Nanograssed Micropyramidal Architectures for Continuous Dropwise Condensation

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Engineering the dropwise condensation of water on surfaces is critical in a wide range of applications from thermal management (e.g. heat pipes, chip cooling etc.) to water harvesting. Surfaces that enable both efficient droplet nucleation and droplet self-removal (i.e. droplet departure) are essential to accomplish successful dropwise condensation. However it is extremely challenging to design such surfaces. This is because droplet nucleation requires a wettable surface while droplet departure necessitates a super-hydrophobic surface. Here we report that these conflicting requirements can be satisfied using a hierarchical (multiscale) nanograssed micropyramid architecture that yield a global superhydrophobicity as well as locally wettable nucleation sites, allowing for ~65% increase in the drop number density and ~450% increase in the drop self-removal volume as compared to a superhydrophobic surface with nanostructures alone. Further we find that synergistic cooperation between the hierarchical structures contributes directly to a continuous process of nucleation, coalescence, departure, and re-nucleation enabling sustained dropwise condensation over prolonged periods. Exploiting such multiscale coupling effects can open up novel and exciting vistas in surface engineering leading to optimal condensation surfaces for high performance electronics cooling and water condenser systems.

1. Introduction

The miniaturization of electronic devices demands novel thermal management techniques to efficiently dissipate heat over a small area. Two-phase heat transfer devices such as condensers allow for high heat transfer coefficients. In particular, dropwise condensation is able to produce heat transfer coefficients an order of magnitude higher than film condensation. Therefore engineering surfaces that enable dropwise condensation is of paramount importance. An ideal condenser surface should be able to shed condensate drops as early and quickly as possible and possess large quantities of nucleate sites that enable rapid drop nucleation and growth for continuous condensation. However it is extremely challenging to design such surfaces. The dilemma lies in the fact that the complex condensation process is influenced by the surface wettability: wettable surfaces are favored for the drop nucleation process whereas superhydrophobic surfaces are favored for drop departure. Previous investigations of condensation on superhydrophobic surfaces or hybrid hydrophilic-hydrophobic patterns have provided important insights on preventing the onset of filmwise condensation while enhancing drop nucleation and growth, but still fail to address the challenge in designing dropwise condensation surfaces to promote both drop growth and drop departure simultaneously. Since wettability is dependent on surface roughness to meet this challenge, we envision designing a three-dimensional (3D) heterogeneous surface that yields a global superhydrophobicity as well as locally wettable patches through spatial control of surface roughness. Here we report such a hierarchical nanograssed micropyramid architecture that promotes drop nucleation as well as drop departure without compromising each other. Specifically, the presence of wettable patches facilitates drop growth and preferential coalescence whereas the global superhydrophobicity promotes spontaneous drop departure without pinning to the substrate. Moreover, synergistic co-operation between the hierarchical roughness structures contributes directly to a continuous process of nucleation, coalescence, departure, and re-nucleation enabling sustained dropwise condensation over prolonged periods. Development of optimal condensation surfaces by exploiting such synergistic coupling in hierarchical structures has important implications for applications such as high performance electronics cooling, heat transfer and water harvesting.

Figure 1a shows a schematic drawing of our designed surface, which consists of micropyramid arrays that are selectively...
covered by nanopillar arrays (nanograin). According to the local surface roughness, we divide the surface into three zones: the relatively smooth sidewalls of the pyramids (smooth patches), the nanograin sidewalls of the pyramids, and the nanograin floor. Nanograin micropyramid arrays with pyramid center-to-center spacing (S) of 20 μm, 30 μm, and 40 μm (S20, S30, S40) were fabricated using a combined anisotropic wet-etching and deep reactive ion etching (DRIE) process. After fabricating silicon pyramid microstructures by tetramethylammonium hydroxide (TMAH) etching, we performed a modified DRIE process for nanograin coating (Experimental Section). Similar to a previous method for etching black silicon, vertically-aligned uniform nanopillar arrays (i.e., nanograin) can be produced by regulating the alternating etching and passivation cycles.\textsuperscript{[20,21]}

To generate relatively smooth patches into the nanograin coating, we intentionally over-etched the nanopillar tops in each etching cycle (Experimental Section) so as to reduce the height of the nanopillars. As a result, the vertical walls underneath the base of the micropyramids were exposed in smooth morphology while the inclined sidewalls and the spaces between the base of the micropyramids were uniformly covered by nanopillar arrays (nanograin). As shown in Figure 1b, the exposed sidewalls are indeed much smoother compared with other areas with uniform nanograin coating. The base dimension of the micropyramids is $14 \mu m \times 14 \mu m$, the pyramid center-to-center spacing is $\sim 20 \mu m$, and the height of the entire micropyramid is $\sim 12 \mu m$ (smooth base: $\sim 2 \mu m$, nanograin top part: $\sim 10 \mu m$). The pillars that comprise the nanograin coating are $\sim 400 \text{ nm}$ in diameter, $\sim 5 \mu m$ in height, and $\sim 200-400 \text{ nm}$ in pitch (Figure 1b, inset). For comparison purposes, baseline samples (i.e., surface with nanograin only, patterned smooth surface surrounded by nanograin and surface with a two-tier roughness, respectively) were fabricated using either wet-etching or dry-etching method. Different from the nanograin micropyramid arrays, the two-tier surface is comprised of vertical micropillar arrays, which are covered by a uniform layer of nanograin except on the side walls of the pillars. All samples were treated with $1 \text{ mM}$ hexane solution of perfluorooctyl trichlorosilane (PFOS). After surface treatment, the static contact angles on the flat surface and nanopillar arrays are $\sim 110^\circ$ and $\sim 160^\circ$, respectively. Condensation dynamics on all the as-fabricated samples was investigated using an environmental scanning electron microscope (ESEM).\textsuperscript{[22]}

During the experiment, all the samples were kept at a tilt angle of $\sim 45^\circ$ from the horizontal, the stage temperature was maintained at $-1^\circ C$, and the water vapor pressure in the ESEM was maintained at $\sim 5.1 \text{ Torr}$ (just above the supersaturation pressure).\textsuperscript{[23]}

2. Results and Discussion

2.1. Microscopic Visualization and Characterization of Dropwise Condensation Using ESEM

To illustrate the utility of smooth patches for enhanced dropwise condensation, we first studied the early stage process of vapor condensation. Figure 2a shows the time-lapse ESEM images of condensation on the hierarchical nanograin micropyramid surface. We intentionally chose a relatively larger viewing area to avoid the electron beam heating problem, as imaging at higher magnification could lead to undesirable evaporation.\textsuperscript{[24]} During the experiment, the surface is first maintained at a dry state and the water vapor pressure is increased to initiate drop nucleation. Although it is challenging to visualize and quantify nanoscale drops on the smooth patches and nanograin zone in the hierarchical surface,\textsuperscript{[25]} from Figure 2a it is evident that once the drops grow in size ($\gtrsim 4 \mu m$ in diameter), they exhibit a near spherical shape.\textsuperscript{[26]} Since the tiny smooth patches (with a height of $\sim 2 \mu m$) are surrounded by non-wettability nanograin, drops can easily recede from these small patches and form a spherical shape.\textsuperscript{[26]} On the contrary, the two-tier surface with large smooth sidewalls (with a height of $\sim 10 \mu m$) is strongly susceptible to contact line pinning (Figure 2b). As condensation progresses, drops condensed on the sidewalls coalesce with neighboring drops, forming bridges between the micropillars that eventually grow into larger size drops that remain strongly pinned to the surface. This illustrates the superiority of the hierarchical nanograin micropyramid surface over the two-tier surface for dropwise condensation. In both cases, interestingly, we observed that the growth rate of condensate drops (when their size is over $4 \mu m$) on the smooth patches is much larger than on the nanograin surface.

In order to accurately characterize the distinct drop nucleation and growth dynamics, we carefully studied the growth rate of drops on a nanograin surface patterned with flat patch arrays (similar to the smooth patches in the micropyramid except that the flat patch is horizontal). The evolution of the average drop radius on the flat and nanograin surface is shown in Figure 2c and 2d. At the very beginning, the exponent ($\alpha$) of the growth power law with time $t$ ($r = r_0 t^\alpha$, $r$ is the radius) of isolated drops on the flat and nanograin surfaces are $\sim 0.4$ and $\sim 0.39$, which follow the well-known $1/3$ power law with time $t$ ($r = t^{1/3}$).\textsuperscript{[27,28]} At the late stage, drop coalescence dominates drop growth, and the growth law exponents $\alpha$ on the flat and nanograin surface are $\sim 1.5$ and $\sim 1.07$, respectively. These differences in drop growth on the flat and nanograin surfaces might be caused by three factors. First, although the nanograin surface has large quantities of random nucleation sites (for nanoscale nuclei, the
Figure 2. Drop nucleation/growth on the smooth and nanograssed surfaces. (a) Environmental scanning electron microscopy (ESEM) images of condensation on the hierarchical nanograssed micropyramidal architecture showing that drops grow much faster on the smooth patches than on the nanoglass (left 2) and as drops grow in size, they depart from the surface in the immediate vicinity of the micropyramids (right 2). (b) ESEM images showing the evolution of drop nucleation and growth on a two-tier surface with large smooth patches along the side walls of the micropillars. As drops grow, liquid bridges form and result in contact line pinning. (c) ESEM images showing the distinct growth process of drops on the surface with patterned flat patches. Drops grow much faster on the flat surface. Small drops at the boundary of the flat surface and nanoglass move towards and accumulate at the flat surface (right 2). (d) Comparison of average drop radius as a function of time for drops growing on the flat and nanoglass surface. (e) Schematic drawing showing the side-view of drops (top) and their liquid-solid contact area on the flat and nanoglass surfaces, respectively (bottom).
intrinsic nucleation energy on the flat and nangrass surface is the same), only the top of the nanopillars serves as active nucleation sites. Yet, the top of nanopillars are convex in shape, which is not energetically favored for fast growth as opposed to the flat surface. Second, for a condensate drop with a base diameter larger than ~400 nm (diameter of a nanopillar), the liquid-solid contact area on the flat surface is much larger than that on the nangrass surface, as illustrated schematically in Figure 2e. The larger contact area on the flat surface results in a lower degree of subcooling in the drops and hence a faster direct phase change of vapor to water. Third, the local wettability difference at the boundaries of the smooth patches and the nangrass might accelerate drop movement (Figure 2c) and coalescence towards the flat surface, which also contributes to a larger growth rate.

After identifying the role of smooth patches for faster drop nucleation and growth, we investigated the condensate drop departure dynamics on the nangrass micropyramid arrays (S20, S30, and S40) as well as baseline nangrass surface. Similar dropwise condensation phenomena were observed on these surfaces. As shown in Figure 3a, on the S20 surface, small spherical drops form at the hierarchical surface and these faster growing drops at the smooth patches frequently coalesce with adjacent drops and the merged drops appear to be suspended on top of the micropyramids, i.e. in the Cassie state (Figure 3b). Some of these Cassie drops, triggered by coalescence, can gain sufficient kinetic energy to spontaneously depart from the surface, either in the format of out-of-plane jumping or random sweeping.29 The random motion effectively sweeps more drops in their paths (as indicated by the dashed circles in Figure 3a) and exposes fresh space for new drop formation, which contributes directly to a continuous process of nucleation, coalescence, departure, and re-nucleation.29,30 The influence of gravity on drop departure is negligible on our surface as the average diameter of departed drops (e.g., 50 μm for the S20 surface) is two orders of magnitude smaller than the capillary length (~2 mm).31,32 This is different from film condensation, in which gravity is the primary force leading drops to depart and the average drop departure size is ~2–3 mm in diameter.31,32

To further compare the dropwise self-removal performance, we quantified both drop number densities and drop departure volume for the nangrass (Nano) and three hierarchical surfaces (S20, S30, and S40). In these calculations, the drop counts were averaged over all the images recorded during 8-min condensation, while drop departure volume was estimated from the departed drops by comparing sequential images taken at ~12 sec intervals. Figure 4a shows the measured drop number densities for the four samples. The drop number density in the field of view (~380 μm × ~290 μm) for these four samples increases from ~1.10 × 10^6 μm^-2 for the nangrass surface to ~1.81 × 10^6 μm^-2 for the S20 surface (~65% increase). The S20 surface shows higher active nucleation site density than S30 and S40 because the more dense the micropyramid array is, the more the preferential nucleation sites. The nangrass surface shows the lowest drop number density due to its lack of 3-D pyramid structures that posses local wettable nucleation sites. This result is similar to the bubble nucleation on the micro/nano-textured surface, which yields higher gas release rate compared to the surface with nanoscale features alone.33,34 Figure 4b shows the time evolution of the cumulative drop departure volumes in the field of view (~380 μm × ~290 μm) for these four samples. After 8-min condensation, the drop cumulative departure volumes for the Nano, S40, S30, and S20 surfaces are ~1.20 × 10^6 μm^3, ~1.82 × 10^6 μm^3, ~3.12 × 10^6 μm^3, and ~6.59 × 10^6 μm^3, respectively. Compared to the nangrass surface, nearly 450% (> 5-fold) increase in the cumulative drop departure volumes was achieved on the S20 surface. Figure 4b also indicates a non-linear increase in the cumulative drop departure volume versus time for the S20 surface. By contrast, the nangrass surface displays a relatively linear increase in the cumulative departure volume with respect to time.

The enhanced drop number density and self-removal volume that we observe for the nangrass micropyramid arrays are caused by the unique features of our surface. First, the introduction of wettable patches in the micropyramid arrays leads to...
continuous and fast drop growth, which in turn increases the probability of preferential drop coalescence, a major mechanism that leads to drop self-removal. Indeed, we observed that the departure took place at the pyramids (the last two images in Figure 2a). This kind of preferential coalescence is different from the random coalescence occurring on a homogeneous surface. This coalescence-induced drop removal is reflected in the sudden spurts in the cumulative drop departure volume vs. time for the S20 surface (Figure 4b). Second, the synergy between the micro and nanoscale roughness features creates a highly stable superhydrophobicity (with negligible pinning effect). The main obstacle to drop motion on a solid surface arises from contact angle hysteresis that pins the drop edge. In our hierarchical surface, the presence of nanograss on the inclined surfaces and the spaces between the micropyramids amplifies the local contact angle. The reduced solid-liquid contact area due to the inclined nature of the pyramids serves to further decrease contact angle hysteresis. Thus, the contact angle and contact angle hysteresis of the nanograssed micropyramid surfaces are \( <160^\circ -165^\circ \) and \( <0.4^\circ -3^\circ \), indicating an excellent depinning ability of our surface. The synergy between the micro and nanoscale roughness features also assists in upwards drop movement, especially when the spacing \( S \) is close to or smaller than the size of the suspended drops. This is because as the droplets grow sitting on the micropyramids, the vertical force on the drop due to surface tension can be scaled as \( F \propto \sigma \sin(\theta - 90^\circ - \phi) \), where \( \sigma \) is surface tension, and \( \phi \) is the apex half-angle of the pyramid. In our case, the local contact angle is \( \theta = 160^\circ \) (because of the presence of nanograss) and \( \phi = 35.3^\circ \), thus the vertical force on the drop is in the upward direction (Figure 3b), indicating that the hierarchical morphology is more readily able to force the drops to the top of the surface than using the nanostructures alone.

Fast drop growth and drop departure can naturally lead to a larger surface coverage of small drops. Small drops contribute to the majority of heat transfer in dropwise condensation because of their small thermal resistances. As shown in Ref. 32, at least 50% of heat transfer takes place through drops that are smaller than 10 \( \mu \)m in diameter. To demonstrate the potential of enhancing the heat transfer rate by our nanograssed micropyramid surfaces, we quantified the drop distribution by showing the histogram of the drop diameters averaged over 8-min condensation (Figure 4c). It is obvious that the S20 surface has the highest percentage of drops with diameter smaller than 10 \( \mu \)m (\( \sim 60\% \)), which suggests that the S20 surface has superior heat transfer rate.

### 2.2. Dropwise Condensation Under Ambient Conditions

We further tested the dropwise condensation stability using a large-area sample (S20, 1 cm \( \times \) 1 cm) under ambient conditions for prolonged duration. The temperature and relative humidity were \( \sim 22^\circ \)C and \( \sim 70\% \), respectively. The S20 sample was placed on a water-cooled cold plate controlled at \( \sim 2^\circ \)C by a circulating chiller (Experimental Section). Figure 5a shows the time-lapse top-view images of dropwise condensation on the horizontally oriented S20 surface visualized by an Olympus microscope with a 10\( \times \) objective. In over a 1-hour experiment, the condensed drops remained spherical and continuously departed from the surface via coalescence with neighboring drops. We used the drop surface coverage to quantify the self-drying ability of
learned in this study, especially the elucidation of the role of surface roughness on drop nucleation, coalescence, and departure, could further stimulate new theoretical and experimental efforts to probe complex condensation phenomena.

4. Experimental Section

Hierarchical surface fabrication: The fabrication steps for nanograss micropyramid structures are described as follows. First, microstructures were patterned using standard photolithography. Tetramethyloxysilane (TMOS) and trifluoropentane were used to etch silicon. To achieve the desired roughness, the reaction rate was controlled by varying the etching conditions. The etching process was monitored using in-situ imaging, and the etching time was adjusted to maintain the desired surface morphology.

Condensation dynamics observation using ESEM: The dynamic behavior of dropwise condensation on the sample surfaces was investigated using environmental scanning electron microscopy (ESEM). The sample substrates were placed in a specially designed chamber to control the environmental conditions. The chamber temperature and humidity were precisely controlled, and the condensation process was visualized in real-time. This allowed for the study of condensation dynamics under various conditions, providing valuable insights into the mechanisms of dropwise condensation.

3. Conclusions

To summarize, we have demonstrated a novel strategy to achieve significant increases in drop number density, drop growth rate, drop departure rate, and surface coverage of small drops, all of which contribute to the enhancement of dropwise condensation heat transfer. By harnessing heterogeneous wettability and hierarchical roughness features in multiscale structures, we can enhance both drop nucleation and drop departure on a condensation surface. Most importantly, the synergy of patterned active nucleation sites with pyramid-shaped hierarchical structures leads to a continuous dropwise condensation process through the constant activation and mobilization of drops. While this study was focused on silicon, the concept of activating the three-phase interfaces by tailoring micro/nanostructures for enhanced dropwise condensation can also be applicable to other material systems. The insights learned in this study, especially the elucidation of the role of surface roughness on drop nucleation, coalescence, and departure, could further stimulate new theoretical and experimental efforts to probe complex condensation phenomena.
testing apparatus was installed under an upright microscope with a 10× lens. Images of water vapor condensing from the air were recorded by a CCD camera at a frame rate of ~1 fps for ~65 minutes.

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