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Anchoring of nematic liquid crystals on terraced silicon surfaces

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Anchoring of nematic liquid crystals on silicon surfaces slightly tilted with respect to the (001), (110), or (111) crystollographic planes is studied. It is found that the silicon crystal and the terraced structure of these surfaces play different roles in the determination of the anchoring directions of the nematic liquid crystals. The first one determines the azimuthal orientation of the anchoring directions that are found to be that of the twofold axes of the silicon crystal parallel to the surface of the terraces. For [001] orientation, this leads to a bistable anchoring; for [111] orientation, the expected tristable anchoring is not observed and only one anchoring direction is induced. The terraced structure determines the tilt of the anchoring directions with respect to the mean surface of the substrate. The experimentally measured tilt is not the one expected if the nematic molecules simply lay parallel to the terraces composing such vicinal surfaces. It is shown that besides this contribution of the terraces, one must also take into account the contribution of the steps separating these terraces.

I. INTRODUCTION

The orienting action of solid surfaces on nematic liquid crystals was first pointed out by Mauguin,[1] who has studied the behavior of nematic liquid crystals on the surface of cleaved mica. Since then, the orientation—or anchoring—of nematic liquid crystals on the cleavage surfaces of different crystals has been studied by several authors.[2–7] Although this kind of substrate is difficult to use for applications, it is very interesting from a fundamental point of view: in contrast to most of the substrates obtained by treating glass surfaces,[8] the crystalline substrates have a well-defined and known structure, which makes it easier to understand the microscopic interactions responsible for anchoring.

We have studied the anchoring directions induced by different commercially available silicon wafer surfaces. These surfaces were obtained by cutting monocrystalline silicon ingots in a direction near—but not along—a cleavage plan and polishing the surface. This means that the surface is made of not one macroscopic plane, as one would obtain by cleavage, but of a succession of terraces separated by steps. Such substrates allow us to study at the same time the influence on the nematic orientation of the silicon crystal on the one hand, and of the terraced structure of these surfaces on the other hand.

We will first describe the method of preparation and the structure of silicon surfaces we have used (Sec. II) and our method of investigation of the anchoring directions of nematic liquid crystals (Sec. III). Section IV will present the different anchorings induced by silicon surfaces depending on the crystallographic orientation of the terraces, the tilt of the mean surface plane with respect to this orientation, and the time interval between the obtention of a pure silicon surface by chemical etching and its use as orienting substrate for nematic liquid crystals. We will show that in the case of pure silicon surfaces, the structure of the silicon crystal is responsible for the determination of the azimuthal orientation of the nematic liquid crystal and the terraces and steps are responsible for the determination of the tilt of the anchoring directions.

II. STRUCTURE OF SILICON SURFACES

The position of silicon atoms located at the surface differs from the one they would have in the crystal bulk. The structure of this first atomic layer depends greatly on the way the surface is cleaned and the conditions under which it is stored. The surfaces we have studied have been chemically cleaned the following way: they have been first cleaned in three successive baths (trichlorethylene, ethanol, and aceton) in order to remove organic impurities. Then they have been put in a buffered hydrofluoric acid bath (NH_4F:HF 7:1) in order to dissolve the layer of native oxide formed at the surface during its stay in the air. Two monolayers of silicon hydroxide have been formed afterwards by putting the wafers in a solution of sulfuric acid and hydrogen peroxide (H_2SO_4:$H_2O_2$1:1). This hydroxide has been finally removed with a solution of hydrofluoric acid in ethanol (C_2H_5OH:HF 10:1) and the surfaces have been rinsed with ethanol and dried with nitrogen. This treatment leads to pure silicon surfaces whose first atomic layer is

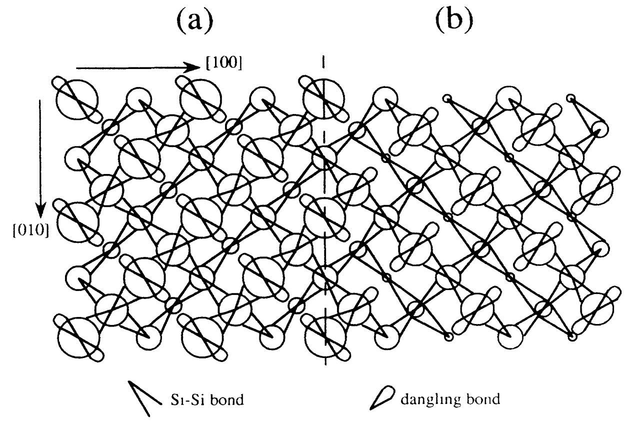

FIG. 1. The structure of two successive terraces on a surface with [001] orientation. The decreasing sizes of the circles correspond to Si atoms belonging to atomic planes located at an increasing depth in the crystal.

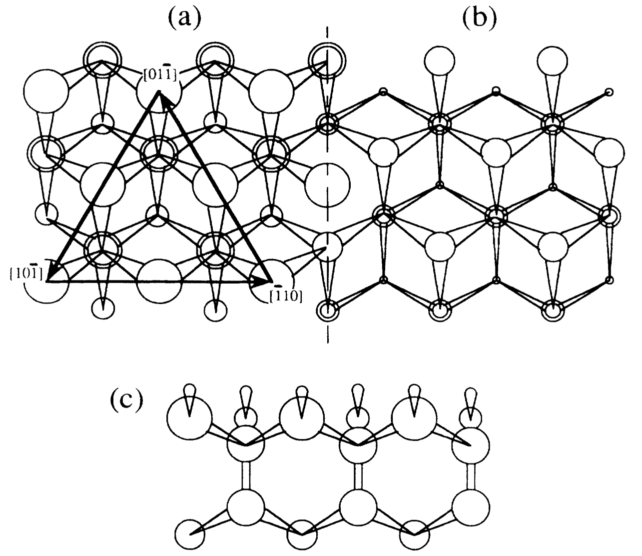

FIG. 3. (a),(b) Same as Fig. 1 for the [111] orientation. (c) Cross section parallel to the [$\bar{1}$10] axis of the terrace presented in (a).

reconstructed locally but in an incoherent way over the whole surface. This incoherence leads to an amorphous first layer.

The surface atoms have dangling bonds; when the surface is kept in air–as was the case with our surfaces—these atoms bond covalently with oxygen atoms to create an oxide layer. The thickness of this layer is about a tenth of a monolayer 1 min after cleaning[9] and reaches an equilibrium value of 14 Å after a few days.[10]

The structure of the surface thus changes with time as the oxide layer grows. Figures 1–3 describe the structures of pure silicon surfaces oriented perpendicular to [001], [110], and [111] axes without any reconstruction of the surface, They correspond to the structures of the surfaces just after cleaning, except the first atomic layer, whose layout is undefined. These structures are altered by the formation of the oxide layer which is amorphous.[11]

III. ANCHORING INVESTIGATION METHOD

The investigation of the anchoring directions has been made by depositing nematic droplets on the surface. This method is based on the selection of anchoring by wetting which has been extensively described elsewhere.[12,13] We recall here only the principle of the method

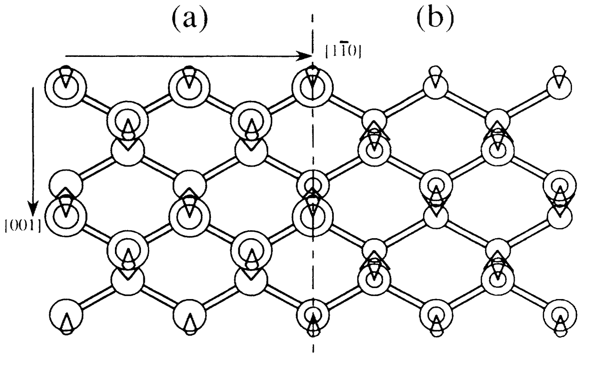

FIG. 2. Same as Fig. 1, for the [110] orientation.

The wetting of a solid substrate by a liquid is a dynamical process uniting two interfaces: the liquid-air interface and the solid-air interface. These two interfaces unite at the contact line whose motion leaves behind the liquid-solid interface.[14] This motion results from a current in the liquid that carries the molecules located at the liquid-air interface towards the contact line until they reach the solid surface where they become at rest with respect to the substrate.[15,16]

When the liquid is nematic, the orientation of the molecules at the nematic-air and nematic-solid interfaces are fixed by the anchoring conditions at these interfaces. In general, this results in a different orientation of the nematic liquid crystal at these two interfaces. When the nematic molecules that are at the nematic-air interface move toward the contact line, they interact progressively with the solid substrate. This interaction makes their orientation evolve and finally adopt a direction corresponding to a minimum of the potential of interaction between the substrate and the nematic liquid crystal. During this evolution, a choice has to be made between the different anchoring directions possible on the substrate. We have shown that this choice depends on the wetting conditions characterized by the direction of the wetting flow and the contact angle.

The spreading of a droplet is a wetting process during which all the points of the nematic-substrate interface created by the spreading are wetted with different conditions. So the inside of the spread droplet is divided into several domains where different anchoring directions have been selected. Moreover, the spreading is radial and the contact angle evolves from π when the droplet touches the substrate to zero when the droplet is completely spread; all the wetting conditions are explored by such a wetting process and all the anchoring directions induced by the substrate are found in the droplet.[17]

From the observation under a polarizing microscope of the texture of a nematic droplet spread on a substrate, one can deduce the following.

(1) The number of anchoring directions induced by the substrate from the number of domains with different orientations existing in the spread droplet.

(2) The azimuthal orientation of the projection of the anchoring directions in the substrate plane by determining the orientations of the substrate for which the extinction of the different domains is obtained.

(3) The tilt of the anchoring directions from the shape of the walls separating the domains with different orientations.

The last determination is only valid for nematic liquid crystals—as the one we have used in the experiments presented here—having homeotopic anchoring conditions at the nematic-air interface, that is to say when the molecules are perpendicular to this interface. In the case of the other anchorings at the free nematic surface (conical or planar), the relation between the droplet texture and the shape of the potential of interaction of the nematic liquid crystal with the substrate is not known yet with a sufficient precision to allow such a determination. Moreover, this determination of the tilt of the anchoring directions is only qualitative: one can distinguish between planar anchorings, with which one gets only diametral walls (Fig. 4), and tilted anchorings, for which at least one wall is a closed line (Fig. 5). From the position of this closed wall in the droplet, one can estimate the order of magnitude of the tilt angle and compare the tilt angles obtained on different surfaces. This method is more sensitive to small tilt angles than other known methods[18] and allows us to detect extremely small anchoring tilt angles (Table I).

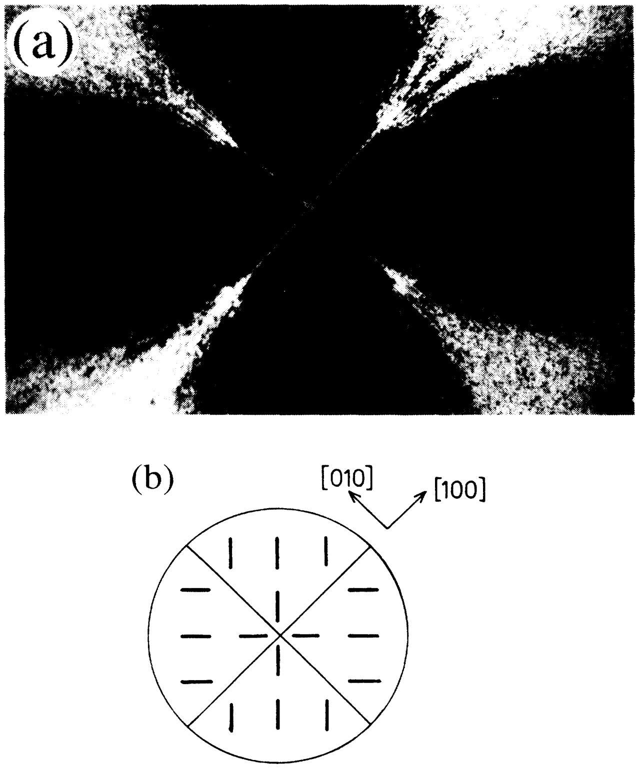

FIG. 4. Texture of a nematic droplet spread onto a [001] silicon surface inducing planar anchoring directions (surface number 1 in Table I). Under a polarizing microscope (a), the droplet appears with four dark domains of uniform orientation, given in (b), separated by bright lines. These lines are walls in which the nematic orientation rotates from one anchoring direction to the other. The walls are diametral straight lines, which is characteristic of a planar anchoring.

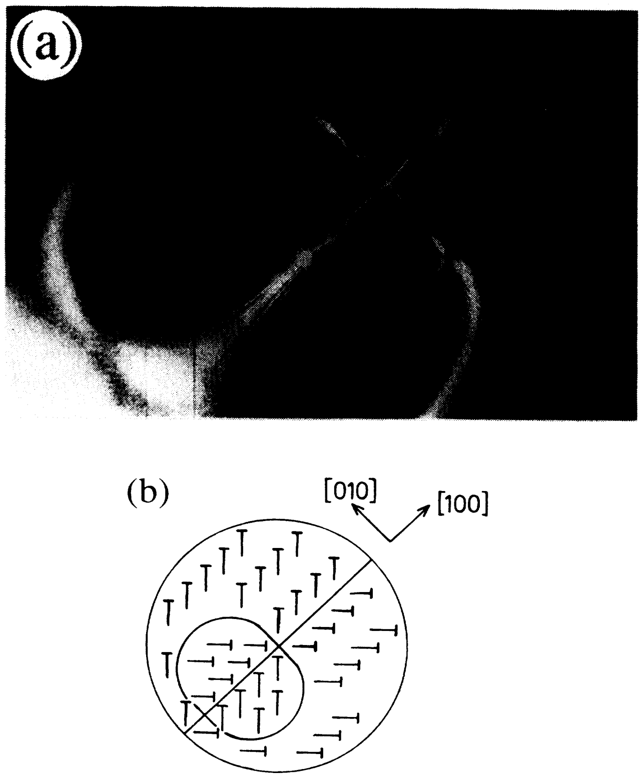

FIG. 5. Same as Fig. 4 for a [001] silicon surface inducing tilted anchoring directions (surface number 3 in Table I). One of the walls separating the domains with different anchoring directions is a solid line, which is characteristic of a tilted anchoring.

IV. ANCHORING INDUCED BY SILICON SURFACES

We have used the nematic mixture *E*8 from British Drug House Chemicals (BDH) which is composed of cyanoalkylbiphenyls, cyanoalkoxybiphenyls, and cyanoalkylterphenyls (*n*CB, *n*OCBB, and *n*CT in Table II). We have first studied the anchoring induced just after cleaning by silicon surfaces slightly tilted with respect to (001), (110), or (111) crystallographic planes (Table I). The values and directions of tilt of the silicon surfaces have been measured by x-ray diffraction. The error over the tilt angle is of the order of 0.1° and over the tilt direction of 1°.

We have used only well-polished surfaces presenting no scratches. When the surface is scratched, the nematic liquid crystal orients parallel to the mean direction of the scratches as it has already often been observed since the first use of rubbed substrates by Chatelain.[19]

From the anchorings observed on the different surfaces

TABLE I. Characteristics of the different silicon surfaces we have studied and the anchoring tilt angle δ_a they induce. α is defined in Figs. 6–8; h, w, β, p, and α_e in Fig. 9.

Orientation	[001]					[110]	[111]			
Step height h (Å)	1.3					1.9	3.0			
Surface number	1	2	3	4		5	6	7	8	9
Figure	6(a)	6(a)	6(a)	6(b)		7	8(a)	8(b)	8(c)	8(d)
Tilt α (deg)	0.3	0.5	4.0	0.8		2.5	<0.2	3.5	1.6	2.3
Terrace width w (Å)	240	138	19	92		44	>859	49	107	75
Angle between anchoring and step directions β (deg)	45	45	45	90	0	3		0	30	46
Effective periodicity p (Å)	339	195	27	92	∞	841		∞	214	104
Effective tilt α_e (deg)	0.2	0.4	2.8	0.8	0	0.1		0	0.8	1.6
Anchoring tilt δ_a (deg)	0	$\sim 10^{-1}$–10^{-2}	~ -1	$\sim 10^{-1}$–10^{-2}	0	$<10^{-2}$	0	0	$\sim 10^{-1}0^{-2}$	$\sim 10^{-1}$–10^{-2}

and given in Figs. 6–8, one can deduce the anchoring directions imposed by the silicon crystal and the effect of the terraced structure of the surfaces.

A. Azimuthal orientation induced by silicon crystals

All the anchoring directions induced by the silicon surfaces we have studied are either planar—laying parallel to the surface—or slightly tilted, with tilt angles of the order of 1° or less depending on the tilt between the mean silicon surface and the crystallographic planes forming the terraces. This means that on an ideal silicon surface made of one macroscopic crystalline plane, planar anchorings would be obtained and this is confirmed by the observations made on the surface number 6 [Fig. 8(a)] presenting no measurable tilt between the surface plane and the (111) crystallographic plane—the surface numbers along with their characteristics are defined in Table I.

All the silicon surfaces we have studied induce anchoring directions in nematic liquid crystals that are parallel to the twofold axes of the surfaces. When the surface is perpendicular to a twofold axis ([110] orientation), there is only one twofold axis and we observe a monostable anchoring (Fig. 7). When the surface is perpendicular to a fourfold axis ([001] orientation), there are two such twofold axes perpendicular to each other and we observe a bistable anchoring (Fig. 6).

For [111] orientation, the surface has three equivalent twofold axes, and we would expect a tristable anchoring. The experiment shows that only one of the three possible anchoring directions is induced by the surface (Fig. 8). This direction is the same over the whole surface and does not change after successive cleanings which remove several atomic layers. Moreover the choice of the anchoring direction shows no correlation with the direction of the steps existing on the surface. This can be seen, for instance, on the surface number 8 [Fig. 8(c)]: the presence of the steps cannot discriminate between the $[0\bar{1}1]$ and $[10\bar{1}]$ directions whereas only the $[10\bar{1}]$ direction is chosen as anchoring direction. This symmetry breaking could be explained by a surface deformation created upon

TABLE II. Composition of the nematic liquid-crystal $E8$ and molecular length of the components.

Nematic liquid crystal	5CB	3OCB	5OCB	8OCB	5CT
Weight proportion (%)	43	17	13	17	10
Molecular length (Å)	18	16	19	23	22

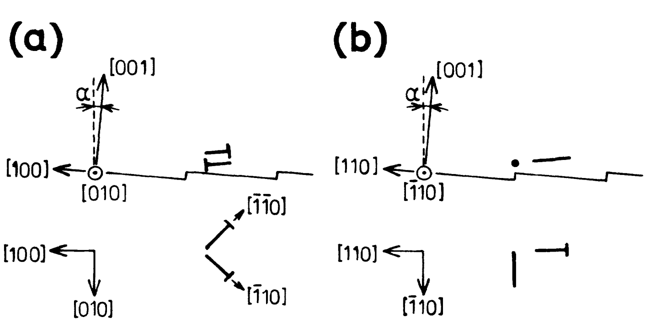

FIG. 6. Anchoring induced by vicinal [001] surfaces cut with different directions of tilt α between the surface normal and the [001] axis: (a) tilt direction [100]; (b) tilt direction [110]. In each case, the figure gives a side view parallel to the steps (up) and a top view (down). The anchoring directions are represented by nails whose heads stick out of the figure plane.

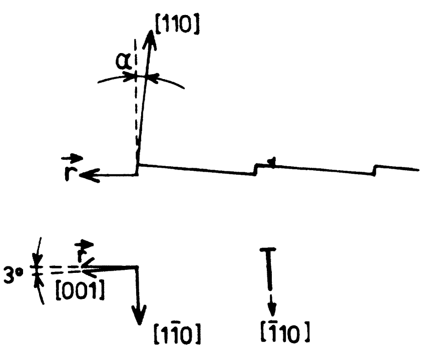

FIG. 7. Anchoring induced by a vicinal [110] surface cut with a tilt α of 2.5° between the surface normal and the [110] axis. The surface normal is tilted towards the direction **r** making an angle of 3° with the [001] axis. See the caption of Fig. 6 for details.

cutting the crystal. But in that case, we would also expect such a deformation to occur on the [001] surfaces.

The choice of the twofold axes as anchoring directions for the nematic liquid crystal on the silicon surfaces may result from two different types of interactions. The first ones are steric interactions: the nematic molecules prefer to lay parallel to the grooves existing between rows of silicon atoms at the surface in the direction of the twofold axes (Figs. 1–3). This seems, in fact, quite unlikely, because as the first atomic layer is incoherently reconstructed, the grooves existing on an ideal nonreconstructed surface must disappear.

The interactions of the second type are the interactions between the nematic molecules and the silicon atoms which result in a potential of interaction whose minima correspond to the twofold axes. There are two components in this potential: the first one is the contribution of the first atomic layer which gives an isotropic term because of its incoherent structure, the second one is the contribution of the rest of the silicon crystal which is responsible for the orientation of the nematic molecules. This shows that the interaction between the nematic molecules with the silicon atoms located in the crystal deeper than the first atomic layer is sufficiently important to provide a good orientation of these molecules. The importance of this interaction of nematic liquid crystals with nonsuperficial layers of the substrate has already been shown in the case of muscovite mica substrates, in which the surface layer inducing orientation in nematic liquid crystals is approximately 14 Å thick.[20]

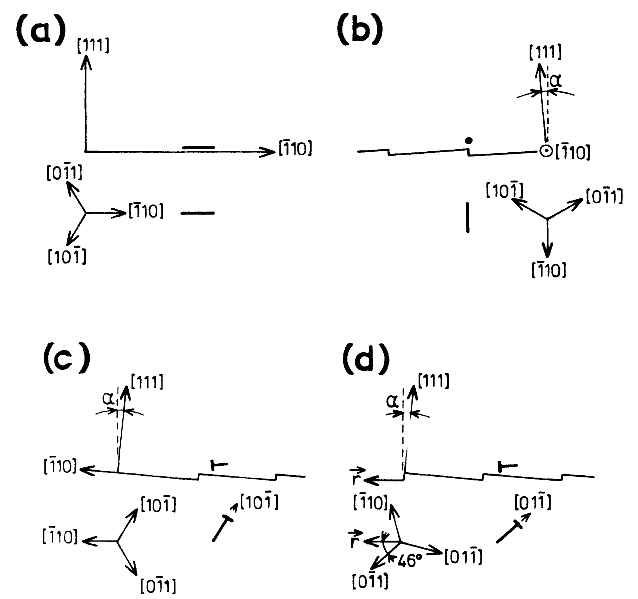

FIG. 8. Same as Fig. 6, for vicinal [111] surfaces: (a) no tilt; (b) tilt around the $[\bar{1}10]$ axis; (c) tilt direction $[\bar{1}10]$; (d) tilt direction **r** making an angle of 46° with the $[0\bar{1}1]$ axis.

B. Tilt induced by the terraced structure of the silicon surfaces

It is natural to think that the existence of the tilt of the plane of the terraces forming the substrate surface with respect to the mean plane of the substrate induces a tilt of the anchoring directions of the nematic liquid crystal. Indeed as the nematic molecules lay parallel to the terraces, they should be tilted with respect to the substrate surface. Because the projection $\mathbf{d}_a$ of an anchoring direction on the plane of the substrate is, in general, not perpendicular to the direction of the steps, the tilt induced by this mechanism is not equal to the tilt α of the terrace plane with respect to the substrate surface but to an effective tilt angle α_e given by (Fig. 9):

$$\tan\alpha_e = \frac{h}{p} , \tag{1}$$

where h is the height of the steps and p is the effective periodicity of the steps along the anchoring direction $\mathbf{d}_a$ (Fig. 9):

$$p = w \sin\beta , \tag{2}$$

β being the angle between $\mathbf{d}_a$ and the direction of the steps.

When the anchoring direction induced by the silicon crystal is parallel to the steps ($\beta = 0°$), the effective tilt is

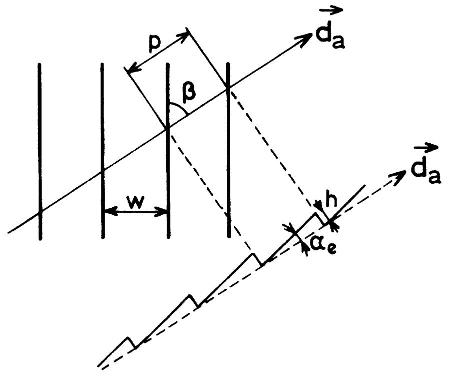

FIG. 9. Definition of the effective periodicity p and effective tilt α_e of the terraces and steps seen by the nematic molecules. $\mathbf{d}_a$ is the projection onto the substrate surface of the anchoring direction, β is the angle between $\mathbf{d}_a$ and the direction of the steps, and w is the width of the terraces.

zero and no tilt of the anchoring is observed. This is the case for the surface number 7 [Fig. 8(b)] and for one of the anchoring directions on the surface number 4 [Fig. 6(b)].

On the surface number 5 (Fig. 7), the effective tilt is 0.1° but the obtained anchoring tilt seems to be much smaller (Table I). On the surface number 1 [Fig. 6(a)], the anchoring directions show no tilt although the effective tilt is 0.2°. Even more striking is the result obtained on surfaces numbers 2–4 [Fig. 6(a)] and 8 and 9 [Figs. 8(c) and (d)]: the anchoring tilt obtained on these surfaces is negative (Table I), which means that the nematic molecules are tilted in an opposite way to the one imposed by the terraces. This shows that the terraces are not the only elements of the surface influencing the tilt of the nematic molecules and that the mechanism described above is not valid.

The other elements that can have an influence on the anchoring tilt are the steps separating neighboring terraces. A simple way of taking this into account is to consider only the steric effects of the steps. When a nematic molecule is located on a step, it mus be tilted with respect to the substrate surface by an angle $-\delta_s$ given by

$$\delta_s = \arcsin\left[\frac{h}{a}\right] , \tag{3}$$

where a is half the length of the molecule (Fig. 10). So the steps induce locally a negative tilt on the nematic molecules.

The macroscopic anchoring tilt angle δ_a observed experimentally results from the propagation to the bulk nematic liquid crystal of the tilt of the molecules located near to the substrate. When this locally induced tilt varies on the substrate surface, δ_a is an average of the different local tilts. So in our case, δ_a must be the sum of two terms, one describing the influence of the terraces and the other describing the influence of the steps.

When the density of steps is sufficiently high, which corresponds to a sufficiently short effective periodicity p, the influence of the steps is greater than the one of the terraces and δ_a is negative. When the periodicity p increases, the influence of the steps decreases and becomes equal to one of the terraces; δ_a is zero as in the case of surface number 1. For even greater periodicities, the terraces dominate and δ_a is positive as in the case of surface number 5.

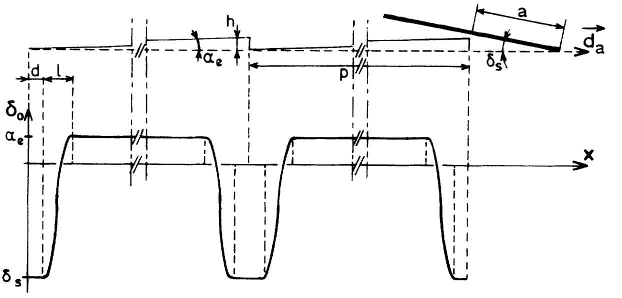

FIG. 10. General form of the variation of the tilt δ_0 imposed locally to the nematic molecules by a terraced silicon surface.

In order to check the validity of this mechanism, we have made a simple calculation of the values of δ_a predicted when the influence of the steps is taken into account and we have compared them with our experimental results.

The principle of our calculation is the following: we consider a (x,z) two-dimensional half-space filled with nematic molecules laying in the (x,z) plane and making an angle $\delta(x,z)$ with the x axis. The half-space is limited in $z=0$ by a terraced surface of periodicity p, step height h, and tilt of the terraces α_e. This surface models the terraced silicon surface seen by the nematic molecules whose projection on the surface plane is $\mathbf{d}_a$ which coincides with the x axis of our model surface (Fig. 10). Our two-dimensional system assumes implicitly that the steps are perpendicular to the (x,z) plane, so it models only the experimental situations where $\beta=90°$; but one can check that the value of the macroscopic tilt δ_a is independent of β when all other parameters are kept constant. Such model terraced surface is of course idealized with respect to real silicon surfaces where multiple steps can occur.[21]

$\delta(x,z)$ satisfies the equation,

$$\frac{\partial^2\delta}{\partial x^2} + \frac{\partial^2\delta}{\partial z^2} = 0 , \tag{4}$$

which results from the minimization of the elastic energy of the nematic liquid crystal assuming the isotropy of the elastic constants.[22] This equation can be solved when the boundary conditions are known. In our case, these boundary conditions are given by the variations of the tilt angle $\delta_0(x)$ induced locally at point x by the substrate. $\delta_0(x)$ is a periodic function of period p, so it can be decomposed in a Fourier series:

$$\delta_0(x) = \sum_n \left[a_n \cos\left[n\frac{2\pi}{p}x \right] + b_n \sin\left[n\frac{2\pi}{p}x \right] \right] . \tag{5}$$

The solutions of Eq. (4) have then the general form

$$\delta(x,z) = \sum_n \left[a_n \exp\left[-n\frac{2\pi}{p}z \right] \cos\left[n\frac{2\pi}{p}x \right] + b_n \exp\left[-n\frac{2\pi}{p}z \right] \sin\left[n\frac{2\pi}{p}x \right] \right] . \tag{6}$$

The macroscopic anchoring tilt δ_a is given by

$$\delta_a = \delta(z=\infty) = a_0 = \frac{1}{p}\int_0^p \delta_0(x)\,dx . \tag{7}$$

In order to take the influence of both the terraces and the steps into account, the function $\delta_0(x)$ must impose that the tilt is equal to α_e on the terraces and to $-\delta_s$ on the steps; this imposes the following general expression, whose representation is given in Fig. 10:

$$\delta_0=\begin{cases}-\delta_s, & 0\le x\le d\\ -\delta_s+(\delta_s+\alpha_e)f\left[\dfrac{x-d}{l}\right], & d\le x\le d+l\\ \alpha_e, & d+l\le x\le p-d-l\\ -\delta_s+(\delta_s+\alpha_e)f\left[\dfrac{p-d-x}{l}\right], & p-d-l\le x\le p-d\\ -\delta_s, & p-d\le x\le p\end{cases} \tag{8}$$

$f(y)$ is a function increasing from 0 for $y=0$ to 1 for $y=1$.

By combining Eqs. (7) and (8), one obtains

$$\delta_a=\alpha_e+(\delta_s+\alpha_e)\frac{\Delta}{p}\ , \tag{9}$$

$$\Delta=-2(d+l)+2l\int_0^1 f(y)dy\ . \tag{10}$$

The coefficient Δ contains all the information about the detailed influence of the steps which is unknown; so we can only evaluate its order of magnitude. The minimum value of Δ is $-2(d+l)$ obtained by taking $f(y)=0$ for $0\le y<1$ and $f(1)=1$. Its maximum value is $-2d$ obtained by taking $f(0)=0$ and $f(y)=1$ for $0<y\le 1$. The values of d and l are difficult to estimate but orders of magnitude of a few angstroms for d and a few angstroms for 10 Å for l seem reasonable.

By combining Eqs. (1), (3), and (9), one finally obtains

$$\delta_a=\arctan\left[\frac{h}{p}\right]+\left[\arcsin\left[\frac{h}{a}\right]+\arctan\left[\frac{h}{p}\right]\right]\frac{\Delta}{p}\ . \tag{11}$$

We have then an expression of δ_a depending on three parameters.

(1) The height h of the steps can be calculated for the surfaces studied experimentally from the crystal structure and the lattice parameter (5.431 Å) of the silicon. The values we find (Table I) agree within 0.1 Å with the values obtained experimentally by tunneling microscopy.[21]

(2) a is half the length of the nematic molecules. The nematic liquid crystal we have used is a mixture of several kinds of molecules[23] whose lengths are known (Table II). We have taken as value of a the average of the values of a for each kind of molecule, which gives $a=9.5$ Å.

(3) Δ is the only unknown parameter. It can be fixed considering the experimental result obtained on surface number 1 (Table I): $\delta_a=0°$ for $p=339$ Å and $h=1.3$ Å. One obtains $\Delta=-9.21$ Å that fits the order of magnitude we had found above. Δ can be expected to depend on the orientation of the silicon surface. But as this dependence is very difficult to estimate and as it should not be very big, we have used the same value of Δ for all the silicon surfaces.

These values of the parameters h, a, and Δ allow us to plot the variations of δ_a with p in the case of the three types of silicon surfaces we have studied, characterized by $h=1.3$ Å for the [001] surfaces (Fig. 11), $h=1.9$ Å for the [110] surfaces (Fig. 12), and $h=3.0$ Å for the [111] surfaces (Fig. 13). We can see that the values of the tilt of

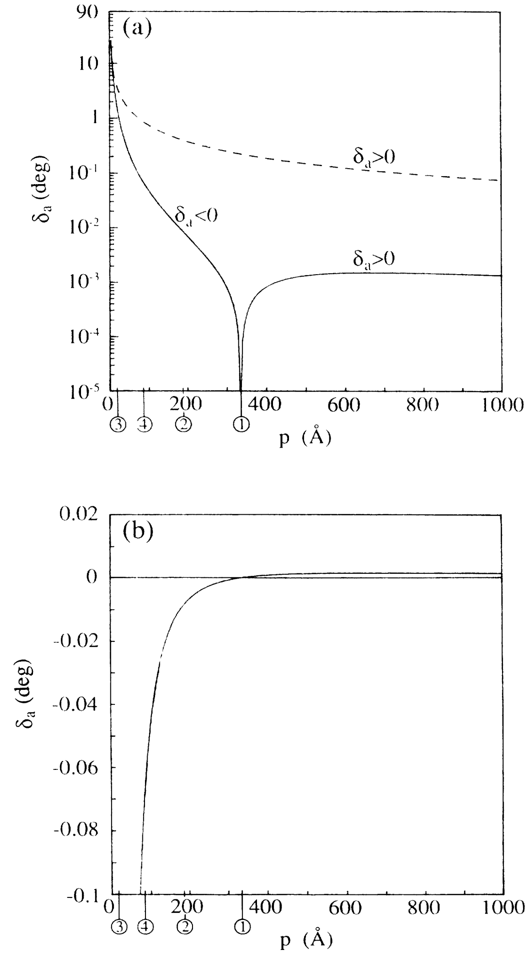

FIG. 11. $\delta_a(p)$ on the [001] surfaces, $h=1.3$ Å. (a) Logarithmic plot of $|\delta_a(p)|$: in-plane line δ_a given by Eq. (11) taking into account the influence of the steps; in the dashed line $\delta_a(p)=\alpha_e$ given by Eq. (1) taking into account only the influence of the terraces; (b) linear plot of δ_a given by Eq. (1). The encircled numbers refer to the surfaces studied experimentally (Table I).

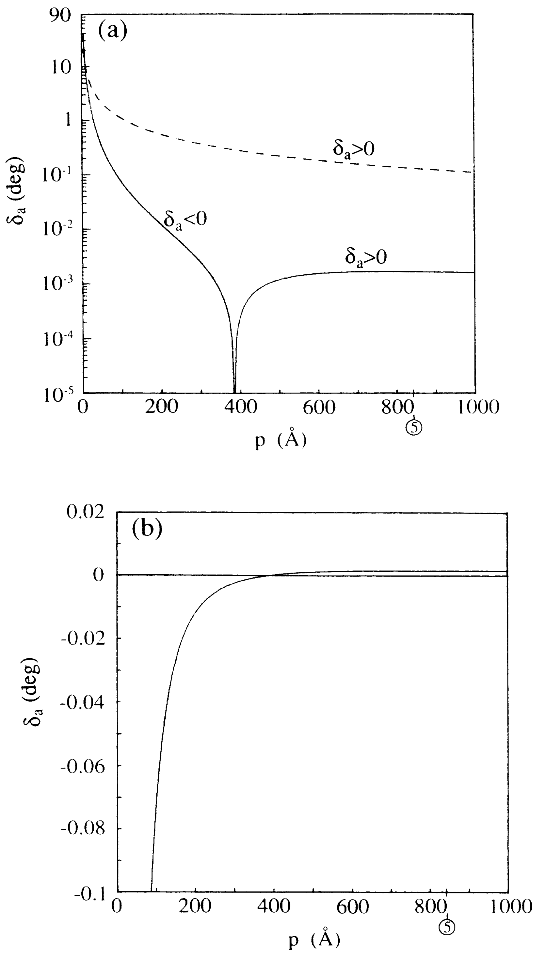

FIG. 12. Same as Fig. 11 for the [110] surfaces; $h = 1.9$ Å.

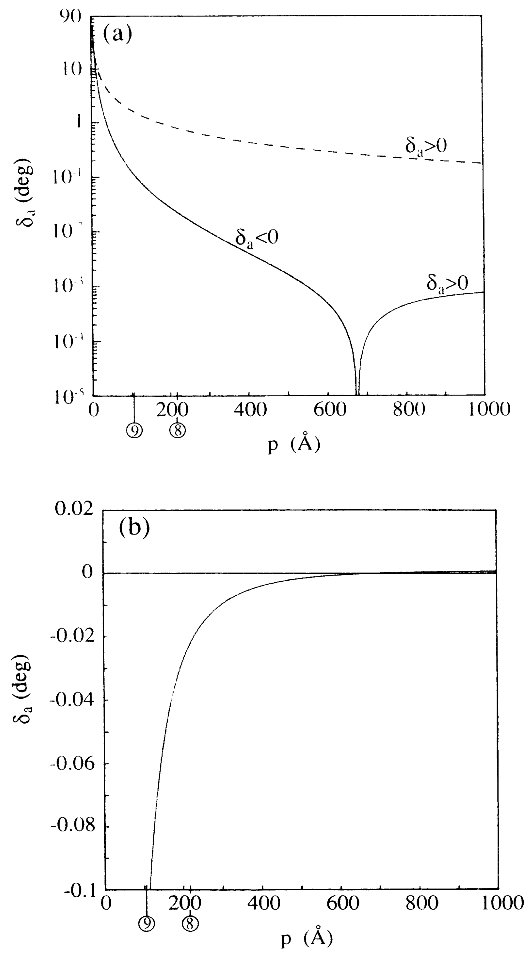

FIG. 13. Same as Fig. 11 for the [111] surfaces; $h = 3.0$ Å.

the anchoring directions predicted by our simple model including the influence of the steps are in qualitative agreement with the results obtained experimentally (Table I).

This model shows that the influence of the steps existing at the substrate surface drastically changes the anchoring tilt with respect to the value α_e expected by considering only the influence of the terraces [Figs. 11(a), 12(a), and 13(a)]. For periodicities p smaller than a threshold value p_c depending on the step height h, the steps impose a negative macroscopic tilt, that is to say in the same way as the one they impose locally. The threshold values are higher than the values of the periodicity generally observed on the commercially available silicon wafers, which means that on nearly all the silicon surfaces, one will get a negative anchoring tilt. For values of p greater than p_c, the anchoring tilt is positive but two orders of magnitude smaller than the tilt α_e imposed by the terraces. the ratio between the respective contributions to δ_a of the terraces and the steps remains approximately constant when p tends to infinity: on the one hand the ratio of the surfaces occupied, respectively, by the steps and the terraces decreases but on the other hand the tilt α_e induced by the terraces decreases too.

C. Evolution of the anchoring with time

When we deposit nematic droplets on a silicon surface periodically after its cleaning, we observe that the anchoring induced by the surface is slowly altered and finally becomes degenerate—all the azimuthal orientations of the nematic molecules giving the same surface energy—after a few days as we can expect from the growth of an amorphous oxide layer. This alteration of the anchoring is not observed in a nematic layer deposited on the silicon surface: the anchoring conditions always remain the same as at the moment of the deposition of the nematic liquid crystal onto the surface.

V. DISCUSSION AND CONCLUSIONS

We have studied the anchoring induced on nematic liquid crystals by silicon surfaces slightly tilted with respect to the (001), (110), or (111) crystallographic planes of silicon. We have observed that the anchoring induced on such surfaces evolves with time from a monostable or bistable anchoring when the surface is of pure silicon to a degenerate anchoring when the surface is covered with a layer of amorphous oxide.

On pure silicon surfaces, the azimuthal orientation and the tilt of the anchoring directions are determined independently by, respectively, the crystal and the terraced structure of the substrate. The nematic liquid crystals align parallel to the twofold axes of the silicon crystal parallel to the surface. We can expect that such anchoring orientations will be obtained on all silicon surfaces parallel to a twofold axis. These preferred anchoring orientations are observed although the first silicon atomic layer is incoherently reconstructed. This shows that the interaction of the nematic molecules with deeper silicon layers is an important contribution to their interaction with the silicon crystal and that the surface seen by these molecules is not limited to the first crystalline layer of the substrate.

The results concerning the effect of the terraced structure of the silicon surfaces on the tilt of the anchoring directions are quite unexpected. The anchoring tilt is not imposed by the tilt of the terrace with respect to the mean substrate surface but it is also drastically influenced by the presence of the steps separating the terraces that impose locally to the nematic molecules a tilt in an opposite way to the one imposed by the terraces. The macroscopic anchoring tilt resulting from these two influences is in most of the experimental cases in the opposite way to the one imposed by the terraces. When it is in the same way, its value is smaller than 10^{-3} deg.

Our model including the influence of the steps on the anchoring tilt angle and accounting for the experimental results we have obtained on silicon surfaces is based on purely steric interactions of the nematic molecules with the terraced structure of these surfaces; so it is likely to be also valid for terraced surfaces of other crystals. However, we emphasize that the variations of the macroscopic tilt angle δ_a with the periodicity p of the steps is sensitive to changes of the parameter Δ which contain all the information about the detailed influence of the steps on the local tilt $\delta_0(x)$ and which is, therefore, very likely to vary from one crystal to the other. The curve $\delta_a(p)$ can have two different aspects.

(1) When $\Delta' = h + \delta_s \Delta$ is positive which implies that $\Delta > -h/\delta_s \simeq a$, $\delta_a(p)$ increases from $-\infty$ for $p \to 0+$ to 0 for $p = p_c = -h\Delta/\Delta'$, reaches a positive maximum for $p = 2p_c$, and then decreases to zero when p tends to infinity.[24] For values of p greater than $2p_c$, the ratio of δ_a to the tilt α_e induced by the terraces is approximately constant and of the order of $1 + \delta_s \Delta / h \simeq 1 + \Delta / a$.

(2) When Δ' is negative, $\delta_a(p)$ is negative for all values of p and increases from $-\infty$ for $p \to 0+$ to 0 for $p \to +\infty$.[24]

In the case of the silicon surfaces we have studied, $\delta_a(p)$ was always of the first type. But when keeping all the other parameters equal to the ones used for the silicon surfaces and taking a value of Δ smaller than $a = 9.5$ Å instead of $\Delta = 9.21$ Å, which corresponds to an increase of the influence of the steps, we obtain a curve $\delta_a(p)$ of the second type. On the contrary, when Δ is increased over the value $\Delta = 9.21$ Å, which corresponds to a decrease of the influence of the steps, the critical value p_c under which δ_a is negative tends to 0 and the ratio $(\delta_a/\alpha_e)_{p > 2p_c}$ tends to 1. For instance, for $\Delta = -8.5$ Å, one obtains $p_c = 86$ Å for $h = 1.3$ Å as in the case of the [001] silicon surfaces and $(\delta_a/\alpha_e)_{p > 2p_c} \simeq 10^{-1}$. So for this value of Δ, the effect of the steps would be already difficult to detect experimentally and it becomes nearly impossible for smaller values of Δ.

The shape of the curve $\delta_a(p)$ is also sensitive to the value of the tilt δ_s imposed locally on the steps. δ_s depends both on the height of the steps, which is a characteristic of the substrate, and on the length of the nematic molecules. Increasing (decreasing) δ_s would change $\delta_a(p)$ in the same way as decreasing (increasing) Δ. But we should *a priori* expect that Δ depends on h and a so the dependence of $\delta_a(p)$ on these two parameters is not easy to estimate.

These dependences of $\delta_a(p)$ with Δ and δ_s show that in the case of other crystalline substrates and other nematic liquid crystals, one can expect to have either a stronger influence of the steps, in which case the observed tilt angle δ_a is always negative, or a weaker influence of the steps, in which case the observed tilt angle is close to the one induced by the terraces on a wide domain of periodicities p.

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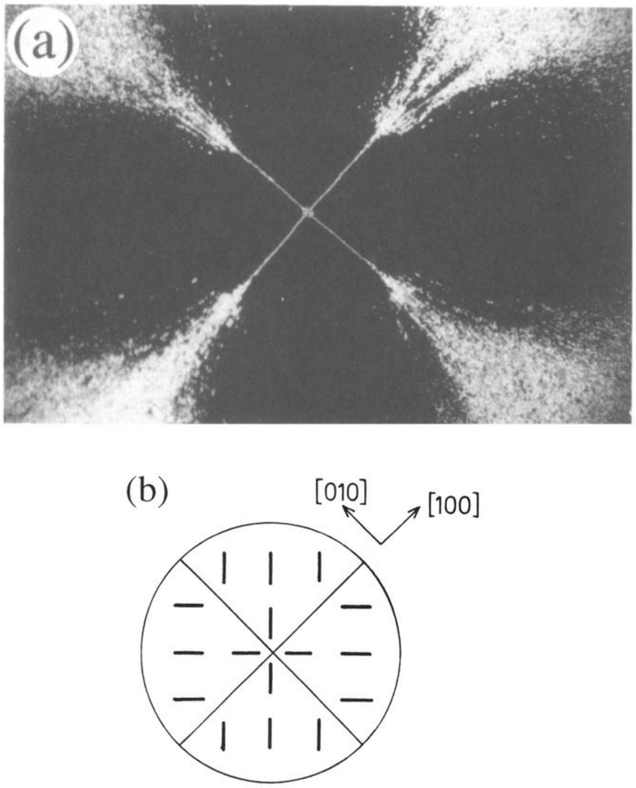

FIG. 4. Texture of a nematic droplet spread onto a [001] silicon surface inducing planar anchoring directions (surface number 1 in Table I). Under a polarizing microscope (a), the droplet appears with four dark domains of uniform orientation, given in (b), separated by bright lines. These lines are walls in which the nematic orientation rotates from one anchoring direction to the other. The walls are diametral straight lines, which is characteristic of a planar anchoring.

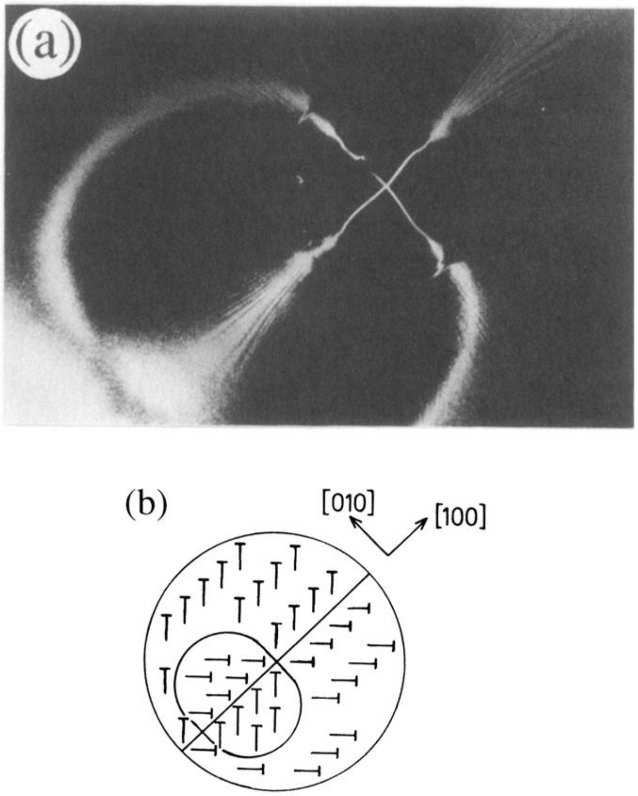

FIG. 5. Same as Fig. 4 for a [001] silicon surface inducing tilted anchoring directions (surface number 3 in Table I). One of the walls separating the domains with different anchoring directions is a solid line, which is characteristic of a tilted anchoring.