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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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Online publication date: 11 November 2010

To cite this Article Lelidis, I. and Öedman, C.(2003) 'Influence of substrate nature and growth conditions on the morphology of thin DMOAP films', *Liquid Crystals*, 30: 6, 643 – 649

To link to this Article: DOI: 10.1080/0267829031000094810

URL: <http://dx.doi.org/10.1080/0267829031000094810>

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Influence of substrate nature and growth conditions on the morphology of thin DMOAP films

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(Received 15 July 2002; in final form 2 December 2002; accepted 5 January 2003)

We report some preliminary results on the morphology of thin *N,N*-dimethyl-*n*-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP) films. When deposited on a glass substrate, DMOAP forms a mono- or multi-layer structure parallel to the substrate. The surface topography of the film is probed by atomic force microscopy. In general, the free surface of such a film is not flat and smooth. Islands and holes are formed on the free surface of the films when a sufficiently flat substrate is used. The thin film surface topography depends strongly on the nature of the bare substrate, the curing conditions, and the immersion time of the substrate in the DMOAP solution. The film is always rougher than the bare substrate used. Annealing roughens the surface of the alkoxy silane thin films deposited on a glass substrate. For films on glass plates covered with an indium tin oxide layer, annealing has minor effects. The surface topography affects the microstructure of homeotropic smectic samples.

1. Introduction

The uniform stable alignment of liquid crystals (LCs) over macroscopic areas on the surface of solid substrates is an important issue for both scientific and technological reasons [1, 2]. This is achieved by a suitable treatment of the substrates used to form the cell [3, 4]. The usual methods for producing uniformly oriented liquid crystal samples are SiO evaporation [5, 6], and coating of the substrate by thin films of polymeric materials [7]. In the latter case the surface anisotropy is usually obtained by rubbing or by photopolymerization [8]. The morphology of these thin films has been extensively studied for planar and tilted alignment by means of scanning probe microscopy [9, 10], X-rays [11, 12], scanning electron microscopy [13], neutron reflectivity [14], as well as by other methods. Less attention has been afforded to the topology of thin films which induce homeotropic alignment of the liquid crystal molecules. The topography of the substrate surface should be important particularly in the case of smectic LCs since smectic phases transmit deformations on a macroscopic scale [15, 16]. This means that even small irregularities on the surface of the substrate cause static deformations of the layers, extending to appreciable depths inside the smectic sample and eventually creating defects. Furthermore, surface defects may act as nucleation centres [17] for dislocation loops,

e.g. under contraction of a smectic sample. Recently, screw dislocations have been observed in homeotropically oriented smectics [18, 19] and they probably originate from substrate irregularities.

In this paper, we present some preliminary results on the surface morphology of thin films of *N,N*-dimethyl-*n*-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP, $\text{CH}_3-(\text{CH}_2)_{17}(\text{Me})_2\text{N}^+(\text{CH}_2)_3\text{Si}(\text{OMe})_3\text{Cl}^-$, where Me denotes methyl) deposited on various types of glass substrates, by dipping the substrate in a DMOAP solution. Topographical data of the substrate and of the thin DMOAP film are obtained by using atomic force microscopy (AFM). The influence of the nature of the substrate and the effect of curing conditions on the silane thin film topography are investigated. The thin film thickness and its profile are studied qualitatively as a function of the immersion time. The quality of the alignment is tested in smectic LC cells by polarizing optical microscopy (POM). The LC sample microstructure depends on the substrate topography. This work is the first part of a project to establish the relationship between surface irregularities on the substrate and screw dislocations [20] in thermotropic smectic liquid crystals.

2. Experimental

Bare float glass and indium tin oxide (ITO) coated float glass plates were used as substrates. The ITO-coated glass plates from Balzers have a squared resistance of 4Ω ,

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and their thickness is 1.2 mm. The bare float glass plates, 2 mm thick, were from Guinhard (Switzerland). In order to remove all organic and inorganic residues, the glass plates were cleaned in an ultrasonic agitator using successively, distilled water, a heated solution of a detergent (Deconex), acetone and isopropanol. Finally, they were rinsed in deionized water and blown dry with nitrogen gas. The glass plates were covered by a thin film of *N,N*-dimethyl-*n*-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP) by dipping in a stirred dilute solution of DMOAP (0.1% silane by volume in 10% distilled water, and isopropanol) for a few minutes (2–5 min). The silanization reaction was performed at room temperature. We did not attempt to study the influence of the silanization temperature on the thin film morphology [21]. Finally, the plates were rinsed with distilled water and dried at 110°C for 1 h under a nitrogen atmosphere.

The alkoxy silane is covalently bound to the substrate hydroxyl groups while the hydrocarbon chains are oriented perpendicular to the glass plates [7]. The molecules are tightly packed due to van der Waals interactions. The height of a monolayer is expected to be 2.7 nm [22], for a closed-packed monolayer (molecules standing upright). The curing process to dry the film, when done above the glass transition temperature, may serve to polymerize the silane monomers to form polysiloxanes, enhancing the stability of the film. Although considerably more than a monolayer of silane may initially be deposited on the substrate, the rinse procedure is believed [7] to leave essentially a monolayer of silane coating on the substrate.

To probe the surface morphology we used a Nanoscope dimension 3000, AFM from Digital Instruments. All scans were performed in the contact mode. The tip, mounted at the free end of the cantilever, was silicon nitride. The liquid crystal alignment was examined in thin cells by POM. We used a Leica DMRP optical microscope with an oven from Instec (mK) mounted on the stage of the microscope.

3. Results and discussion

3.1. AFM measurements

3.1.1. Insulating substrate

Figure 1 is an AFM image of a bare glass plate. The grey scale of the picture corresponds to the height range of the surface. The black level corresponds to the minimum of the height range and the white level to the maximum height. The full vertical, z , range from black to white is 6.6 nm. The surface is flat with a distribution of defects having lateral dimensions in the range 0.1–0.2 μm . The root mean square (rms) roughness ($R_q = (L^{-1} \int_0^L z^2 dx)^{1/2}$, where L is the linear dimension of the scanned area) is $R_q = 0.7$ nm, and the largest peak to valley height (LPVH) is 4.1 nm.

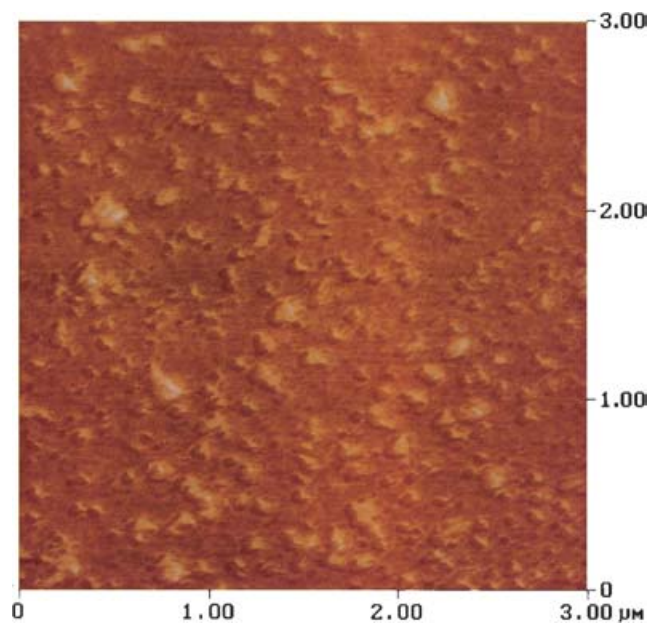


Figure 1. AFM image in contact mode of a bare glass substrate. The vertical range is 6.6 nm.

Table. Root mean square (rms) roughness and largest peak to valley height (LPVH) of the different substrates and of DMOAP thin films, for various drying conditions.

Substrate	Drying time /h	Drying temperature /°C	rms Roughness /nm	LPVH /nm
Bare glass			0.7	4.1
DMOAP film on glass plate	1	110	2.8	25.
After a first annealing	1	120	4.1	
After a second annealing	3	180	6.7	30.
After a second annealing	12	180	17.	
ITO-covered glass plates $R_{sq} = 4 \Omega$			1.8	8.1
DMOAP film on ITO-covered glass plates, $R_{sq} = 4 \Omega$	1	110	5.0	23.
DMOAP film on ITO-covered glass plates, $R_{sq} = 500 \Omega$	1	110	0.5	3.0

Figure 2 shows a region of the same glass plate after the deposition of a thin DMOAP film followed by a curing at 110°C for 1 h. The surface topography is characterized by hills and pores homogeneously distributed to the scanned surface. The diameter of the islands is around 40 nm. The rms roughness R_q has increased to 2.8 nm while the LPVH has become 25 nm, nevertheless the defect height does not exceed 15 nm from the background surface. The depth of the surface holes gives an estimate of the minimum film thickness. The deeper holes are 10.1 nm, i.e. the film is composed of at least four layers of DMOAP. From the differences in depth between surface holes we estimate the mean layer thickness to be 2.5 nm, in good agreement with the length of a monomer (2.7 nm).

Thus both the roughness of the bare glass and the LPVH are enhanced by the deposition of a DMOAP film. Note also that the film is at least four layers thick.

Curing the sample at 120°C for 70 min increases the roughness to 4.1 nm while the pores begin to disappear, whereas the surface hills grow. Additional annealing of the film for 3 h at 180°C yields the surface morphology shown in figure 3. The pores have completely disappeared. The rms roughness has increased to 6.7 nm, and the LPVH is now 30 nm. Upon annealing of the film for 12 h at 180°C the roughness reaches a value of around 17 nm. Figure 4 shows the roughness of the DMOAP film, annealed at 120°C, as a function of the annealing time for three samples. For sufficiently long annealing times all samples seem to attain an equilibrium state.

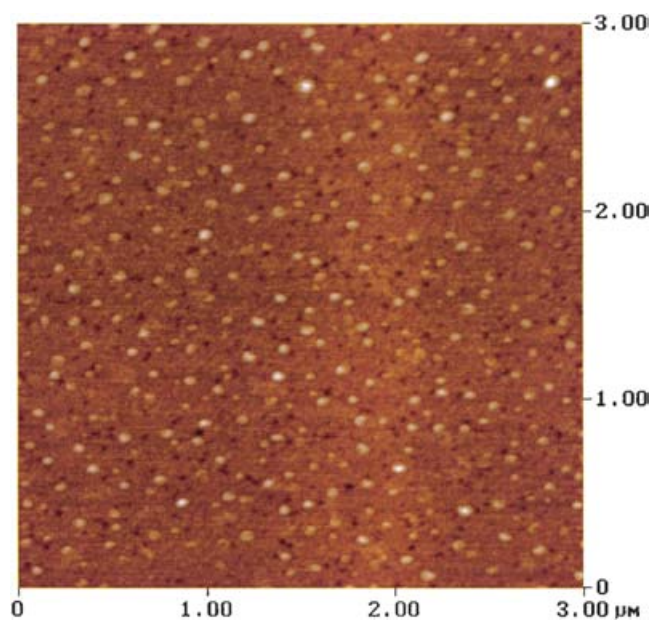


Figure 2. AFM image in contact mode of a DMOAP thin film deposited on a glass substrate and dried at 110°C for 1 h. Circular domains appear on the surface that are either valleys or hills.

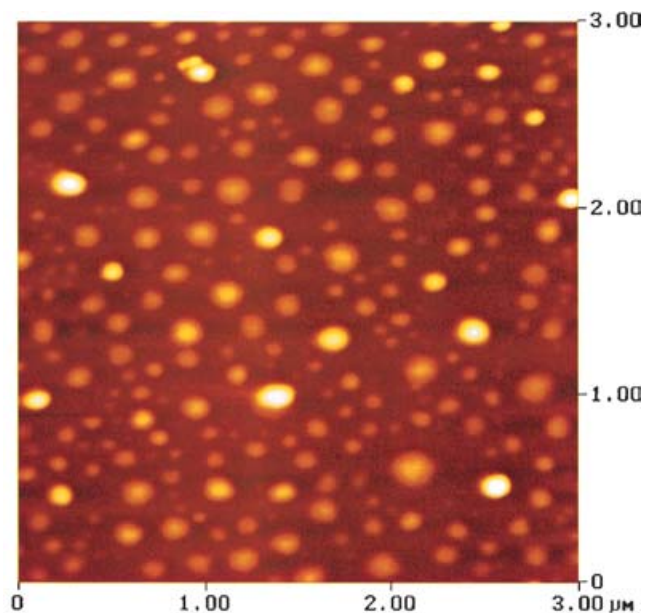


Figure 3. The DMOAP thin film shown in figure 2 after an additional drying at 180°C for 3 h. The valleys have disappeared while the hills have been enhanced.

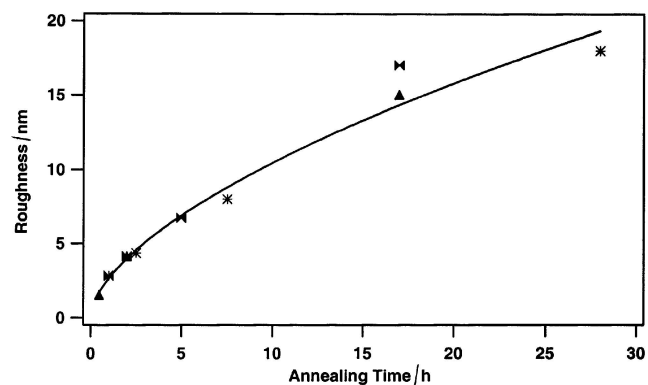


Figure 4. The dependence of roughness surface on annealing time for three samples of thin DMOAP films deposited on bare glass and annealed at 120°C.

We conclude that curing a DMOAP thin film, deposited on a glass plate, increases its roughness. Upon annealing, the number of circular domains at the free surface of the sample decreases while their diameter increases. The typical diameter of a domain initially is 40 nm. After the second annealing process it becomes 100 nm. This behaviour may mean that during annealing at temperatures higher than the glass transition temperature, T_g (90°C), of the polymer, islands on the top silane layer could serve as aggregation centres for molecules diffusing on the substrate during the thermal annealing procedure. The aggregates may grow by branching. In order to explain why the aggregation centres do not only grow laterally but also vertically, one could envisage permeation effects [23] due probably to desorption and to the different expansion

coefficients between the substrate and the polymer (their ratio is of the order of 10^3). As the silane film expands at the contact surface, significant stresses may appear and a way to relieve these may be via the permeation of molecules from the lower layers towards the free surface.

3.1.2. Conducting substrate

Figure 5 shows the typical surface morphology of an ITO covered glass plate with a square resistance $R_{sq} = 4 \Omega$. The surface is homogeneous and the microstructure is granular with a Gaussian distribution. The rms roughness is $R_q = 1.8 \text{ nm}$ and the LPVH is 8.1 nm . The typical grain diameter is around $0.4 \mu\text{m}$ with a height of 4.5 nm . Thus and as expected, low square resistance ITO-covered plates are rougher than float glass plates.

Figure 6 shows the surface morphology of a DMOAP thin film deposited on a glass plate coated with an ITO electrode; the film was dried at 110°C for 1 h. The surface morphology is similar to that seen before the deposition of the alkoxy silane film. The rms roughness increases to 5 nm and the LPVH is now 23 nm . The typical grain diameter remains around $0.4 \mu\text{m}$.

We note that the ITO-coated glass roughness is increased by deposition of DMOAP. Further annealing of the polysilane thin film reveals no significant influence on the roughness. This behaviour may indicate that on sufficiently rough substrates the diffusion of the silane molecules slows down.

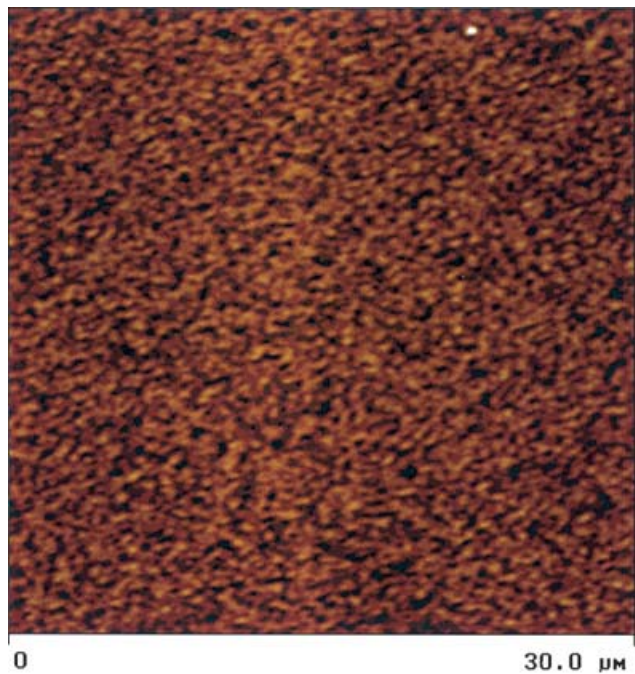


Figure 5. AFM image in contact mode of an ITO-covered glass substrate with $R_{sq} = 4 \Omega$. The surface morphology is granular.

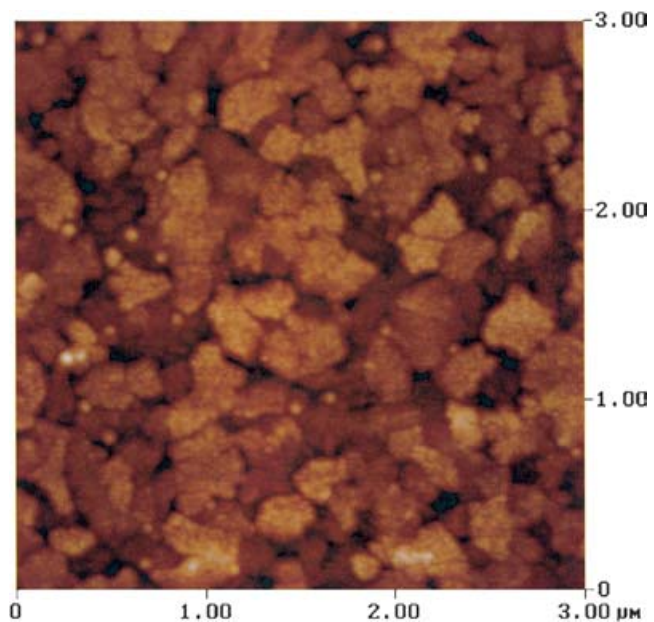


Figure 6. AFM image in contact mode of a DMOAP thin film deposited on an ITO-covered glass substrate and backed at 110°C for 1 h.

In order to establish the influence of the substrate roughness on the DMOAP film roughness without changing the nature of the substrate, we deposited a DMOAP film on a glass plate covered with an ITO layer of $R_{sq} = 500 \Omega$. As the grain size of ITO is much smaller, the substrate roughness reduces to the Ångstrom range. Figure 7 shows

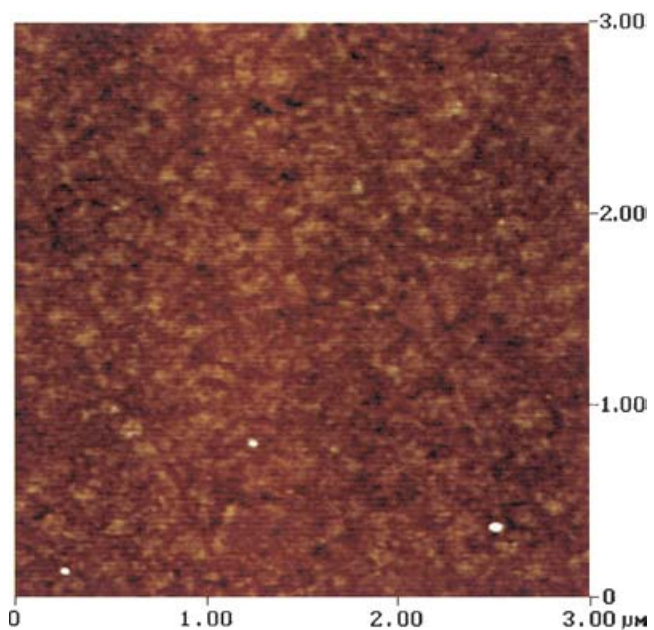


Figure 7. AFM image in contact mode of a DMOAP thin film deposited on a glass substrate with $R_{sq} = 500 \Omega$, and annealed at 110°C for 1 h. The film is flat and featureless.

the thin DMOAP film topography, which is essentially flat and featureless. The rms roughness is 0.6 nm, i.e. one order of magnitude lower than the observed roughness of DMOAP films on ITO, with an $R_{sq} = 4 \Omega$, covered glass plates. This measurement clearly demonstrates that the surface topography of the thin DMOAP film depends directly on the roughness of the substrate used to deposit the film.

Figure 8 gives a cross-section of a silane film, cured at 110°C for 1 h, on: (a) a bare glass plate and (b) an ITO (with $R_{sq} = 4 \Omega$) covered glass plate. Comparing the bare glass substrate with the ITO-coated glass, one notes that the latter is rougher (before prolonged annealing). Another difference between the morphology of silane-coated bare glass and ITO covered glass is that in the former case closed spike-like textures on a base line are observed while in the latter case the textures are open as can be seen in figure 8. The typical diameter of the domains for the film on ITO-covered glass plates is one order of magnitude larger than the diameter of the domains on the bare glass plates.

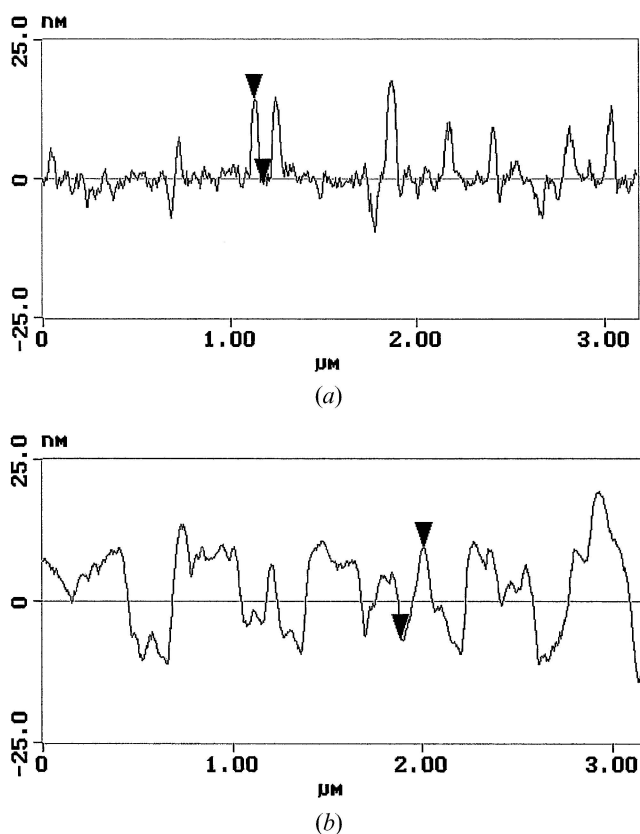


Figure 8. The surface profile along a line of a DMOAP thin film deposited: (a) on a bare glass plate, and (b) on an ITO-covered glass plate. Closed structure is observed on the former substrate, and open structure on the latter. Both films were cured at 110°C for 1 h.

3.2. Immersion time

As the thin film is deposited by dipping the glass plates in a DMOAP solution it is expected that the morphology of the film surface should be influenced by the immersion time [21]. For very short immersion times (less than 30 s) DMOAP islands appear on the substrate and with increasing immersion time (up to 60 s) an almost entire layer covers the substrate but it appears to be porous. The typical pore diameter is about $2 \mu\text{m}$. Both films were cured for 1 h at 110°C . Figure 9 shows the topograph of a glass plate immersed in the silane solution for 120 s and cured for 1 h at 110°C . Large silane islands appear on an otherwise perfect silane monolayer. The height of the islands is a multiple of the height of a monomer. Finally, for very long immersion times (more than 10 min), large aggregates of DMOAP appear on the surface. No further study of the coverage fraction as function of the immersion time has been attempted in the present work.

3.3. 2D Fourier Transform

The structure of the surface of the thin films can be deduced from reciprocal space by performing 2D Fourier Transform (2D-FT) on the images in the real space. For figure 2, that contains hills and holes, we performed a 2D-FT for each species. Both are isotropic diffuse rings but with different characteristic lengths: for the hills $\xi_+ = 0.16 \mu\text{m}$ and for the holes $\xi_- = 0.3 \mu\text{m}$. The 2D-FT obtained from figure 3 exhibits only one diffuse isotropic ring, i.e. the topology can be described by a unique

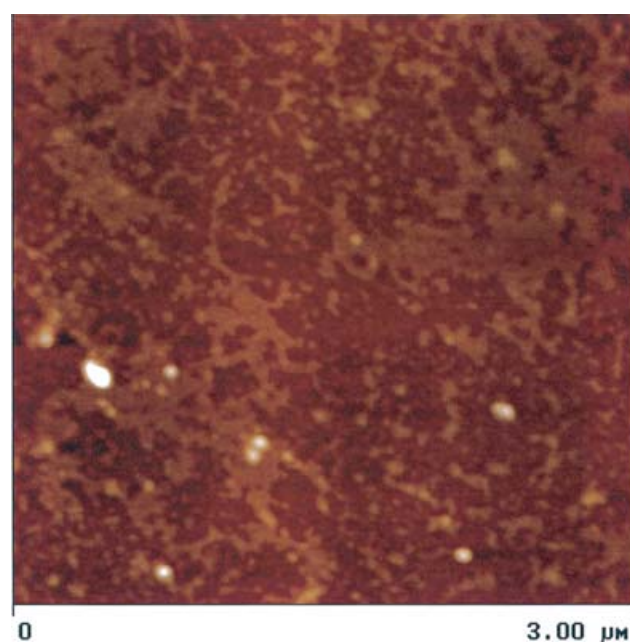


Figure 9. AFM image of a DMOAP thin film deposited on a glass plate, immersion time 120 s. Large islands are superimposed on a perfect silane monolayer. The step height is 2.5 nm.

characteristic length $\xi_+ = 1.4 \mu\text{m}$ corresponding to the hills. After annealing the holes disappeared. The characteristic length ξ_+ increases with time during annealing of the sample. At times $t = 60$ and 300 min, ξ_+ increases from 0.16 to $1.4 \mu\text{m}$. In conclusion the topology of the hills described by the evolution of a characteristic length, i.e. a spatial self-similarity describes the evolution of the morphology. In the case of films deposited on ITO-covered glass, the granular structure of the substrate dominates the surface topography, and therefore we were unable to extract information concerning the structure of the DMOAP thin film.

3.4. Anchoring

It is well known that glass plates covered by alkoxy-silane thin films are used as anisotropic substrates to orient liquid crystals, inducing homeotropic anchoring. The liquid crystal alignment is examined in thin cells by POM. A typical cell is composed of two glass plates, and this is filled with the fluorinated octyloxyphenyl octyloxybenzoate (BDH173), which exhibits an isotropic–smectic A (SmA) phase transition at 77.7°C , and a monotropic SmA–SmC transition at 55°C . The liquid crystal is introduced into the cell in the isotropic phase by capillary action. All cells gave good uniform homeotropic alignment for immersion times from 1 to 5 min. Cells made using glass plates immersed for much longer times in the DMOAP solution contained many defects when observed by optical microscopy, probably due to silane aggregates on the glass plates. A more sensitive method with which to reveal any influence of the glass plate surfaces on the smectic phase microstructure, should be the observation of the microstructure of smectic defects which do not significantly alter the homeotropic orientation of the LC molecules, e.g. edge dislocations. Therefore, we prepared cells with a wedge geometry and cooled the sample close to the SmA–SmC transition. As expected [24], edge dislocations appear (figures 10, 11). Their microstructure is quite different depending on the density ρ of undulations or spikes on the cell solid boundaries (a detailed study will be presented in ref. [25]). Figure 10 shows edge dislocations in a cell with $\rho = 1.5 \times 10^7 \text{ cm}^{-2}$ while in the case of figure 11 the density is $\rho = 3 \times 10^5 \text{ cm}^{-2}$. Both cells are $2 \mu\text{m}$ thick. The edge dislocations are fragmented due to their pinning on other defects which are identified elsewhere as screw dislocations [26]. These preliminary results show the importance of the anchoring quality on the smectic microstructure. The latter should be the origin of the discrepancies that prevent measurements of the smectic modulus of compression.

4. Conclusions

In this work, we have investigated the surface topology of thin DMOAP films, deposited from a solution of the

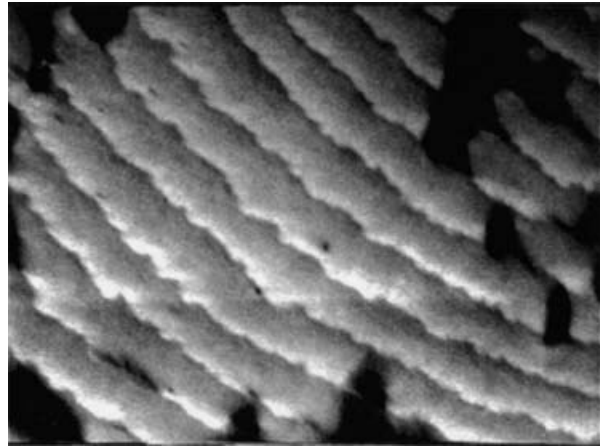


Figure 10. Edge dislocations, under slightly uncrossed polarizers, in a wedge-like smectic A cell: the edge dislocations are fragmented and cause strongly pinned-on screw dislocations. The period of dislocations is $11.8 \mu\text{m}$.

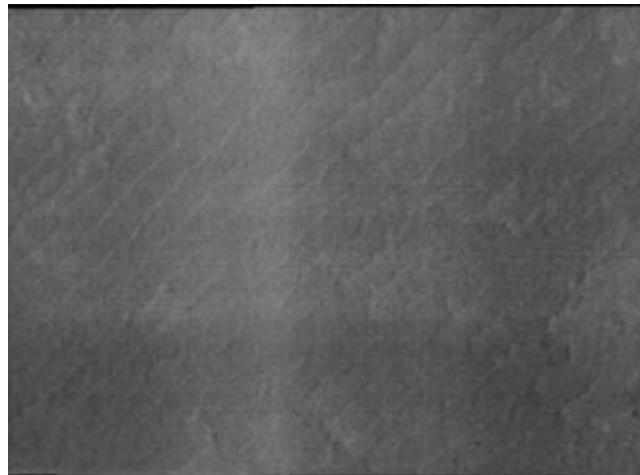


Figure 11. Edge dislocations in a wedge-like smectic A cell: the edge dislocations are less fragmented than those in figure 10. The period of dislocations is $11.6 \mu\text{m}$.

alkoxysilane on glass substrates. AFM studies reveal that the roughness of a thin alkoxy-silane film is affected by the substrate nature, the immersion time, the drying time and the drying temperature. The deposition of an alkoxy-silane film increases the roughness of the substrate for both bare glass plates and ITO-covered glass plates. In the case of thin films deposited on glass plates, the surface roughness is further enhanced by annealing, while this has a minor influence on thin films deposited in ITO glass plates. In the case of a bare glass substrate coarsening processes are observed. Excess alkoxy-silane monomer aggregate to some centres on the surface. It would be interesting to study the growth kinetics during annealing of the circular domains that appear when DMOAP films are deposited on bare glass substrates. The DMOAP thin film deposited on a bare glass substrate

is usually composed of several layers. The smectic phase microstructure is related to the substrate surface as the microstructure around edge dislocations reveals.

We would like to acknowledge M. Kléman and J.-L. Martin for suggestions and critical reading of the manuscript. We thank A. Karimi for use of the AFM facility. Finally, we acknowledge financial support from the Fonds National Suisse de la Recherche Scientifique.

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