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2016

Zhao, Y., & Yang, C. (2016). Retarded condensate freezing propagation on superhydrophobic surfaces patterned with micropillars. *Applied Physics Letters*, 108(6), 061605-.

<https://hdl.handle.net/10356/82792>

<https://doi.org/10.1063/1.4941927>

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Citation: [Applied Physics Letters](#) **108**, 061605 (2016); doi: 10.1063/1.4941927

View online: <http://dx.doi.org/10.1063/1.4941927>

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Retarded condensate freezing propagation on superhydrophobic surfaces patterned with micropillars

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(Received 10 October 2015; accepted 2 February 2016; published online 12 February 2016)

Previous studies have shown ice delay on nano-structured or hierarchical surfaces with nanoscale roughness. Here we report retarded condensate freezing on superhydrophobic silicon substrates fabricated with patterned micropillars of small aspect ratio. We further investigated the pillar size effects on freezing propagation. We found that the velocity of freezing propagation on the surface patterned with proper micropillars can be reduced by one order of magnitude, compared to that on the smooth untreated silicon surface. Additionally, we developed an analytical model to describe the condensate freezing propagation on a structured surface with micropillars and the model predictions were compared with our experimental results. © 2016 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4941927>]

Ice and frost accretions may cause severe consequences in numerous applications. Though various de-icing or anti-icing techniques have been developed, more desirable approaches would be to retard or prevent ice formation instead of removing ice with physical and chemical means.

Owing to rapid development of the micro- and nano-fabrication methods, bio-inspired superhydrophobic (SHPB) surfaces with tunable surface morphology at micro/nano scales and interfacial energy have drawn great attention.^{1–5} Numerous studies showed that the use of SHPB surfaces can effectively retard heterogeneous ice nucleation^{6,7} and reduce ice adhesion.^{8,9} However, it was found that surface “icephobicity” does depend not only on surface wettability but also on complex surface morphology.^{10,11} Jung *et al.*¹² reported that the design of anti-icing surfaces must consider the competing influences of both wettability and roughness. The results of Varanasi *et al.*⁹ and Meuler *et al.*¹³ provided experimental evidences of failure of SHPB surfaces for reducing condensate frosting. On the other hand, Lee *et al.*¹⁴ and Stone¹⁵ showed that under certain conditions, zwitter-wettability or even hydrophilic surfaces could have better performance in icephobicity. Nonetheless, based on these works, one cannot conclude that SHPB surfaces are always icephobic. Furthermore, the high aspect ratio asperities on SHPB surfaces appear to be readily damaged during thermocycling or wetting processes.^{16,17} Such structure degradation would result in superhydrophobicity deterioration and therefore impair surface icephobicity.

Given a surface with sufficiently low temperature in ambient air, condensate frosting is inevitable. Moreover, to study how freezing propagation is of significance as heterogeneous nucleation usually is inevitable.^{3,18,19} Unfortunately, little information is available on quantitative study of freezing propagation. In this letter, we report an investigation of the condensate freezing propagation on SHPB surfaces fabricated with patterned micropillars of small aspect ratios. Numerous experiments were conducted to study the pillar

size effect on the freezing propagation. Importantly, different from most previous studies reporting that nano-structured or hierarchical surfaces with nanoscale roughness can effectively retard frosting invasion, we found that our SHPB surfaces with micropillar patterns also can profoundly suppress the frost invasion and hence reduce freezing propagation velocity. An analytical model was derived to provide a quantitative description of freezing propagation velocity on an SHPB surface with patterned pillars and to elucidate the mechanism of ice bridging between a frozen droplet and a condensate droplet.

We fabricated a series of silicon-based cylindrical micropillar patterned substrates with pillar sizes varying from 5 μm to 200 μm . These pillar patterns were made using the standard photolithography and the deep reactive ionic silicon etching. Once etching off mask layers, we modified the surface energy of silicon to promote hydrophobicity through chemical vapor deposition (CVD) of trichloro(1H,1H,2H,2H-perfluorooctyl)silane monolayer (Sigma Aldrich) right after an oxygen plasma treatment. A schematic diagram showing such surface fabrication procedure is illustrated in supplementary Figure S1.²⁰ Figure 1 shows the scanning electronic microscopy images (FESEM, JEOL7600) of silicon substrates with patterned pillars for three different pillar structure parameters, the surface chemistry modification with silanization, and the wettability characterization of a fabricated SHPB surface. The fabricated silicon based surfaces consist of an array of micron-sized circular pillars, with d , h , and l denoting the pillar diameter, height, and interspacing, respectively. For these engineered SHPB surfaces, two structure parameters, (i) d/l and (ii) h/d , are kept constant with their values as 1 and 2, respectively.

We built an isolated cryostage together with a precise thermal control unit and a high-speed visualization to study condensate freezing propagation (see Figure S2 (Ref. 20)). Prior to experiment, the testing surfaces were flushed with deionized (DI) water and then dried in nitrogen gas flow. During experiment, the substrate temperature was maintained at a constant temperature -10°C using a proportional-

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FIG. 1. Fabricated micropillars on silicon substrates: characterization and chemical modification. (a) Scanning electronic microscopy images of pillars with three different diameter/inter-spacing/height = $d/l/h$; (b) surface hydrophobic treatment with silanization via chemical vapor deposition; (c) schematic illustration of the pillar geometry; (d) static contact angle of 167.5° for a $5\ \mu\text{l}$ deionized water droplet on a $25/25/50\ \mu\text{m}$ pillar patterned and silanized silicon surface.

integral-derivative controller via a LabView data acquisition input and output module (National instrument, NI 9219 and NI 9264). The condensate freezing propagation experiments were conducted in an enclosure chamber filled with a mixture of nitrogen gas and water vapor with a dry-bulb temperature and relative humidity as $25 \pm 1^\circ\text{C}$ and $40 \pm 5\%$, respectively. In-chamber pressure was balanced with ambient pressure via a one-way valve.

As the energy barrier for heterogeneous nucleation is smaller at substrate edges, ice nucleation is triggered at edges and then invades inwards. By setting a $700 \times 700\ \mu\text{m}^2$ observation window close to a boundary edge of the testing structured surface, we could thus observe a unidirectional freezing propagation. Figure 2 shows a comparison of snapshot images taken at three different times for condensate freezing on three kinds of surfaces, one smooth hydrophobic surface (silanized using the same CVD treatment as shown in Figure 1) and two surfaces with patterned pillars of $5\ \mu\text{m}$ and $50\ \mu\text{m}$ in diameter. Setting t_0 as the time of first emergence of ice phase within the observation window, we obtained the time taken for freezing front to travel across the observation window on these three surfaces as 34.5 s, 56.6 s, and 207.6 s, respectively; this gives their mean propagation velocities as $20.3\ \mu\text{m/s}$, $12.4\ \mu\text{m/s}$, and $3.37\ \mu\text{m/s}$, respectively. Corresponding videos captured for these three surfaces are provided in multimedia views. Additionally, the condensate freezing experiment was also conducted on a smooth untreated silicon surface, on which an average freezing propagation velocity of $36.1\ \mu\text{m/s}$ was obtained, and its video is shown in supplementary movie 1.²⁰ These results show that through modifying the interfacial energy and choosing proper size of patterned micropillars, the freezing

FIG. 2. Freezing propagation on smooth and two different micropillars ($5\ \mu\text{m}$ and $50\ \mu\text{m}$ in diameter) patterned SHPB silicon surfaces. Freezing begins at sample edges and then invades inwards as shown. t_0 is set as the time that the first ice crystalline appears in the observation window which locates closely along the left-side boundary of samples. Bright thick lines indicate the location of freezing front. (Multimedia view) [URL: <http://dx.doi.org/10.1063/1.4941927.1>]

propagation velocity of condensate frosting on an SHPB surface patterned with $50/50/100(d/l/h)\ \mu\text{m}$ pillars can be reduced to one order smaller than that on the smooth untreated silicon surface.

Since ice nucleation is triggered at substrate edges, condensate nucleation and following droplet growth/collision determine the size and distribution of condensate droplets. These are crucial factors affecting freezing propagation. For a smooth hydrophobic substrate with uniform surface chemistry, condensation occurs homogeneously all over the surface, showing no spatial preference.²¹ As the droplet size grows, collision and coalescence among individual droplets happen so as to minimize interfacial energy. Freezing front propagates horizontally from droplet to droplet along the solid substrate. For a surface fabricated with patterned micropillars, however, the growth rate of condensate nucleation sites is much faster at the pillar tops and pillar edges. The pillar tops collect most of condensate because the gradient of water vapor is much larger than that on the pillar side and bottom surface.^{22,23} Instead of a random distribution and a continuous growth, both condensate droplet size and location are confined by the pillars. Therefore, we can modulate the condensate droplet size and distribution by using different micropillar sizes.

Supplementary movie 2 (Ref. 20) provides more details about freezing front propagation from a frozen droplet to a condensate droplet. A subcooled water droplet starts freezing into an ice crystal when an ice bridge is formed from one of

its neighboring frozen droplets. The physical contact between ice bridge tip and subcooled liquid is necessary to trigger heterogeneous ice nucleation. An experimentally observed ice bridge is shown in Figure 3(a).

To quantitatively describe inter-pillar freezing propagation, we developed an analytical model on the basis of the following four major assumptions: (1) the freezing propagation is through ice bridging between one frozen droplet and one condensate droplet by neglecting effects of other surrounding frozen and condensate droplets. (2) The formation of an ice bridge is modeled as one-dimensional water vapor diffusion mass transfer from liquid to ice phases. (3) The shape of an ice bridge is approximated as a circular cone (see Figures 3(a) and 3(b)). (4) The time required to complete an intra-droplet freezing is neglected. Specifically, the last assumption is related to two stages involved in freezing a droplet.^{24,25} Based on our droplet size, such intra-droplet freezing time is much smaller than the interdroplet freezing time, namely, the ice bridge formation time. Letting R_d , R_p , and θ , respectively, be the droplet radius, pillar radius, and static contact angle (see Figure 3(b)), a simple geometry relationship among them holds $R_d = R_p / \sin \theta$. For a hydrophobic surface, $90^\circ \leq \theta \leq \theta_c$, where θ_c is the critical angle above which the condensate droplet cannot be held on the pillar top. Quantitatively, θ can be correlated to the total amount of condensate which depends on condensation time, substrate temperature, and relative humidity.^{10,18} The time Δt required to build up an ice bridge can be related to the freezing propagation velocity u and the mass transfer rate $\dot{M}_v$, and thus we can write

$$\Delta t = \frac{l + 2R_p}{u} = \frac{\rho_{ice} V_{ice_b}}{\dot{M}_v}, \quad (1)$$

where ρ_{ice} is the ice density and V_{ice_b} is the volume of ice bridge. The latter can be determined from a geometric relationship for a circular cone (see Figure 3(b)), $V_{ice_b} = \pi \{ (-R_d \cos \theta)^2 [l - R_d(1 - \sin \theta)] - R_d^3 (2 + \sin \theta)(1 - \sin \theta)^2 \} / 3$. According to the theory of mass diffusion, we have

$$\dot{M}_v = \vec{j}_v \cdot \vec{s}, \quad (2)$$

$$\vec{j}_v = -D \nabla c, \quad (3)$$

FIG. 3. (a) Experimental observation before and after formation of an ice bridge; (b) schematic diagram of an ice bridge between a frozen droplet (right) and a condensate droplet (left) on pillar top. The geometry of the ice bridge is considered to be of a circular cone shape for our analysis.

where $\vec{j}_v$ and $\vec{s}$, respectively, denote the mass flux of water vapor and the projected area of the ice bridge that from the water droplet to the ice crystal, D is the diffusion coefficient for water vapor in air and is chosen as $10^{-5} \text{ m}^2/\text{s}$,²⁶ and c is the density of water vapor. The use of ideal gas law gives $c = P_{\text{vapor}} M / RT$ (Here, P_{vapor} is the vapour partial pressure, T the vapour temperature, $R = 8.31 \text{ J/mol K}$ the universal gas constant, and $M = 18 \text{ g/mol}$ the molar weight of water). Since the observation time shown in Figure 2 is in the order of $t_c = 10 \text{ s}$, the thermal penetration length during this period can be estimated using a scaling law of heat transfer as $\delta_{Th} \sim \sqrt{\alpha t_c}$ which is about 1 cm by assuming the thermal diffusivity of water vapour $\alpha = 10^{-5} \text{ m}^2/\text{s}$. This suggests that the vapour temperature around pillars can be treated the same as the substrate temperature, -10°C .

Applying a linear approximation to the concentration gradient, $|\nabla c| \approx \Delta C / l = (P_{\text{vapor,water}} - P_{\text{vapor,ice}}) M / RT$ and expressing the projected area $\vec{s}$ as $|\vec{s}| = R_d^2 (\theta - \sin \theta \cos \theta)$, we can obtain

$$\dot{M}_v = \frac{DMR_d^2 (P_{\text{vapor,water}} - P_{\text{vapor,ice}}) (\theta - \sin \theta \cos \theta)}{RTl}. \quad (4)$$

The values of vapour partial pressures of ice and water can be obtained elsewhere.²⁷ Finally, the freezing propagation velocity can be determined by

$$u = \frac{(l + 2R_p) \dot{M}_v}{\rho_{ice} V_{ice_b}}. \quad (5)$$

Figure 4 shows a variation of the freezing propagation velocity with pillar diameter for the case of $l = d (= 2R_p) = h/2$. Here, both experimental data and theoretical results calculated from the analytical model given by Eq. (5) are included for comparison. Also, the freezing propagation velocity for the smooth hydrophobic surface is depicted with a horizontal dash line. Clearly the analytical model can largely capture the trend of our observed experiments. Specifically, during a

FIG. 4. Variation of freezing propagation velocity with pillar diameter, d . The pillar size ratios are maintained as $d/l/h = 1/1/2$. Solid line and symbols represent the calculated results based on our analytical model expressed by Eq. (5) and the experimental data, respectively. The horizontal dash line denotes the smooth hydrophobic substrate. The insets show distinguished behaviours of condensate freezing on three different surface regimes with, (I) relatively small, (II) medium, and (III) relatively large pillar diameters (also inter-pillar spacings).

certain pillar diameter range (about 10–100 μm), the theory agrees with the experiment reasonably well, showing that the freezing propagation velocity decreases as increasing the pillar diameter.

The inset images in Figure 4 exhibit distinguished behaviours of condensate freezing on three different surface regimes with, (I) relatively small, (II) medium, and (III) relatively large pillar diameters and inter-pillar spacing. In Regime I involving fine patterned surfaces with small pillars (10 μm and less), the absolute surface areas in Regime I are much larger than those of smooth/coarse patterned surfaces, and thus inter-droplet collision and coalescence mostly occur. This leads to drastically reducing the number of droplets and thus ice bridges but at the same time results in increasing the size and inter-spacing of condensate droplets (see the 5 μm pillar case in Figure 2). Therefore, these two competing effects determine the eventual freezing propagation velocity. When we increase the diameter and inter-spacing of pillars to be in Regime II, both condensate droplet size and location are confined by the pillar tops, as shown in the inset in Figure 4. A larger gap between inter-droplets suggests the need of building a bigger volume of ice bridges, giving rise to a slower freezing propagation on such medium pillar size patterned surfaces. In Regime III involving more coarse patterned surfaces with large pillars (100 μm and above), droplets locating at the pillar sidewalls are more likely to grow faster than those on the pillar top (see supplementary movie 2 (Ref. 20) and the inset in Figure 4). Instead of connecting prime droplets on the pillar tops as shown in Figure 3, ice bridges appear to be built up between droplets on sidewalls as well. Thus, the effective droplet spacing or the size of ice bridges is reduced considerably. These ice bridges change into a more “slim” mode stemming from the pointy nature of frozen ice droplet tip,^{7,28} leading to increasing the freezing propagation velocity. Here, it needs to be mentioned that in our experiments we kept $d/l/h = 1/1/2$. If we fix d/h while changing l , similar phenomena as shown in Figure 4 may be expected. Also, there could be a critical value for d/l , where the minimum freezing propagation velocity may occur. Certainly more experiments are needed to examine how changing l will affect the freezing propagation. It also should be pointed out that our analytical model which is derived based on the physical model illustrated in Figure 3(b) can only describe the freezing propagation on patterned surfaces in Regime II. Noticeable differences between the theory and the experiment are found for patterned surfaces in Regimes I and III because those mechanisms and phenomena discussed for these two regimes are not reflected in the model. In addition, only mass diffusion of water vapour is considered. Other factors such as ice volume expansion, temperature gradient, and induced mass diffusion (Soret effect) are not taken into account. This can lead to underestimation of the freezing propagation velocity as shown in Figure 4.

In summary, we have investigated the condensate freezing on silicon based SPHB surfaces with patterned pillars ranging from 5 μm to 200 μm in diameter. Also, we have quantitatively examined the freezing propagation velocity. Specifically, it was shown that compared to the smooth untreated silicon surface, the freezing propagation velocity

on the SPHB surface with patterned pillars of 100 μm in diameter and inter-spacing is about one order of magnitude slower. In addition, we have derived an analytical model to describe the freezing propagation velocity. Through comparing with our experimental results, we found that the model can reasonably explain our experimental findings in Regime II shown in Figure 4. The present study provides insights into the effect of surface microstructure on condensate freezing. Due to unavoidable geometry/chemistry defects, an absolute ice free surface is not achievable. Hence, this work shows a promising way of generating a temporary ice (ice delay) free surface via patterned micropillars of small aspect ratios, which would be more robust and durable.^{16–18}

Y.Z. acknowledges the support from the Nanyang Technological University PhD Scholarship via Nanyang Environment & Water Research Institute (NEWRI).

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