

Nano-domains formation on photoalignment thin film by self-organized dewetting

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Abstract— A novel discontinuous photoalignment surface with nano-domains for liquid crystal is developed. The formation of the discontinuous structure is created by self-organized dewetting, which is regarded as one of the most promising bottom-up approaches to fabricate nano-structure. Different dewetting conditions, such as surface roughness, thickness and viscosity, have been investigated. Such discontinuous photoalignment layer can be fabricated on top of another continuous alignment layer to form a new kind of heterogeneous nano-structured alignment surface – stacked alignment layers. This heterogeneous alignment surface can be used to produce arbitrary pretilt angles for the liquid crystal display. Simulation model has been built to understand the dewetting mechanism. Experiments using photo-aligned and photo-polymerisable polymer have been done to verify the dewetting theory. The produced stacked alignment layers are proved to be robust. Moreover, the dewetting processing is a fully controllable process and is compatible with existing manufacturing techniques.

Keywords — dewetting, nanostructure, photoalignment.

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Recently, different kinds of nanostructured alignment layers have been successfully fabricated for liquid crystal display. Unlike the homogeneous alignment layers, the heterogeneous alignment layers contain more than one alignment material with different alignment property and can produce arbitrary pretilt and azimuth angles or variable anchoring energy.^{1–11} These nanostructured alignment layers can either be formed by phase segregation⁹ or by stacking a nano-network on top of another homogeneous alignment layer.² In this paper, we study the formation of a discontinuous photoalignment thin film by dewetting technique. Self-organized dewetting formation is generally regarded as one of the most promising bottom-up approaches for fabricating nano-domains structure without the need of using any photo-mask. This discontinuous photoalignment layer can be created on another conventional continuous alignment layer to form a stacked structure.^{2,11} The self-organized dewetting process of the planar-aligned (PA) photoalignment polymer forms nano-structured islands and domains on top of another vertical-aligned (VA) polyimide. In addition, by varying the dewetting conditions, precise control of the domain ratio becomes possible and allowing to produce any pretilt and azimuth angles for the liquid crystal molecules.¹ Many applications can be made possible if such pretilt angles are available, such as bistable display devices¹² and no-bias-bend fast switching display devices.¹³ Furthermore, this stacked alignment layers are able to fill the technology gap for fabricating spatially varying pretilt angles within a single substrate. The generated pretilt angles can be spatially varied by controlling the exposure light profile for the photoalignment polymer. A liquid crystal lens, by using the stacked alignment layers, has been successfully fabricated.¹⁴

Hence, we have proven that alignment surfaces produced by using the dewetting technique are robust and are compatible with existing liquid-crystal display manufacturing processes.

In recent years, much effort has been put into understanding the dewetting phenomenon in thin films on solid substrates, both experimentally and theoretically.^{15–20} Indeed, thin liquid films on solid substrates are present in everyday life, for example, ink on a transparency. In some cases, these films are not stable on their substrate and bead up, a phenomenon that is easily observable if one tries to paint oily surface. A liquid film on a non-wettable substrate is not stable and will bead up. While viscous flow is generally considered as the dominant mechanism, dynamics are driven by pressure gradients within the films, which are primarily dominated by the surface energy of the thin liquid film and the effective interface potential to the substrate. When a thin liquid film beads off a solid substrate, it is eventually transformed into an ensemble of individual liquid droplets.

Liquid surfaces are never completely flat. Because of temperature fluctuations, there is always a spectrum of capillary waves present. The stability of the film is determined by the transient behavior of fluctuations on its surface. The schematic drawing of the instabilities of the thin film is sketched in Fig. 1. The instabilities of thin films are analyzable using hydrodynamics. For the motion of a Newtonian fluid with viscosity η , density ρ , the Navier–Stokes equation is given by

$$\rho(\partial_t v + (v \cdot \nabla)v) = -\nabla p + \eta \nabla^2 v + \rho g \quad (1)$$

where p is the pressure within the film. If the viscosity of the applied fluid such as a polymer is very high, the convective

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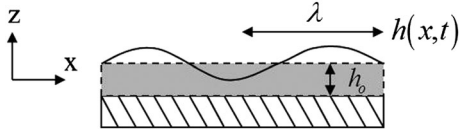


FIGURE 1 — Schematic of a liquid thin film on a solid substrate.

term $(v \cdot \nabla)v$ can be ignored. Furthermore, since the resulting dynamics is very slow, the velocity profile can always be considered to be $\partial v \rightarrow 0$. Therefore, gravity effect g is also not important at this case as well. With the aforementioned considerations, Eq. (1) can be rewritten as

$$\nabla^2 v = \frac{1}{\eta} (\nabla p) \quad (2)$$

It can be seen that the velocity only depends on the z -coordinate. The corresponding integration with the boundary conditions gives

$$v = \frac{1}{2\eta} (\nabla p) z^2 - \frac{h}{\eta} (\nabla p) z \quad (3)$$

Hence, the mean velocity can be obtained:

$$\bar{v} = \frac{h^2}{3\eta} (-\nabla p) \quad (4)$$

Consider that the liquid is incompressible; the change in volume must simply be due to a variation in the level of the fluid. It can be expressed as $\partial_t h = \nabla \cdot (h\bar{v})$. Therefore

$$\partial_t h + \frac{1}{3\eta} \nabla \cdot (h^3 (\nabla p)) = 0 \quad (5)$$

For the pressure within the film, it actually depends on the film thickness. The pressure may come from several contributions, atmospheric pressure, surface tension pressure, and excess intermolecular force. The importance of the various terms depends on the experimental conditions. Here, we only consider the most important term, the excess intermolecular force. R. Seemann, S. Herminghaus and K. Jacobs *et al.*^{21–23} have suggested that the excess intermolecular force or effective interface potential for this system can be written as

$$p_{vdW}(h) = \frac{B}{h^8} - \frac{A}{12\pi h^2} \quad (6)$$

where A is the effective Hamaker constant to describe the long range van der Waals force and B describes the short range repulsive interactions. Assuming only non-retarded van der Waals forces within the thin film geometry, therefore, there are only two possible scenarios for the film. In the first scenario, the Hamaker constant is negative, which means that the van der Waals forces are repulsive, pushing the film apart. Hence, the film can minimize its free energy by increasing its thickness. In other words, the film is wetting

the surface and is stable. However, if the Hamaker constant is positive, which means the van der Waals forces are attractive when $\langle h \rangle > h_c$, the film reduces its free energy by thinning. The film is hence unstable and dewets. Such dewetting is called spinodal dewetting in which capillary waves are spontaneously amplified. Another dewetting rupture mechanism is caused by nucleation, which may be initiated by defects or thermal. In this paper, we will only consider the spinodal dewetting. The spinodal dewetting can only take place when the second derivative of the excess intermolecular force with respect to the film thickness is negative, that is, $p''_{vdW}(h_0) < 0$, where h_0 is the initial homogeneous film thickness.

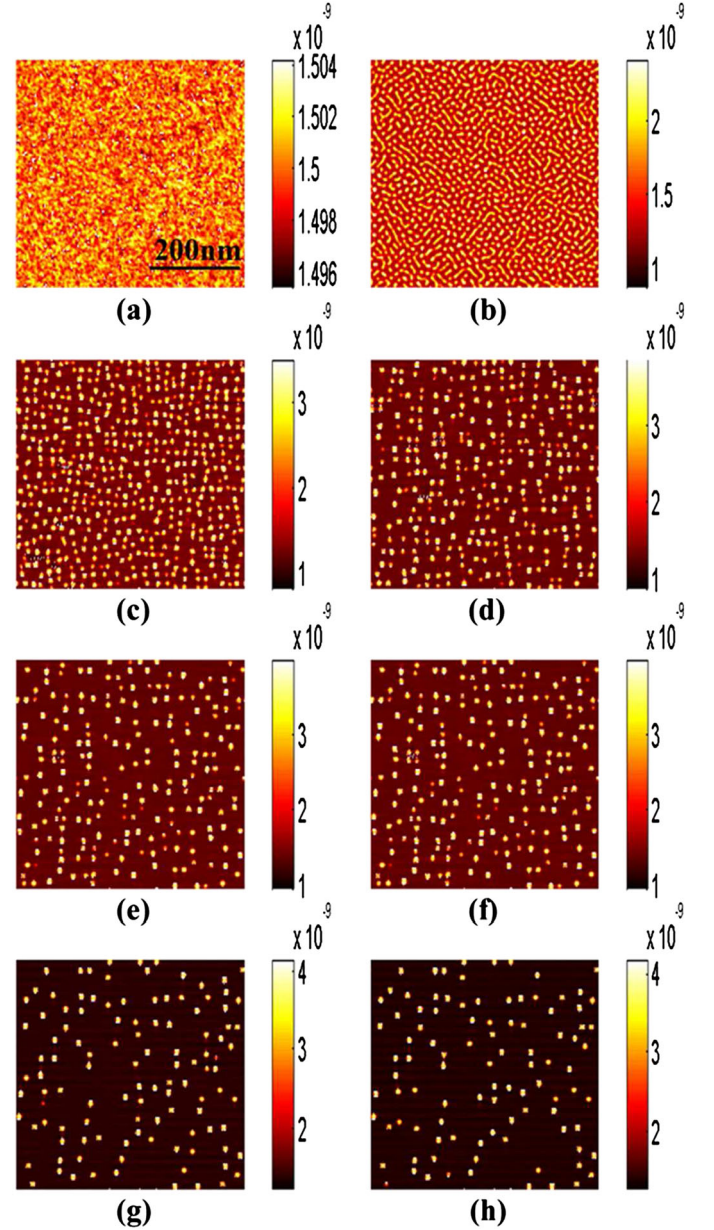


FIGURE 2 — The dynamics of a dewetted thin film with mean thickness 1.5 nm at time: (a) 0 μ s, (b) 0.08 μ s, (c) 3.75 μ s, (d) 6.7 μ s, (e) 142 μ s, (f) 680 μ s, (g) 850 μ s, and (h) 1.5 ms.

By substituting Eq. (6) into Eq. (5), we can obtain the final equation to describe the dynamics of the thin film on the substrate:

$$\partial_t h + \frac{1}{3\eta} \nabla \cdot [h^3 (-\gamma \nabla^2 h + \partial_h p_{vdW}(h) \nabla h)] = 0 \quad (7)$$

Numerical simulation using time iteration method on 250×250 lattices with periodic spacing of 2.5 nm and time step of 0.1 ns had been performed. The surface tension was 30 mNm^{-1} , viscosity 30 mPas , short range repulsive interactions $6 \times 10^{-75} \text{ Jm}^6$, and the effective Hamaker constant $5.3 \times 10^{-19} \text{ J}$. Based on the numerical model, we were able

to investigate the dewetting pattern with different mean thin film thicknesses (1.5 nm, 3 nm, 4 nm, 5 nm, and 7 nm) at different time steps as shown in Figs. 2–6. When the film thickness increases, the growth of instability is retarded owing to the spinodal decomposition effect becoming weaker. Figure 7 shows the simulated arithmetic average roughness of thin film with surface tension equals to 30 mNm^{-1} and 60 mNm^{-1} , respectively. As expected, from Fig. 7, it can be observed that the thin film will eventually become flat as the thickness increases. Figure 8 plots the simulated pretilt angles of a dewetted (discontinuous) PA alignment film on a continuous VA alignment layer against a wetted (continuous) PA alignment film on a continuous VA alignment layer. The

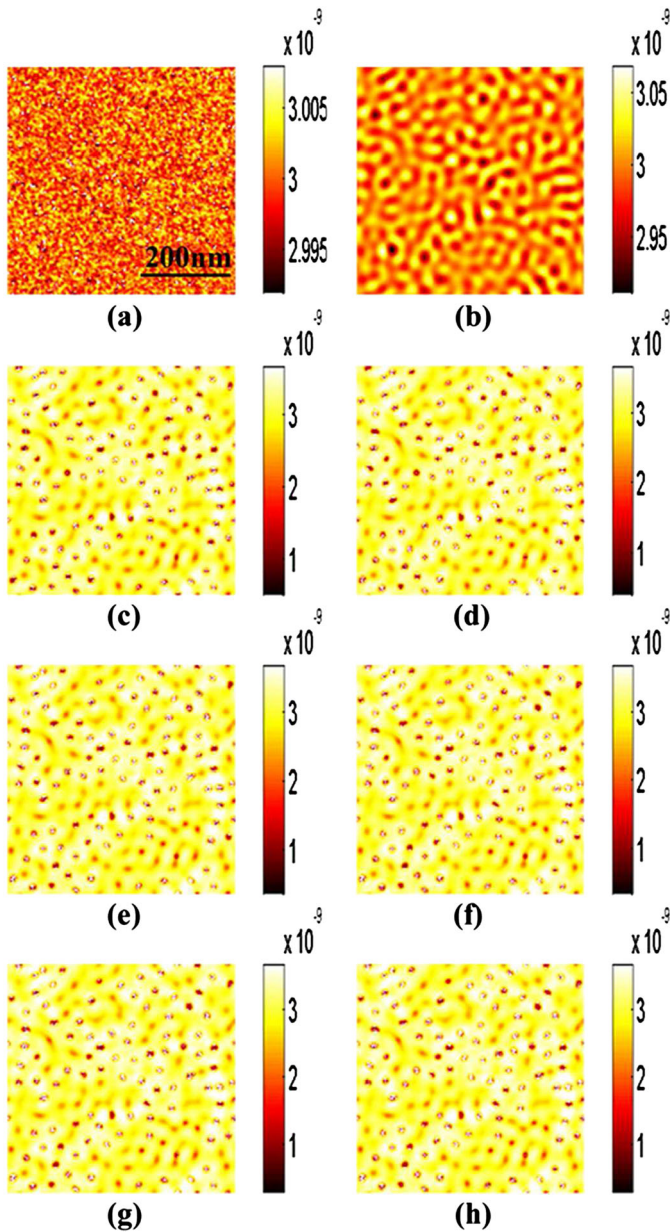


FIGURE 3 — The dynamics of a dewetted thin film with mean thickness 3 nm at time: (a) 0 μs , (b) 0.3 μs , (c) 7 μs , (d) 15 μs , (e) 37 μs , (f) 65 μs , (g) 122 μs , and (h) 262 μs .

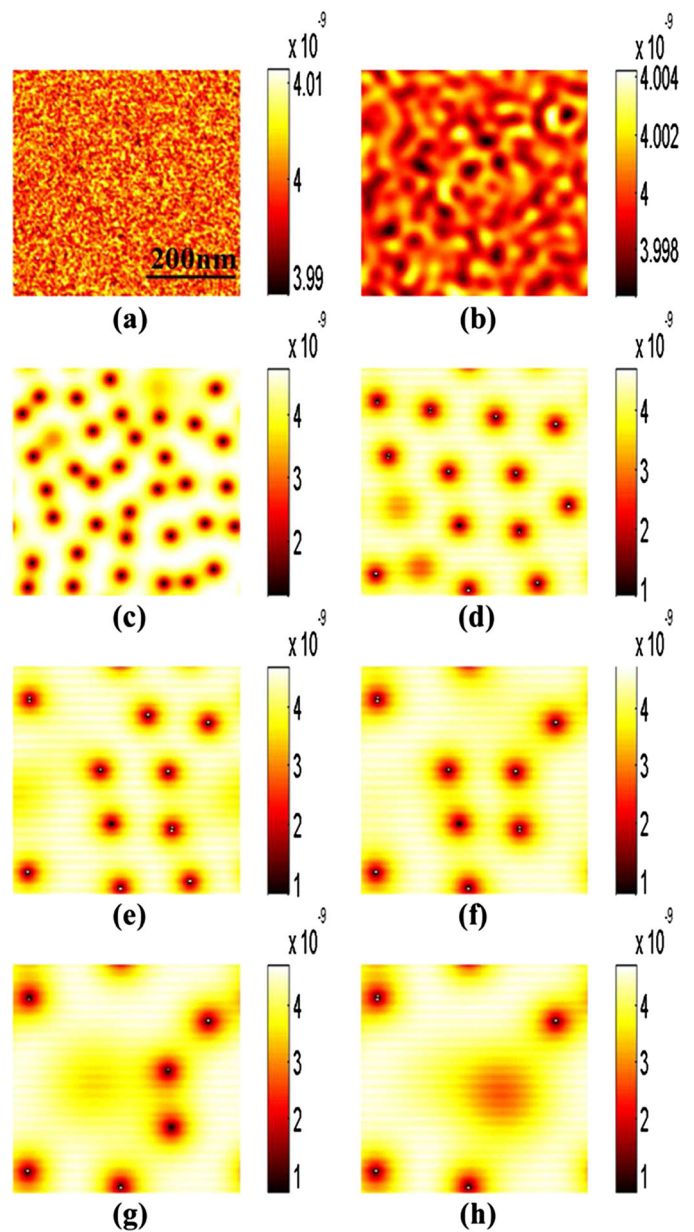


FIGURE 4 — The dynamics of a dewetted thin film with mean thickness 4 nm at time: (a) 0 μs , (b) 0.5 μs , (c) 16 μs , (d) 22 μs , (e) 50 μs , (f) 76 μs , (g) 124 μs , and (h) 215 μs .

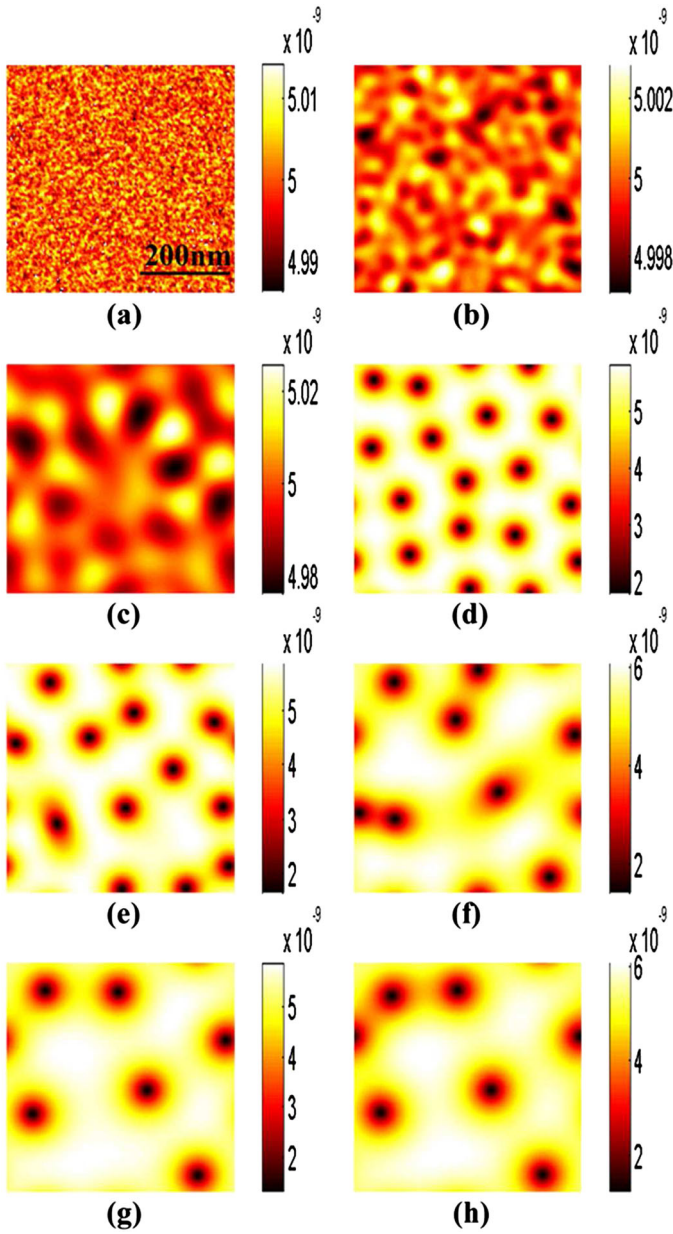


FIGURE 5 — The dynamics of a dewetted thin film with mean thickness 5 nm at time: (a) 0 μ s, (b) 0.17 μ s, (c) 11 μ s, (d) 22 μ s, (e) 81 μ s, (f) 108 μ s, (g) 147 μ s, and (h) 204 μ s.

dark curve represents the wetted film, while the blue and red curves represent the dewetted film with different surface tensions. The result indicates important facts that the domains effect indeed existed because of thin film thickness fluctuation. In addition, the intermediate pretilt angles transition range for the dewetted film is about three to five times wider than the wetted film. A stronger surface tension film will induce thick and large domains. Hence, for the application of generating arbitrary pretilt angles, a dewetted film is indeed better than a wetted film as the pretilt angles are changing gradually. For a weak surface tension film, the effect is similar to wetted film. The pretilt angles tend to change abruptly against the film thickness. Such effect may suitable for some sensor applications.

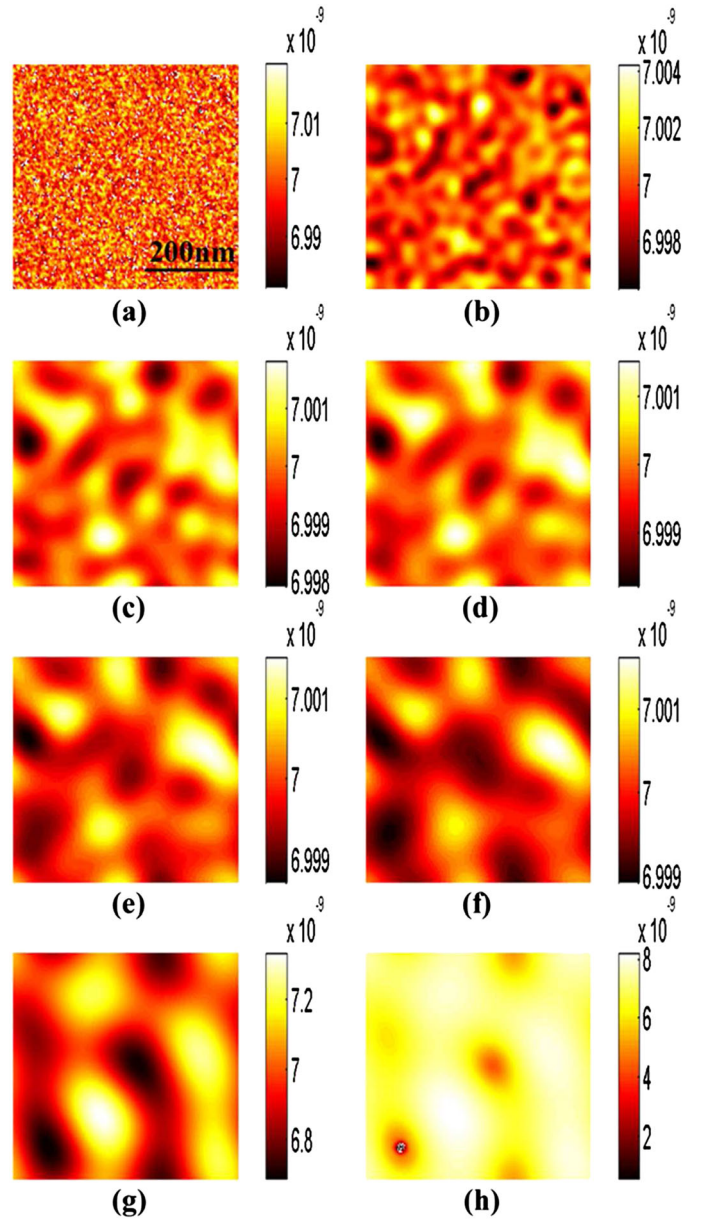


FIGURE 6 — The dynamics of a dewetted thin film with mean thickness 7 nm at time: (a) 0 μ s, (b) 0.06 μ s, (c) 4 μ s, (d) 8 μ s, (e) 40 μ s, (f) 81 μ s, (g) 162 μ s, and (h) 292 μ s.

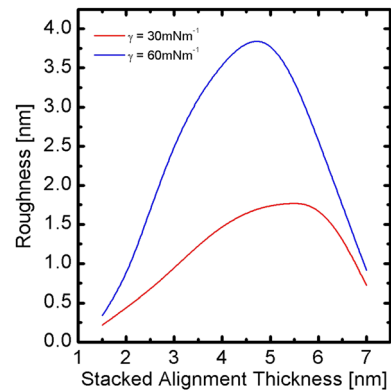


FIGURE 7 — Simulated roughness of stacked alignment layers with different surface tensions.

In order to verify the theory, several experiments have been done. First, an indium tin oxide glass substrate was prepared. The substrate was spin-coated with different concentrations of a PA photo-polymerizable photoalignment polymer, ROP-103, provided by Rolic Technology Ltd, Switzerland. The thickness of the ROP-103 film was adjusted by dissolving different concentration (0.06 wt.%, 0.08 wt.% and 0.1 wt.%) of

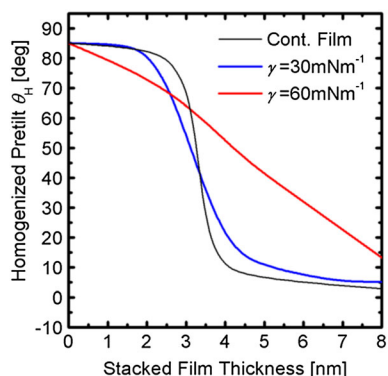


FIGURE 8 — Simulated pretilt angles produced by stacked alignment layers with wetted and dewetted top layer.

ROP-103 into solvent Cyclohexane. Because low viscosity solvent was applied, thin photoalignment film would be formed during spin coating, and dewetting was expected to occur. The polymer was then polymerized by using linearly polarized ultra-violet exposure. Atomic force microscopic pictures were scanned afterward and shown in Fig. 9. From Fig. 9(a) and (b), it can be seen that the alignment layers are indeed discontinuous and the “valley” and “hill” are uniformly distributed within the substrate. The average domain size is about 100 nm to 250 nm. However, when the concentration of the ROP-103 increased to 0.1 wt.%, thicker film would be obtained after spin coating. Eventually, the coated film cannot undergo dewetting as it is too thick. Hence, a continuous alignment layer was formed as shown in Fig. 9(c).

The effect of the surface tension had also been verified by experiments. Two substrates (S1 and S2) were coated with same VA polyimide JALS2021 provided from JSR Corporation, Japan; but were prepared by different cycling temperatures, 180°C and 230°C, respectively. The corresponding surface contact angles were measured by exposing the substrate under dimethylformamide solvent vapor in a dry box. It can be observed from Fig. 10 that the two substrates

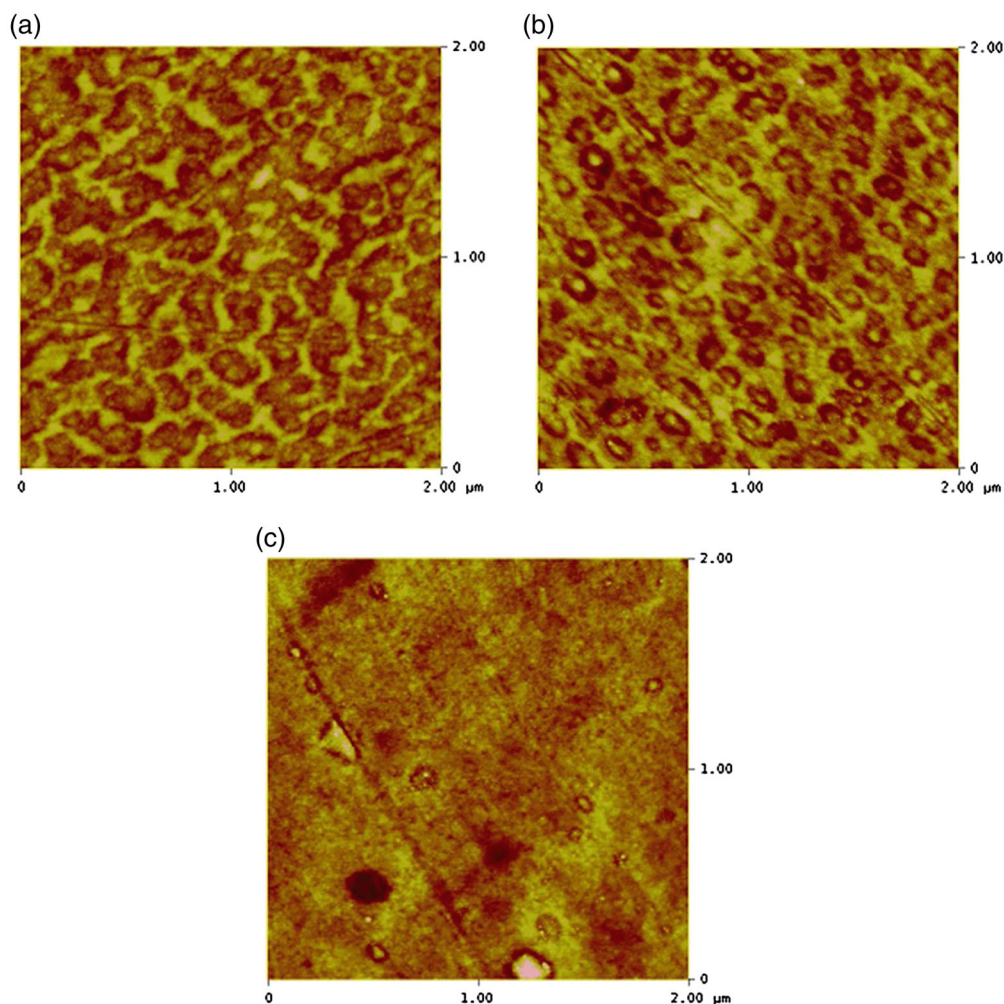


FIGURE 9 — Atomic force microscopy pictures of photoalignment thin films with different concentrations: (a) 0.06 wt.%, (b) 0.08 wt.%, and (c) 0.1 wt.%.

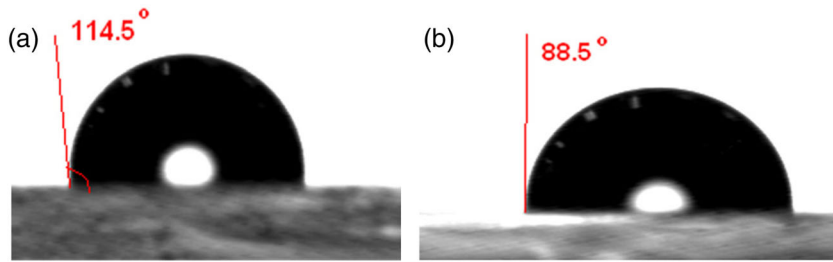


FIGURE 10 — Measured contact angles of vertical-aligned polyimide surfaces with different cycling temperatures: (a) 180°C and (b) 230°C.

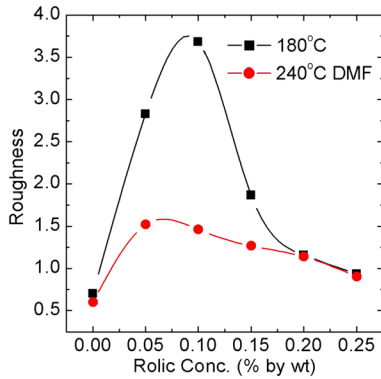


FIGURE 11 — Measured roughness of stacked alignment layers on substrate with different surface tensions.

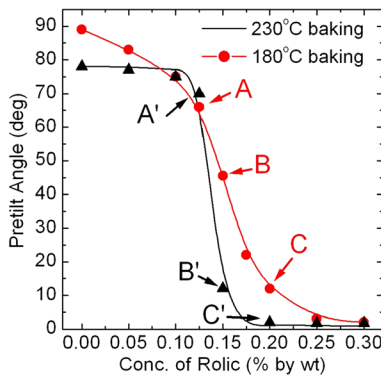


FIGURE 12 — Measured pretilt angle of stacked alignment layers with different dewetting conditions.

resulted in different contact angles indicating that they were having different surface tension.

The substrates were further coated with different concentration of ROP-103 solutions on top to form stacked alignment surfaces. The roughness and pretilt angle of the stacked alignment surfaces had been investigated. The measured results are plotted in Figs. 11 and 12. It is found that the stronger surface tension alignment layer, such as substrate S1 will induce thicker and larger domains. The corresponding pretilt angles will change in a more gradual way. On the other hand, we found abrupt drop of pretilt angle for substrate S2 which has lower surface tension. Such findings agreed with our previous simulations.

In conclusion, we have demonstrated that thin photoalignment film on solid substrate is not stable and will

dewet. A discontinuous photoalignment layer can be fabricated by using the dewetting phenomenon. A dewetting model based on Navier–Stokes equation has been built. From the simulation results, it is proven that different nano-pattern can be formed by controlling the dewetting conditions. By stacking such discontinuous photoalignment layer on top of a conventional continuous alignment layer, heterogenous liquid crystal alignment surface can be produced. The stacked alignment layers are capable of generating arbitrary pretilt and azimuth angles. The results are highly repeatable because of the promising dewetting process.

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