 cm/day) to induce nucleation, and afterwards subsequent crossings will occur at much slower rates (0.1 to 0.5 cm/day) to obtain slow growth rates.

We find that the maximum single crystal size usually obtained in a cell after one crossing was 4 mm² and the estimated thickness was 20 to 40 μm. A picture of the cell after a growth experiment is given in Fig. 5(a). One may notice that the average size of the crystals along the moving direction is increased. The crystals are largest in areas where the hermetic cell was cooled down first: The growth period after nucleation was longer there, and solute material was still supplied through diffusion and/or convection during the whole experiment. A picture of a very homogeneous high-optical quality monocrystal resulting from this method is shown in Fig. 5(b).

This method is surprisingly efficient, and lead to 40 μm thick and 4 mm² single crystals. The thickness depends on the cell's geometry, and therefore an improved geometry would allow the fabrication of thinner crystals.

This method is certainly promising for growing homogeneous single crystalline thin films. A drawback is that it is difficult to take out the crystals from hermetically sealed cells. For the same reason there is also a lack of surface finish control.

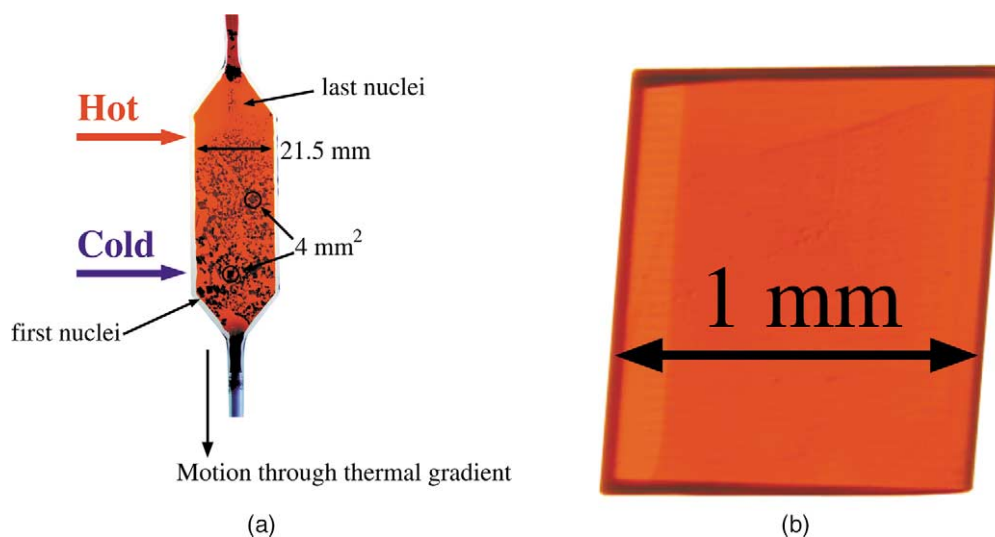


Figure 5. (a) Growth cell after the travelling heater zone refiner experiment, (b) cross-polarized picture of a single crystal grown by this method.

4.4. Capillary method

For 2D growth from the melt, the capillary method was already published in the literature (see Table 1). The set-up consists of two parallel substrates that stand vertically in a closed system (bottle) filled about one fourth with the liquid mother-phase. The liquid is pulled up between the substrates by capillary force. The same capillary effect keeps the substrates parallel, too, if they are not externally clamped together. The saturated solution should be at an initial temperature T_i ($= 55\text{ }^\circ\text{C}$) considerably higher than the environmental temperature T_e ($= 27\text{ }^\circ\text{C}$) where the bottle will be kept during growth. Here a rapid cooling down of the solution is preferred to force nucleation. Due to relative inefficient diffusion of solute material in a low-concentration solution, polynucleation will preferentially occur during this cooling step. Controlled slow growth will start as soon as the solution in between the substrates will not be saturated anymore, and will thus require solvent evaporation as the steering force for undercooling. By this means we know that the system is always on a vertical line in the solubility diagram (Fig. 1).

The driving force for undercooling is the preservation of the saturation in the solution. After nucleation, a low temperature is required to obtain slow growth rates. There are four ways to minimize the evaporation rate:

- (i) A special substrate geometry could diminish the specific perimeter contact with the air/environment gas, using, for example, discs instead of rectangular substrates;
- (ii) The use of a partially sealed pair of substrates would have the same effect, and would fix the spacing between the substrates;
- (iii) It would be very useful to dip the two substrates in the saturated solution to a larger extent (e.g. two thirds of the substrate height);
- (iv) Finally, one could start the experiment at a higher temperature to provoke a quick solvent saturation in the vapor phase inside the growth bottle, or even extend the idea to proceed under constant lower pressure.

For the capillary method to grow DAST thin films we used cells of type 3 (Fig. 3). Initial rapid undercooling was applied from 55 to $27\text{ }^\circ\text{C}$ to force nucleation. Monocrystals reached 12 mm^2 , and their estimated thickness was $20\text{ }\mu\text{m}$. Not surprisingly, the growth rates decrease with time as the vapor

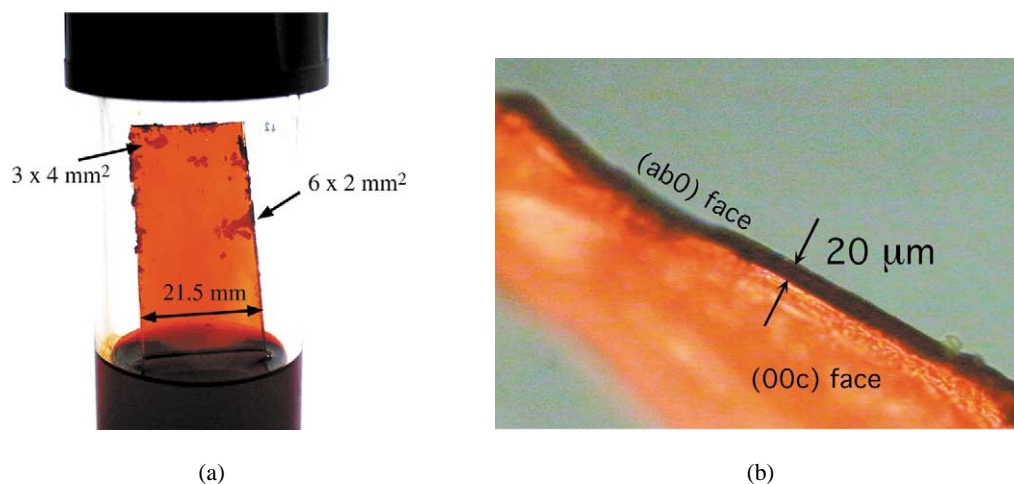


Figure 6. (a) Growth bottle during capillary-evaporation experiment, (b) single crystal grown by this method, side view.

surrounding (air) becomes saturated with the solvent evaporated from the solution (methanol), implying a decreasing material supply. The thin DAST crystals kept growing during at least four months. A picture of the growth bottle is given in Fig. 6(a) and a picture of a related as-grown monocrystal is given in Fig. 6(b). Clearly, the main disadvantage is a poor surface quality of the crystals grown by this method.

Because the crystallization process is slow, there is a chance for improving the crystal quality although an industrial production using this method seems quite difficult. However, first high-quality single crystals for scientific investigations can be easily obtained. Similar to liquid crystals, the molecular orientation during growth might be optimized for velvet-rubbed substrates, and further rubbing techniques should be investigated.

A further possibility is an extension of the method by adding a temperature difference. As an example we placed the same capillary system in an oil-bath warmer than air (typically $\Delta T = 5^\circ\text{C}$). The idea is to improve the solute supply in the capillary method with the hotter up-streaming solution typical of the ΔT method. We obtained the highest 2D growth rates with this method, up to an area of 43 mm^2 and a thickness of $30\text{ }\mu\text{m}$ in three days. Due to water contamination, the hydrated phase of DAST was obtained instead of the pure substance. This might be another reason for the rapid growth rates and a straightforward comparison should be avoided. Pure DAST grew by this method only up to an area smaller than 2 mm^2 .

4.5. Undercooled flow cell method

The development of this method was originally inspired from the two-bath circulating crystallizer [33]. Using this method the solution is pumped from a saturated solution container through a so-called flow cell by a peristaltic pump ($\mu\text{L}/\text{minute}$) as shown in Fig. 7. The cell is locally cooled down to saturate the flowing solution and induce growth at this point. Critical points of the set-up are the following. The whole system has to be well temperature-controlled and the connecting tubes should be kept at a slightly higher temperature than the rest of the system, since undesired heterogeneous nucleation may occur especially there. The cell's walls have to be thin to avoid undercooling of the complete cell with respect to the flowing solution (like for all the experiments), because the solute would crystallize at the entrance of the cell, stopping the solution to flow. The flow has to be laminar to grow good quality single crystals, which justifies the use of a micro-pump.

Nucleation is forced by starting the experiment without any flow. Polynucleation is to be thwarted by back-dissolution. In our case we illuminated the undesired seeds with a high-power lamp to dissolve them.

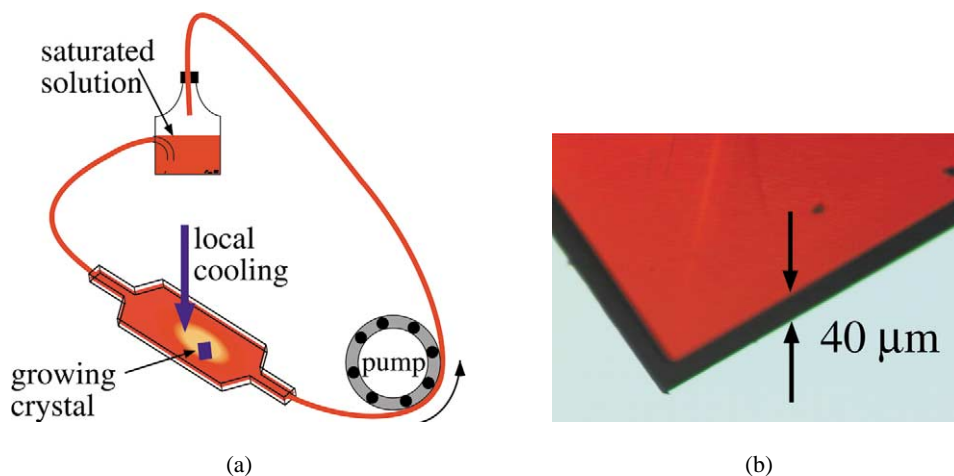


Figure 7. (a) Schematic undercooled flow cell growth set-up; (b) As-grown single crystal.

We obtained 11 mm^2 and $40 \mu\text{m}$ thick single crystals. As it was very difficult to locally undercool the cell, polycrystalline growth occurred all through the cell. Due to the solution flow, the nuclei could leave the cell and stick inside the connecting tubes. Hence special attention was given to control the temperature of the connecting tubes.

4.6. Molecular solution epitaxy

We also investigated the approach of self-assembled multilayers by taking advantage of the fact that DAST is a salt. We treated the surface of an optically flat quartz substrate with a tailored silanisation, as illustrated in Fig. 8. We covered the surface with 2-(4-chlorosulfonylphenyl)-ethyltrichlorosilane, providing an acidic $\text{O} \dots \text{H}$ surface. Then we bathed the surface with a toluene solution containing the cation of DAST.

The next step is to put this substrate in a slightly saturated DAST/methanol solution and let the solute grow by the usual bulk growth slow cooling technique. The anions in the solution are supposed to see the stilbazolium surface as a molecular plane of a growing bulk DAST crystal and self-assembly of DAST's

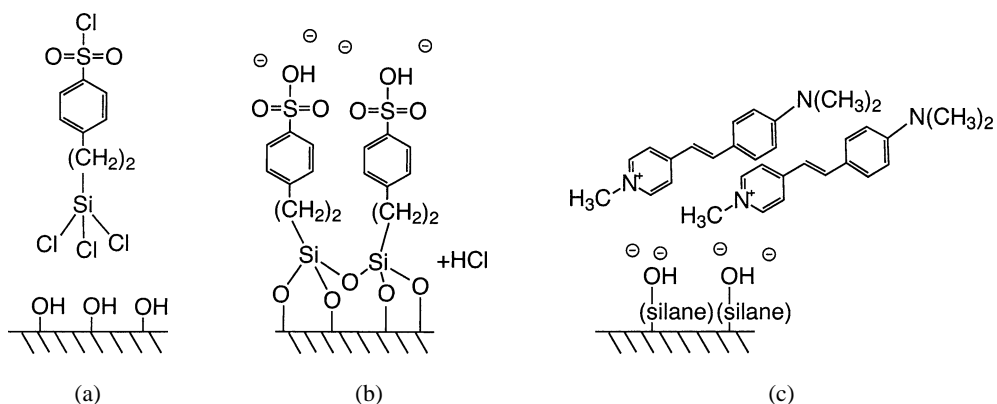


Figure 8. (a) 2-(4-chlorosulfonylphenyl)-ethyltrichlorosilane getting close to the quartz substrate. (b) The silanes are bound to the surface, rejecting HCl during the wet reaction. (c) 4'-dimethylamino-N-methyl-4-stilbazolium (the cation of DAST) approaching the acidic surface.

Figure 9. Microscope picture between crossed polarizers of a DAST single crystal with an area of 4 mm^2 grown by solution epitaxy. The measured thickness was between 10 and $35 \mu\text{m}$.



single crystal: $2 \times 2 \times 0.01\text{--}0.035 \text{ mm}$

anions and cations should start. We obtained single crystals with a surface area of 4 mm^2 as shown in Fig. 9. Nucleation in general was favored on such a surface-treated substrate. Although the crystal morphology was clearly modified in the thin plates solution epitaxy is a very promising approach and has to be further explored.

5. Conclusions and outlook

We have discussed established methods and new approaches for the fabrication of single crystalline thin films for electro-optic and nonlinear optical applications. Out of the new methods investigated, the most promising ones are the capillary method and solution epitaxial growth. Solution epitaxial growth showed good results, in particular with respect to the large area (4 mm^2) of these as-grown monocrystals. The thickness is to be further controlled with the growth temperature and temperature gradients.

The minimum thickness obtained throughout the different experiments was $10 \mu\text{m}$ (in the capillary growth with cell 3). Since the thickness depends mainly on the cell geometry, one has to concentrate on the development of a thinner cell, with the additional possibility to remove the films after growth.

Although we have concentrated our discussion on novel exploratory methods to grow thin films of DAST, most of the techniques can be extended to other material systems. We believe that our approaches will be very useful in the future and that there is large chance that the growth of high-quality single crystalline films for electro-optic and frequency-conversion devices becomes a reality.

Acknowledgements. This work has been supported in part by the Swiss National Science Foundation. Three of the authors dedicate this article to the memory of Marcel Ehrensperger our long-term crystal growth expert who unexpectedly died in 2000.

References

- [1] J. Zyss, I. Ledoux, *Chem. Rev.* 94 (1994) 77–105.
- [2] C. Bosshard, M. Bösch, I. Liakatas, M. Jäger, P. Günter, in: P. Günter (Ed.), *Nonlinear Optical Effects and Materials*, Springer-Verlag, 2000, p. 163.
- [3] L.R. Dalton, A.W. Harper, B. Wu, R. Ghosn, J. Laquindanum, Z. Liang, A. Hubbel, C. Xu, *Adv. Mater.* 7 (1995) 519–540.
- [4] Y.Q. Shi, C. Zhang, H. Zhang, J.H. Bechtel, L.R. Dalton, B.H. Robinson, W.H. Steier, *Science* 2888 (2000) 119–121.
- [5] S.R. Marder, J.W. Perry, C.P. Yakymyshyn, *Chem. Mater.* 6 (1994) 1137–1147.
- [6] F. Pan, G. Knöpfle, C. Bosshard, S. Follonier, R. Spreiter, M.S. Wong, P. Günter, *Appl. Phys. Lett.* 69 (1996) 13–15.
- [7] R. Spreiter, R. Bosshard, F. Pan, P. Günter, *Opt. Lett.* 22 (1997) 564–566.
- [8] S. Follonier, C. Bosshard, F. Pan, P. Günter, *Opt. Lett.* 21 (1996) 1655–1657.
- [9] U. Meier, M. Bösch, C. Bosshard, F. Pan, P. Günter, *J. Appl. Phys.* 83 (1998) 3486–3489.

- [10] P.Y. Han, M. Tani, F. Pan, X.-C. Zhang, *Opt. Lett.* 25 (2000) 675–677.
- [11] C. Bosshard, R. Speiter, P. Günter, *J. Opt. Soc. Am. B* 18 (2001) 1620–1626.
- [12] T. Kobayashi, S. Isoda, T. Maeda, A. Hosino, *Cryst. Prop. Prep.* 32–34 (1991) 731.
- [13] T. Gotoh, S. Fukuda, Yamashiki, in: S. Miyata (Ed.), *Nonlinear Optics*, Elsevier, Amsterdam, 1992, p. 219.
- [14] C. Cai, M.M. Bösch, Y. Tao, B. Müller, Z. Gan, A. Kündig, Ch. Bosshard, I. Liakatas, M. Jäger, P. Günter, *J. Am. Chem. Soc.* 120 (1998) 8563–8564.
- [15] J. Sakata, M. Mochizuki, *Thin Solid Films* 195 (1991) 175–184.
- [16] C. Bosshard, K. Sutter, P. Prêtre, J. Hulliger, M. Flörsheimer, P. Kaatz, P. Günter, *Organic Nonlinear Optical Materials*, Gordon and Breach, Amsterdam, 1995.
- [17] C. Bosshard, M. Küpfer, in: F. Kajzar, J.D. Swalen (Eds.), *Organic Thin Films for Waveguiding Nonlinear Optics*, Gordon and Breach, Amsterdam, 1996, p. 163.
- [18] D. Elwell, H.J. Scheel, *Crystal Growth from High-Temperature Solutions*, Academic Press, 1975.
- [19] F. Pan, K. McCallion, M. Chiapatta, *Appl. Phys. Lett.* 74 (1999) 592–595.
- [20] M. Thakur, Y. Shani, G.C. Chi, K. O'Brien, *Synt. Met.* 28 (1989) D595–D604.
- [21] P.J. Halfpenny, E.E.A. Shepherd, J.N. Sherwood, G.S. Simpson, in: G.R. Moehlmann (Ed.), *Proceedings of the SPIE*, Vol. 2025, 1993, p. 171.
- [22] S.T. Ko, T. Senge, S. Umegaki, *Nonlinear Opt.* 15 (1996) 197–204.
- [23] W. Qingwu, D.B. Sheen, J.N. Sherwood, G.S. Simpson, in: *Conference on Electro-Optics and Lasers*, OSA Technical Digest, Paper CWF37, Optical Society of America, Washington, DC, 1996, p. 281.
- [24] S. Gauvin, J. Zyss, *J. Cryst. Growth* 166 (1996) 507–527.
- [25] I.F. Nicolau, *J. Mater. Sci.* 6 (1971) 1049–1060.
- [26] M. Thakur, J. Xu, A. Bhowmik, L. Zhou, *Appl. Phys. Lett.* 74 (1999) 635–637.
- [27] K. Komatsu, H. Nanjo, Y. Yamagishi, T. Kaino, *Thin Solid Films* 393 (2001) 1–6.
- [28] T. Takayama, M. Yoshida, H.H. Deng, K. Komatsu, T. Kaino, *Nonlinear Opt.* 25 (2000) 413–418.
- [29] K. Takayama, K. Komatsu, T. Kaino, *Jpn. J. Appl. Phys.* 40 (2001) 5149–5150.
- [30] G.L. Bryant, C.P. Yakymyshyn, K.R. Stewart, *Acta Cryst. C* 49 (1993) 350–351.
- [31] W.S. Wang, J. Hulliger, H. Arend, *Ferroelectrics* 92 (1989) 113–119.
- [32] I.F. Nicolau, *J. Mater. Sci.* 5 (1970) 623–639.
- [33] J.C. Bryce, *The Growth of Crystals from Liquids*, North-Holland, Amsterdam, 1973.
- [34] M. Thakur, S. Meyler, *Macromolecules* 18 (1985) 2341–2344.
- [35] D. Zhi, M. Thakur, in: *Quantum Electronics and Laser Science Conference*, OSA Technical Digest, Paper QWD23, Optical Society of America, Washington, DC, 1995, p. 134.
- [36] L. Zhou, M. Thakur, *J. Mater. Res.* 13 (1998) 131–134.
- [37] Y. Kubota, Y. Yoshimura, *Appl. Phys. Lett.* 53 (1988) 2579–2581.
- [38] C. Bosshard, J. Hulliger, unpublished work, 1992.
- [39] A. Leyderman, Y. Cui, *Opt. Lett.* 23 (1998) 909–911.
- [40] T. Suhara, K. Suemoto, N.H. Hwang, H. Nishihara, *IEEE Photon. Tech. Lett.* 3 (1991) 241–243.