Alignment of Liquid Crystals on Stepped and Passivated Silicon Templates Prepared in Ultrahigh Vacuum

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We report on the orientation of nematic liquid crystals supported on highly regular, periodic, nanometer-scale structures formed from atomic steps on the surface of miscut silicon crystals thermally annealed in ultrahigh vacuum (UHV). Prior to removal from UHV, the silicon templates were passivated by reaction with methanol, acetone, or hydrogen and characterized by ultraviolet photoelectron spectroscopy using synchrotron radiation. In contrast to silicon substrates prepared in the past by wet chemical methods and substrates prepared by oblique deposition of metal and metal oxide films, the passivated templates prepared in UHV have highly regular single and bunched atomic steps that can be observed by scanning tunneling microscopy. Three independent measurements of the orientation of nematic liquid crystals of 4-cyano-4′-pentylbiphenyl (5CB) on these templates revealed the alignment of 5CB to be parallel to the atomic step edges on samples with periodic single atomic steps (~0.3 nm height, ~15 nm width) as well as bunched atomic steps (~5 nm height, ~70 nm width). Because the nanometer-scale structures of these surfaces are well-defined and readily manipulated on spatial scales comparable to the sizes of a range of biological species, these surfaces may be useful as templates for the detection of the binding of biological species through changes in the orientation of liquid crystals.

Introduction

The alignment of liquid crystals near interfaces has received widespread attention due, in part, to the application of this phenomenon in a variety of optical devices, including flat-panel displays.[1] More recently, the behavior of liquid crystals near nanostructured interfaces has been proposed as the basis for detection of the specific binding of biological molecules to receptors hosted at these surfaces.[2] Because nematic liquid crystals possess large orientation correlation lengths,[3] it is possible to amplify the binding of nanometer-sized biological molecules at interfaces into changes in the orientation of $10-100$ μm thick films of liquid crystal.[2,3] Whereas past studies have used substrates with complex nanometer-scale structures induced by the oblique deposition of metallic films,[4] our procedures here permit formation of well-defined nanostructured surfaces that can be prepared with systematic and predictable changes in their nanometer-scale topography. Because the nanometer-scale structure of these surfaces can be systematically varied to match the size of the biological species, we believe these substrates may provide materials for biological assays tailored for the detection of species with a particular size or shape.[2,4] We also believe that these substrates may be generally useful as templates in directing the organization of arrays of

colloids, magnetic nanoparticles, etc., for single-particle per-bit memory[5] and the organization of micelles, organic molecules, etc., for molecule-based electronics.[6] Recently, arrays of silicon steps have been fabricated with epitaxial CaF_2 stripes,[7] and small molecules have been selectively adsorbed on such striped structures.[8]

The surfaces used in this investigation are prepared by miscutting single crystals of silicon along the (111) crystallographic face in a direction near, but not along, the cleavage plane.[9,10] The miscut Si(111) substrates form a 7×7 reconstruction, thereby leading to a regular array of atomic step edges across the surface of the substrate.[11] By controlling specific parameters such as the angle of miscut, the direction of miscut, and the thermal annealing of substrates, past studies have demonstrated that it is possible to prepare single-domain arrays of steps that

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(10) Lin, J. L.; Petrovykh, D. Y.; Viernow, J.; Men, F. K.; Seo, D. J.; Himpsel, F. J. *J. Appl. Phys.* **1998**, *84*, 255. (b) Men, F. K.; Liu, F.; Wang, P. J.; Chen, C. H.; Lin, J.-L.; Himpsel, F. J. Unpublished results. We have found that the step height is doubled during bunching on the Si(111) miscut toward the [112] direction, so the samples in the study are 2.6° (not 1.3°) and 5.6° (3.5°), miscut toward [1 1 2]. The average facet angle is 12°.

(11) The 7×7 reconstruction results from the rebonding of silicon atoms at the clean Si(111) surface to minimize the number of broken bonds.[22]

Figure 1. Silicon surfaces with (A) single and (B) bunched atomic steps used as templates for the alignment of liquid crystals. Derivative of surface topography obtained by STM for (C) single- and (D) bunched-step surfaces (scanned from the left size of the image). The steps were oriented downward from left to right, resulting in the appearance of the dark lines. (E) Illustration of the molecular structure of 5CB.

possess well-defined widths and heights on the $\sim$0.3–100 nm length scale.[9,10,12] In this study, we have prepared two types of substrates that present arrays of atomic steps on their surfaces: single and bunched atomic steps, each with kink densities below one per 20 000 lattice sites on the surface. The single-step substrates have arrays with terraces $\sim$15 nm wide, separated by steps with heights of two silicon atoms ($\sim$0.3–0.4 nm) (Figure 1A). These substrates are formed by miscutting the samples at an angle of $\sim$1.1° from the (111) plane toward the [11$\bar{2}$] direction. In contrast, the bunched-step substrates possess terraces with widths of $\sim$65–85 nm, separated by bunched steps with heights of $\sim$5 nm (Figure 1B). These substrates are formed by miscutting the surface of the crystal at an angle of $\sim$2° toward the [11$\bar{2}$] direction. Here we demonstrate that these steps persist when exposed to the conditions used in studies of the alignment of liquid crystals.

Although the surfaces of miscut silicon substrates have been explored in the past for the alignment of liquid crystals, the structure and the chemical species on the surfaces were not determined prior to the deposition of liquid crystals.[13] Our attempts to repeat the wet chemical procedures of past studies yielded surfaces without identifiable steps when analyzed by scanning tunneling microscopy (STM). The goal of the research described in this paper, therefore, was to prepare well-defined, well-characterized surfaces and to explore the orientation of liquid crystals on these substrates. Here we describe methods to passivate the broken surface bonds of the clean Si(111) 7 $\times$ 7 surface so that the step structure remains intact when removed from UHV. The structure of the resulting surfaces is characterized by STM, and the chemical passivation of these surfaces is characterized by ultraviolet photoelectron spectroscopy (UPS) using synchrotron radiation. To permit comparison to past studies, we also prepared Si(111) through methods similar to those

of past studies of the anchoring of liquid crystals, i.e., wet oxidation and etching wafers without preparation of the 7 $\times$ 7 surface structure.[13]

We measured the in-plane orientation of liquid crystals on stepped silicon surfaces by three independent techniques. The first method is based on the orientation of the disclination line formed within a small drop of liquid crystal ($\sim$1 mm) placed onto the substrate.[14,15] The second method is based on the alignment of liquid crystals confined within a cell where one surface has a known alignment and the other surface is a stepped silicon substrate.[16] The third method uses reflectance difference/anisotropy spectroscopy (RDS/RAS).[17] This approach uses a polarization modulation scheme to obtain the difference in optical reflectivities of light polarized parallel and perpendicular to the steps. We measured the orientation of nematic 4-cyano-4′-pentylbiphenyl (5CB) on substrates with single and bunched atomic steps passivated by methanol, acetone, or hydrogen.

Materials and Experimental Methods

Materials. The liquid crystal 5CB (T_{ni} = 34.5 °C), manufactured by BDH, was purchased from EM Industries (Hawthorne, NY). Acetone, $H_3C(CH_2)_{14}SH$, and methanol (99%) were purchased from Aldrich (Milwaukee, WI) and used without further purification. Ethanol was purchased from Aaper (Shelbyville, KY). We synthesized $HOOC(CH_2)_{10}SH$ and $HO(CH_2CH_2O)_2$-$(CH_2)_{10}SH$ by using previously published methods.[18] Silicon (111) n-type wafers with miscuts between 1° and 4° and doping levels in the 10^{18} cm^{-3} range were obtained from MEMC (St. Peters, MO). Glass microscope slides were purchased from Fisher (Los Angeles, CA). Titanium (99.999%) and gold (99.999%) were purchased from Advanced Materials (Spring Valley, NY).

Preparation of Stepped Silicon Substrates. Methods of producing high-quality arrays of atomic steps on vicinal Si(111) 7 $\times$ 7 surfaces have been reported recently.[9,10,12] Substrates having single atomic steps with heights of 0.31 nm and bunched atomic steps with heights of $\sim$5 nm and facet angles of $\sim$12° can be prepared. For comparison, a 5CB molecule with a length of $\sim$1.9 nm and a diameter of $\sim$0.7 nm is shown in Figure 1E.[19] Single steps are obtained by a miscut toward the [$\bar{1}\bar{1}$2] azimuth, whereas bunched steps are obtained by a miscut toward the opposite [11$\bar{2}$] azimuth. We prepared substrates with five different types of miscut angles and directions, i.e., <0.2° ("flat" surface), 1.1° and 2° toward the [$\bar{1}\bar{1}$2] azimuth, and 2.6° and 4° toward the [11$\bar{2}$] azimuth. All samples were prepared in ultrahigh vacuum ($\sim$10^{-10} Torr).

The single-step samples (and the flat surface) were prepared by a heating sequence that produced large, single-domain 7 $\times$ 7 reconstructions and avoided the bunching of steps near the 7 $\times$ 7 to 1 $\times$ 1 phase transition at 870 °C.[5] This process was performed by outgassing the sample for 30 min at 700 °C. Next, the sample was flashed to 1250 °C to remove the oxide layer. The sample was cooled in 1 min to 1060 °C, where the single steps are stable, and then quenched to 850 °C within 3 sec to avoid the bunching of steps. The sample remained at 850 °C for about 1 h to produce a long-range 7 $\times$ 7 reconstruction with straight step edges. Figure 1C shows a STM image of a sample prepared by this procedure when using a substrate with a 1.1° miscut in the [$\bar{1}\bar{1}$2] direction. The 2° miscut produced single steps with terraces

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~8 nm wide and occasional bunches of ~4 atomic steps. The nominally flat sample possessed terraces with widths >80 nm.

The preparation of surfaces with bunched steps required a heating procedure that facilitated the formation of wide terraces (~70 nm) separated by facets of the bunched steps. The heating procedure involved flashing the sample to 1250 °C, cooling it to 1060 °C in 1 min, and then cooling it slowly through the phase transition at a rate of 0.5 °C per minute to 650 °C. The sample remained at 650 °C for at least 30 min to enlarge the width of the terraces to a self-limited maximum size. Figure 1D shows a STM image of a bunched sample with a 4° miscut prepared by this procedure. The heights of the bunched steps are 4.9 nm for the substrate with a miscut angle of 4° and 3.1 nm for the substrate with a 2.6° miscut. Both miscuts were made in the direction of the [$1\bar{1}2$] azimuth.

Passivation of Silicon Substrates. Clean Si(111) 7×7 surfaces have two types of dangling bonds that are highly reactive when exposed to air—adatoms and rest atoms.[20] The adatoms are electron acceptors, whereas the rest atoms are electron donors. Typically, a native oxide layer with thickness ~1 nm forms on the surface of the silicon upon exposure to air. Although the step structure is preserved to some degree during oxidation (see below), we sought to identify passivating agents that would prevent oxygen from disrupting the back bonds and roughening the surface. We have exposed Si(111) 7×7 substrates to a variety of passivation agents by vapor-phase deposition of hydrogen, methanol, acetone, diethylsilane, benzene, and hexylamine. The details of the passivation procedure have been published previously.[21] In this study, the surface was passivated with methanol, acetone, or hydrogen at ~10^{-7} Torr (exposure to 2−4 Langmuirs of the passivating agent) onto substrates heated to 100 °C. For purposes of comparison, we also prepared samples of silicon that were not passivated.

Scanning Tunneling Microscopy (STM). We visualized the silicon substrates using scanning tunneling microscopy (Omicron) at a tunneling current of 0.4−0.8 nA and a sample bias of +2 V. To enhance the appearance of the steps in the images reported in this paper, we present the derivative of the topography in the x-direction. The terraces decrease in height from the left to the right side of each image.

Ultraviolet Photoelectron Spectroscopy (UPS). Ultraviolet photoelectron spectroscopy performed at the Synchotron Radiation Center (Stoughton, WI) was used to identify the atomic composition and electronic structure of the flat silicon surfaces passivated with acetone and methanol. Samples were passivated with either methanol or acetone dosed to 4 Langmuirs within the UPS chamber. The chamber pressure during acquisition of all UPS spectra was ~2.0×10^{-9} Torr, the spot size was 0.5 mm $\times$ 5 mm, and the takeoff angle was 50°. Monochromatic incident UV radiation was obtained from the synchrotron beam line at 54 eV for acetone passivation and at 66 eV for methanol passivation. Five to fifteeen survey scans were acquired on each sample at a resolution of 0.1 eV. The binding energies were referenced to the Fermi energy of a polycrystalline tantalum foil (61.05 eV).

Measurement of Alignment of Liquid Crystals. Once passivated, the silicon templates were removed from the UHV chamber, placed into a nitrogen chamber, and introduced to 5CB within 15 min. As described below, we used three methods to determine the orientation of the nematic phase of 5CB on the surfaces of the silicon templates.

Observation of Disclination Lines in Nematic Droplets Using Polarized Light Microscopy. First, we determined the orientation of nematic 5CB on single-step, bunched-step, and flat silicon surfaces passivated with hydrogen, acetone, or methanol by observing the optical appearance of drops of the nematic liquid crystal through cross polars. A small droplet of 5CB (~1 μL) in the isotropic phase (~35 °C) was dispensed from a hypodermic needle onto a substrate maintained at ~35 °C. The sample was then transferred to the stage of a BX-60 Olympus

(Tokyo, Japan) polarized light microscope (operating in reflectance mode), where the sample was cooled into its nematic state (room temperature). Finally, the optical appearance of the nematic droplet was visualized between cross polars using a Sony CCD camera and recorded onto a computer using NIH Image. Because the droplets of liquid crystal spread on these substrates, the optical appearance of the droplets was sometimes complex and difficult to interpret. We therefore confirmed our conclusions with two additional measurements that permitted determination of the alignment of liquid crystals on these substrates.

Orientation of 5CB Using Optical Cells. The second method used to determine the orientation of 5CB on the silicon substrates was based on the use of cells in which the liquid crystals were sandwiched between two surfaces. We prepared the cells from a silicon template (one surface) and a self-assembled monolayer formed from $H_3C(CH_2)_{14}SH$ on an obliquely deposited film of gold (the other surface). We used the SAM supported on the obliquely deposited, semitransparent film of gold because the alignment of 5CB is known on this surface.[16] The two surfaces were aligned (facing each other) such that the direction of deposition of the gold and the direction of step edges in each film were perpendicular. The surfaces were spaced apart with a thin film of Mylar or Saran Wrap (nominal thickness of 2 or 12 μm). A drop of 5CB heated into its isotropic phase ($T < 40$ °C) was then drawn by capillarity into the cavity between the two surfaces of the optical cell. The cell was subsequently cooled to room temperature, and the optical textures were analyzed by polarized light microscopy in reflectance mode (transmission through the gold film; reflection from the silicon surface).

Reflectance Difference Spectroscopy (RDS). The third technique used to determine the in-plane orientation of 5CB was based on measurements of the difference in reflectivity of UV light polarized parallel and perpendicular to the steps of the silicon substrate (see Figure 6A for a sketch of the experimental setup).[17] Polarized light was reflected from the surface at an angle of 45° from the step edges, which were oriented along the [110] crystallographic axis. By using an analyzer oriented along the [110] direction and a lock-in amplifier, we obtained an output signal directly proportional to the reflectance difference between the [110] and [$11\bar{2}$] axes, $\Delta r = r_{1\bar{1}0} - r_{11\bar{2}}$. Rotation of either the sample or the analyzer by 90° in the setup shown in Figure 6A gives rise to spectral peaks with opposite signs (caused from the reflectance difference between the [$11\bar{2}$] and [110] axes). A modulation technique provides a sensitive measurement of the relative reflectance difference, $\Delta r/r$, between cases where the polarization is parallel and perpendicular to the steps. The modulation was accomplished by using a photoelastic modulator (PEM) at a frequency of 50 kHz.

Results

Characterization of Stepped Silicon Substrates. The topographies of the stepped silicon surfaces were characterized by STM prior to the placement of liquid crystals onto these surfaces. Typical images are shown in Figure 2 for the case of silicon surfaces with single atomic steps. The clean Si(111) 7×7 surface in Figure 2A exhibits atomically straight step edges which run parallel to natural grooves of the 7×7 reconstruction on the terraces. As shown in the line trace below Figure 2A, the step edges are 2.3 nm apart, which corresponds to the 7 atomic rows or half the diagonal of the 7×7 unit cell. After exposure to methanol vapor in the vacuum chamber (Figure 2B), the 7×7 structure almost disappears, with only traces of the deep corner holes of the 7×7 unit cell apparent in the image. As shown in the line trace below Figure 2B, the steps remain straight except for an occasional 2.3 nm kink, visible in Figure 2B. Panels C and E of Figure 2 show a surface passivated with methanol after exposure to 1 atm of dry nitrogen for 15 min (a typical handling time before exposure to liquid crystals). While the noise in the STM image increased due to the presence of loosely bound species that created instabilities in the tunneling current, the steps were still straight and well-oriented.

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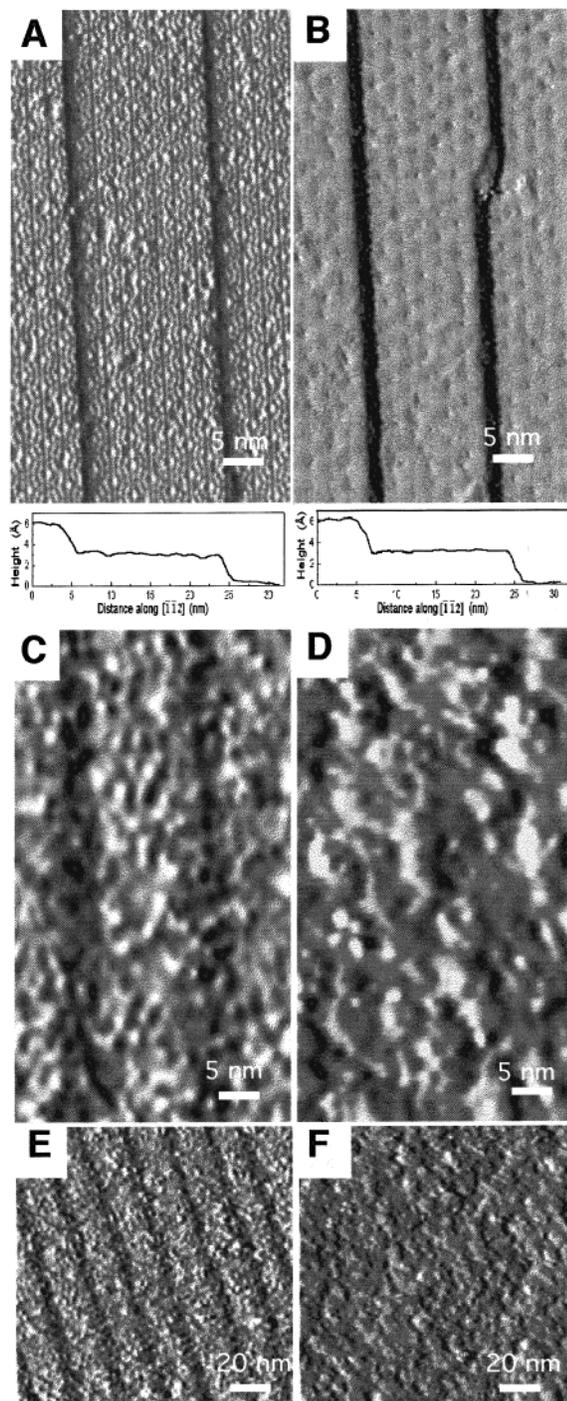
Figure 2. Derivative of topography of Si(111) substrates with single atomic steps obtained by STM: (A) clean Si(111) 7 × 7 surface with atomically straight single steps imaged in UHV; (B) substrate in panel A passivated by exposure to 5 Langmuirs of methanol at room temperature. The line scans below A and B show characteristic cross sections taken from the images in A and B. (C and E) Substrate in B after exposure to dry nitrogen at atmospheric pressure for 15 min over two different line scans, 30 and 200 nm. (D and F) Si(111) wafer treated by the wet chemical methods of Jérôme et al.[13]

For comparison, panels D and F of Figure 2 show scanning tunneling micrographs of silicon substrates that were prepared in UHV and then treated by a wet oxidation/etching cycle similar to that used for silicon substrates in past studies on the alignment of liquid crystals.[13] Through STM, we could not find any evidence of the stepped structure on the substrate prepared by the wet chemical procedure. Similarly, a two-dimensional Fourier transform
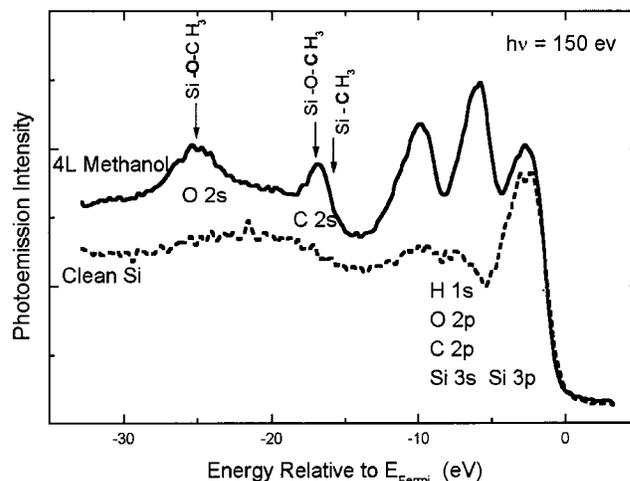
Figure 3. Ultraviolet photoelectron spectra of methoxy species on Si(111) 7 × 7 after exposure to 4 Langmuirs of methanol.

of the STM image (topographical image) did not reveal any evidence of the stepped structure in these samples. We conclude, therefore, that the substrates prepared by the UHV procedures were substantially different from those prepared by the wet chemical method.

To characterize the surface chemistry associated with the passivation of substrates with methanol and acetone in UHV, we performed UPS on the valence orbitals. The surface sensitivity of the synchotron radiation was optimized by tuning the photon energy (*hν*) to a value where the mean free path of the photoelectrons was minimized (typically 0.5 nm) and the cross section specific to the adsorbate orbitals was maximized. A typical ultraviolet photoelectron spectrum is shown in Figure 3. We used the 2s orbitals of C and O for fingerprinting the adsorbed species. These peaks are at energies below that of the complex spectrum of features that contain many bonding and antibonding combinations of the Si valence band and the majority of the adsorbate orbitals. The C and O 2s peaks, however, are still sensitive to the bonding configuration and permit determination of the local bonding configuration of C and O atoms. For example, the bonding of carbon to oxygen in a methoxy group produced a downward shift of the C 2s peak because the electronegative oxygen caused an attractive, positive potential at the carbon site. In contrast, the bonding of carbon to less electronegative atoms, such as C, Si, or H, resulted in a higher energy for the C 2s peak, such as that for a methyl group,[21] as indicated in Figure 3. Likewise, we used the O 2s level to determine if oxygen remains at the surface after the reaction of the methanol with the surface. Comparison of the methanol-passivated surface to the O 2s peaks for SiO_2 in Figure 3 indicated that the oxygen does not leave the methoxy group. The area of the O and C 2s peaks relative to the clean Si background is a measure of the oxygen and carbon coverage when normalized by surfaces with known coverages. By comparing the spectrum in Figure 3 to those in past work[21] on ethyl and methyl groups on Si, we conclude that the methanol-passivated surface contains fewer C atoms than in the apparent monolayer in methoxy groups. This low coverage is partly explained by the 7 × 7 reconstruction of the clean Si(111) surface, which reduces the density of dangling bonds to $^{19}/_{49}$ of a monolayer. Previous photoemission work on the adsorption of methanol on Si(111) 7 × 7 indicates that the methoxy groups attack the rest atoms only and

not the adatoms.[22] Adatom sites are predominantly quenched by hydrogen produced as fragments of methoxy formation. The slow kinetics of the Si−H bond formation and the competitive recombination and desorption of H−H illustrate the difficulty in quenching adatom surface states.[22]

Alignment of Liquid Crystals. *Observations of Disclination Lines in Nematic Droplets.* We determined the in-plane orientation of 5CB on silicon substrates by placing a drop of 5CB onto a substrate and observing the optical texture within the nematic droplet using a polarized light microscope operated in reflectance mode. Even though the droplet of 5CB spreads onto the silicon template, we observed the optical textures of these drops to be similar to those which did not spread in past studies.[14a,15] A disclination line (the threadlike structure passing through the core of the droplet in Figure 4B,C) dominated the appearance of each droplet. The formation of these types of defects is the result of perpendicular anchoring of 5CB at the air−5CB interface and uniform planar (or near-planar) anchoring at the silicon−5CB interface (Figure 4A). The origin of the disclination line, which runs perpendicular to the azimuthal direction of anchoring on the silicon template, is caused by a reversal of the handedness of the twist distortion within the droplet (Figure 4A).

Figure 4B shows the optical appearance of a droplet of 5CB supported on a single-step silicon surface passivated with methanol. As shown by the arrow marked "1", a complex disclination line propagated through the center of the drop in a direction perpendicular to the orientation of the steps on the surface. The disclination line is not sharp because the height profile of the liquid crystal is almost flat near the center of the drop. While we have not directly measured the out-of-plane orientation of 5CB on these surfaces, the location of the disclination line at the center of the drop suggests that the orientation of 5CB is either parallel or nearly parallel to the surface.[14b] A disclination loop (the arrow marked "2") positioned ∼150 μm from the center of the drop corresponds to the location where 5CB transitioned from an isotropic to nematic state as it spread across the surface. Rotating the droplet between cross polars, we observed a modulation in the intensity of light reflected from the droplet, consistent with the conclusion that the liquid crystals were oriented on the surface in an azimuthal direction parallel to the edges of the single atomic steps.

Figure 4C shows a droplet of nematic 5CB supported on a bunched-step silicon template passivated with hydrogen. Similar to the sample in Figure 4B, the disclination line formed in the droplet of 5CB was observed to be perpendicular to the bunched steps, indicating that the orientation of 5CB is parallel to the bunched steps on the surface. In contrast to Figure 4B, the loop disclination corresponding to the transition from isotropic to nematic structure does not appear in Figure 4C. For comparison, Figure 4D shows the optical appearance of a representative "flat" (no deliberate miscut) silicon substrate passivated with methanol. The optical appearance of the droplet was complex and was observed to be similar for all types of surface passivation. We observed at least two in-plane orientations of 5CB on these substrates. We also observed a disclination loop of the type shown in Figure 4B (by arrow "2"). The two domains are indicated by arrows "3" and "4" and are separated by additional disclination loops (arrow "5").

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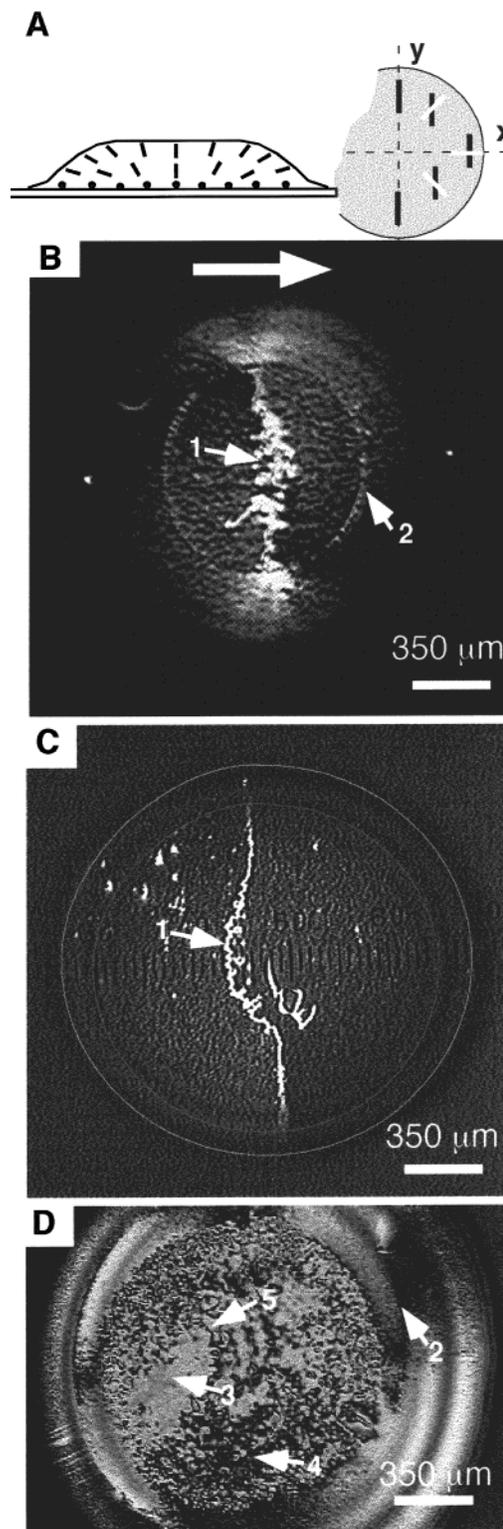
Figure 4. (A) Schematic illustration of a droplet of nematic liquid crystal supported on a stepped silicon surface. The side view shows the orientation of 5CB within a droplet cut by a plane along the disclination line. The top view shows the reversal of handedness of the 5CB twist distortion on either side of the disclination line (which propagates long the *x*-axis). (B) Optical texture of a drop of 5CB placed on a single-step surface passivated with methanol at a 1.1° miscut (crossed polars using reflection-polarized light microscopy). The arrow across the top of panel B indicates the direction of the steps on the silicon substrate. (C) Optical texture of a drop placed on a bunched-step silicon surface passivated with hydrogen at a 3.5° miscut. (D) Optical texture crossed polars of a drop of 5CB on a flat Si(111) surface passivated with methanol.

Orientations of Liquid Crystals Obtained by Fabrication of Optical Cells. Because the optical appearance of the droplets in Figure 4 was more complex than that observed in our past studies, we supported our conclusions regarding the orientations of liquid crystals on the stepped silicon by fabrication of optical cells.[14a,15] The cells were fabricated from two surfaces: a lower silicon substrate and an upper surface formed by the self-assembly of $H_3C(CH_2)_{14}SH$ on an obliquely deposited film of gold (Figure 5A).[4a,16] The region between the two surfaces was filled with liquid crystal, and the optical appearance of the liquid crystal was determined by reflection-polarized light microscopy. Figure 5B shows the optical texture of 5CB confined to an optical cell with a lower surface comprised of a silicon substrate supporting bunched steps. As shown in Figure 5B, the optical cell appeared dark when viewed between crossed polars with bunched steps parallel to the polarizer. In contrast, the film of liquid crystal appeared bright when rotated by 45° (Figure 5C) from the polarizer. These optical characteristics and others indicated that 5CB was oriented uniformly without distortion within the optical cell. Because the orientation of 5CB on the top surface is known, we conclude that the in-plane orientation of 5CB on the bottom surface is parallel to the step edges. This conclusion was reached for silicon substrates with both single and bunched steps, and it confirmed the conclusions based on inspection of the droplets of liquid crystals supported on the silicon templates. We observed these orientations to be stable over 24 h.

Reflection-Difference Spectroscopy (RDS). Figure 6A shows the experimental setup for performing RDS. To calibrate the RDS system, we measured the in-plane orientation of 5CB supported on SAMs formed from either $HOOC(CH_2)_{10}SH$ or $HO(CH_2CH_2O)_2(CH_2)_{10}SH$ on obliquely deposited films of gold; the SAMs are known to orient 5CB in orthogonal azimuthal directions.[23,24] In the RDS measurements, the in-plane orientations are determined through the biphenyl (4.6 eV, 3.7×10^4 cm^{-1}) absorption bands (from the 5CB).[25] This band is primarily due to a $\pi \rightarrow \pi^*$ intramolecular electronic transition that has been investigated in optical absorption studies.[25] The spectra obtained using the SAMs displayed absorbances with opposite signs (Figure 6B,C), consistent with the known orthogonal orientation of the liquid crystal on these samples.[24] We observed the signs of the absorbances to invert when the samples were rotated by 90°. By using this result as a reference, we confirmed by RDS that the in-plane orientation of 5CB on single-stepped and bunched silicon templates was parallel to the step edges. Figure 6D shows a representative RDS spectrum for 5CB oriented on a single-step silicon surface passivated with methanol.

Discussion

Our measurements of the orientation of nematic 5CB on stepped silicon substrates indicate that the in-plane orientation of 5CB is independent of the chemical nature of the passivated surface and the miscut angle on single-step (miscut angles of 1.1° and 2°) and bunched-step samples (miscut angles of 2.6° and 4°). Droplets of liquid crystal placed on all these substrates possess a disclination line that spans the diameter of the droplet. We did observe some minor differences in the defect structure of droplets

(23) Shah, R. R.; Abbott, N. L. *J. Am. Chem. Soc.* **1999**, *121*, 11300.

(24) The azimuthal orientation of 5CB on SAMs from HOOC(CH₂)₁₀-SH is parallel to the deposition direction of the gold. In contrast, SAMs formed from HO(OCH₂CH₂)₂(CH₂)₁₀SH cause an azimuthal alignment of 5CB that is perpendicular to the deposition direction of the gold.

(25) Khoo, I.-C.; Wu, S.-T. *Optics and Nonlinear Optics of Liquid Crystals*; World Scientific: Singapore, 1993.

Figure 5. (A) Schematic illustration of the orientation of 5CB within optical cells with one surface prepared from single-step silicon passivated with methanol and an opposing surface supporting a SAM formed from $H_3C(CH_2)_{14}SH$ on an obliquely deposited film of gold. The arrow indicates the direction of deposition of gold onto the top substrate. Optical texture of 5CB in such a cell when observed with crossed polars using reflection-polarized light microscopy at (B) maximum extinction and (C) 45° rotation from maximum extinction.

of liquid crystals placed on single- and bunched-step-samples (e.g., looped disclination line). We are not yet able, however, to interpret these minor differences in terms of the interaction between the liquid crystals and the substrate. The use of liquid crystal cells and RDS revealed no difference in the alignment of 5CB on single- and bunched-step samples. Because a preferred orientation was not observed on the silicon surfaces without a

Figure 6. (A) Schematic illustration of the experimental apparatus used to measure the in-plane orientation of 5CB by reflectance difference spectroscopy (RDS). See the text for details. The molecular structure for 5CB is shown in Figure 1E. (B) Spectra for 5CB on a SAM formed from $HOOC(CH_2)_{10}$-SH on obliquely deposited gold where the orientation of the liquid crystal is parallel to the direction of the gold deposition. (C) Spectra for the same 5CB as in panel B but with the substrate rotated by 90°. (D) RDS spectrum of 5CB on a 1.1° miscut Si(111) wafer with single atomic steps after methanol passivation.

deliberate miscut (for all types of passivation), we conclude 5CB aligned in a preferred direction because of the presence of steps (single or bunched) on the silicon surface.

The results of our study lead us to conclude that arrays of single and bunched atomic steps on silicon surfaces do influence the in-plane alignment of 5CB. In contrast, Jérôme et al. concluded in a past study that the terraced structure determined the out-of-plane orientation of liquid crystals (<1° measured from the surface) and the crystal structure (underlying the steps on the surface), not the stepped surface, determines the in-plane orientation.[13] We believe that the structure of the surfaces used in our study likely differs from those used in past studies of the orientations of liquid crystals on silicon surfaces prepared by wet chemical methods. Whereas steps are apparent in

STM images of silicon surfaces we had prepared in UHV and exposed to atmosphere, as shown in panels C and E of Figure 2, we were not able to visualize steps on vicinal silicon surfaces after treatment in buffered hydrofluoric acid. We also point out that our experiments were based on use of 5CB, whereas the experiments of Jérôme and co-workers used E8, a mixture of mesogens (including 43% 5CB).[13]

Another significant distinction between the results of Jérôme and co-workers and our work is the issue of the alignment of liquid crystals on passivated Si(111) surfaces without a deliberate miscut. As illustrated in Figure 4D, we did not observe a unique anchoring direction on samples without a deliberate miscut. In contrast, Jérôme and co-workers report a unique anchoring direction on samples prepared without a miscut.[13] One possible explanation for the orientation of liquid crystals along the [110] direction observed by Jérôme and co-workers may be a minor residual miscut which produced steps along [110] or equivalent directions.[13] Wet chemical etching in buffered HF has been demonstrated to produce single steps along the [110] direction, whereby the [11$\bar{2}$] direction points downhill.[26] On clean Si(111) 7 × 7, the steps run along the [110] direction, but the [11$\bar{2}$] direction points uphill for single steps and downhill for bunched steps.

Although we have measured the alignment of nematic 5CB to be similar on silicon surfaces with arrays of single and bunched atomic steps, it is plausible that the interactions contributing to this alignment are substantially different on these two surfaces. On substrates presenting arrays of single atomic steps, a short-range interaction between the mesogens and the terraced substrate (e.g., edges of atomic steps) likely orients the liquid crystal. We note that the size of a 5CB molecule (0.7 nm diameter and 1.9 nm length)[19] is comparable to the width of the terraces; thus, a molecular-level description (not continuum description) of the interaction is needed. On substrates with bunched steps, however, it is plausible that an additional long-range elastic interaction influences the alignment of 5CB. On these substrates, the wavelength of the topography is large compared to the size of a 5CB molecule, and thus, it is possible that a significant contribution to the anchoring energy may result from distortion of the director over the topography of these substrates.[4a] This mechanism of anchoring can be captured through a continuum description of the liquid crystal.

Because the interaction between the liquid crystal and surface is plausibly different for single- and bunched-step substrates, when they are used as templates on which to transduce the specific binding of biological species, liquid crystals may respond differently to the formation of biological complexes on each type of substrate. Unlike the obliquely deposited films of gold in past studies, where systematic manipulation of the surface topography was not easy, the nanoscale topography and anisotropy of the silicon templates described herein can be changed in a predictable manner by manipulation of the direction and angle of the miscut.

Conclusions

In summary, we have reported on the alignment of nematic liquid crystals on the surfaces of silicon that presented regular arrays of single and bunched atomic steps. The substrates were prepared in ultrahigh vacuum and chemically passivated; they were confirmed to possess

(26) Huang, Y.-C.; Flidr, J.; Newton, T. A.; Hines, M. A. *Phys. Rev. Lett.* **1998**, *80*, 4462 and references therein.

well-defined arrays of atomic steps prior to contact with the liquid crystals. In contrast to the conclusions of past studies of the anchoring of liquid crystals on the surfaces of miscut silicon, three independent measurements of the orientation of nematic 5CB lead us to conclude that the liquid crystal orients parallel to the edges of the atomic steps on surfaces with both single and bunched steps. Thus, we conclude that the orientation of the steps on these samples directs the alignment of the liquid crystals. Because the periodicity of the arrays of atomic steps can be systematically manipulated by the angle of miscut of the silicon, we believe that these substrates are likely to be useful in studies of liquid crystals transducing the formation of biological complexes on surfaces.