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研究課題名（和文）New antifrosting strategies based on spatial control of nucleation combined with nanostructured anticondensation surfaces.

研究課題名（英文）New antifrosting strategies based on spatial control of nucleation combined with nanostructured anticondensation surfaces.

研究代表者

ムテルドゥ　ティモテ・マリ・フランソワ（Mouterde, Timothee）

東京大学・大学院工学系研究科（工学部）・講師

研究者番号：４０９１２５３０

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研究成果の概要（和文）：湿り空気中の冷却基板上では凝縮液滴により視界が制限されてしまう。そこで、表面に疎水性ナノ構造を設けることで液滴が合体自発跳躍により表面から排出され、表面被覆率を低減することが可能である。しかし、液滴間の距離と液滴のサイズは密接に結びついており、ランダムな核生成位置が上記の防曇性能を制限していた。
本研究では、親水性領域の間隔を最適化し、凝縮液滴の位置を制御するバイフィリックパターニング法を開発した。この手法と液滴の自発跳躍を組み合わせることで、液滴の体積と表面被覆率において最適な防曇性能を達成し、表面の親水性パターン設計によってその特性を調整することが可能であることを示した。

研究成果の学術的意義や社会的意義
Control of condensation is important for industrial process and in daily lives as it can limit vision through transparent surfaces or limit the longevity of materials due to water accumulation. Here we combined biphilic surface chemistry with nanostructures to obtain the best antifogging surface.

研究成果の概要（英文）：On a cold substrate placed in a humid atmosphere, condensation droplets form on the surface limiting the visibility. If the surface is covered with hydrophobic nanostructures condensation droplets are ejected from the surface upon merging. This allows to reduce the surface covered by condensation. However, the random nucleation position of the droplets limits the performance of the surface: droplets nucleating far from each other are large when they jump, and small if they appear very close.
In this research we developped a biphilic patterning method which allow to control the position of the droplets of condensation. We understood the optimal spacing between hydrophilic areas that allow for a perfect nucleation control. We combined this nucleation control with the jumping droplet property, this allows to make the best antifogging surface in terms of droplets volume, and surface coverage. These properties can be controlled by the design of the surface biphilic pattern.

研究分野：Fluid mechanics

キーワード：antifogging　anticondensation　nanostructures　superhydrophobic

１．研究開始当初の背景（Background at the beginning of the study）

Condensation and frosting are prevalent phenomena, and managing their behavior is essential for various applications (e.g., antifrosting, better visibility, and water harvesting). To mitigate the impact of condensation, antifogging surfaces have been developed using chemical and physical surface modifications. There are two primary pathways to achieve this: (1) superhydrophilic wet-style antifogging surfaces, where the surface spreads the condensation into a liquid film, preventing the scattering of light by the condensation droplets, and (2) superhydrophobic dry-style antifogging surfaces, where condensation droplets are ejected from the surface upon merging due to the release of excessive surface energy. The dry-style antifogging surfaces are more resistant to contamination and avoid large water accumulation on the surface. However, they involve drop-wise condensation, where droplets inevitably scatter light to some degree.

To enhance visibility and reduce droplet surface coverage, two approaches are known. The first approach is the jumping effect, which maintains constant droplet surface coverage due to continuous condensate ejections. The second approach is biphilic condensation control, where condensation is spatially controlled on hydrophilic sites surrounded by hydrophobic areas. Previous research successfully reduced droplet surface coverage by making the hydrophilic patches sparse enough. However, in the absence of the jumping effect, surface coverage inevitably increased over time.

２．研究の目的（Purpose of the study）

The goal of this research project is to explore how it is possible to combine biphilic control of nucleation with the jumping droplet surfaces to obtain the best antifogging surfaces. In particular, the goal was to understand how condensation nucleation is controlled by biphilic patterns, how such patterns can be used on nanocones for jumping droplet removal and finally how the biphilic antifogging surfaces perform.

３．研究の方法（Research Methods）

We divided this research in three main parts that we will now describe.

(1) Fabrication of biphilic patterned surfaces

The biphilic patterning of surfaces was done by first covering a hydrophilic surface (silicon wafer, or nanocones) by a layer of photoresist. The photoresist is then patterned using a laser lithography (DWL66+, Heidelberg - Takeda Super Clean Room), once developed only cylindrical resist patterns remain on the surface. The surface is then coated with a hydrophobic coating (1H,1H,2H,2H-Perfluorooctyltrichlorosilane, Fujifilm) by chemical vapor deposition. This forms a hydrophobic monolayer on the substrate not covered by the photoresist. The protective photoresist is then removed by sonication in hot acetone and the surface is cleaned. The resulting surface is biphilic and we made sure to always use fresh biphilic patterns as the hydrophilic areas tend to get polluted by airborne contaminant.

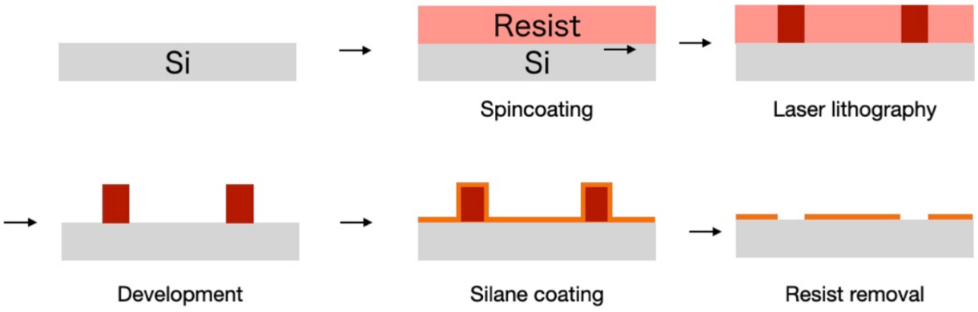

Figure 1. Schematic of the biphilic patterning on a flat silicon chip.

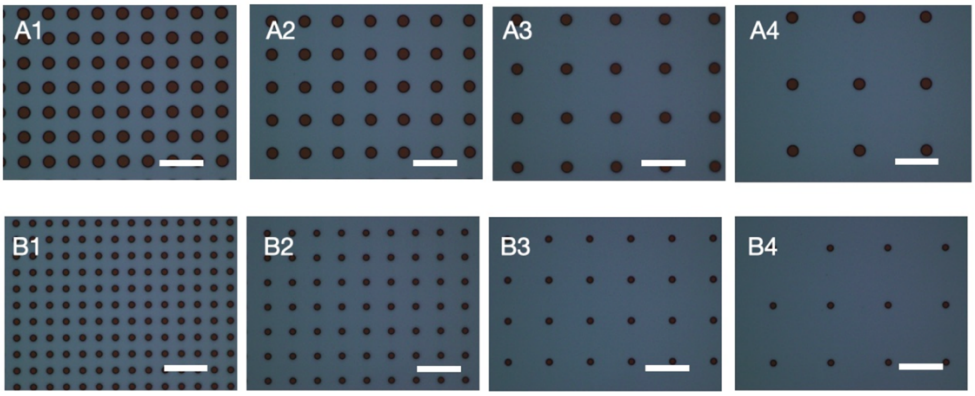

Figure 2. Optical microscope images of the resist patterns with different geometries. The scale bars represent 60 μm.

(2) Understanding of nucleation control on flat surface

To understand the nucleation control on flat surfaces, we used the previously describe biphilic silicon wafer. The surfaces hydrophilic pattern is made of a squared grid of cylindrical hydrophilic pattern. The grid pitch denoted l is varied from 20 μm to 140 μm depending on the surfaces. We then performed condensation experiments under controlled humidity and temperature and the condensation droplets are observed with a microscope and a camera. We quantify the condensation control by evaluating the number of hydrophilic patches covered with a condensation droplet (controlled nucleation) and the number of droplets that nucleate in the hydrophobic region (uncontrolled nucleation). We quantify the condensation control by introducing two metrics, P_1 the probability for a hydrophilic patch to be covered by a condensation droplet, and P2 the number of droplets outside of a hydrophilic patch normalized by the total number of patches. A perfectly controlled nucleation would be $P_1 = 1$ and $P_2 = 0$. The results will be described in part 4.

(3) Biphilic antifogging surfaces

To reduce the volume and surface covered by the condensation, we propose to combine the biphilic control with a hydrophobic nanocones surfaces which is known to be the best existing antifogging surface due to its high jumping probability and low surface coverage (proportion of the surface covered by condensation droplets). To reduce the surface coverage and the droplet volume, we design pairs of biphilic patches. The distance between both patches of a is a and the distance between the pairs is b (Figure 3), the patch diameter is denoted as d.

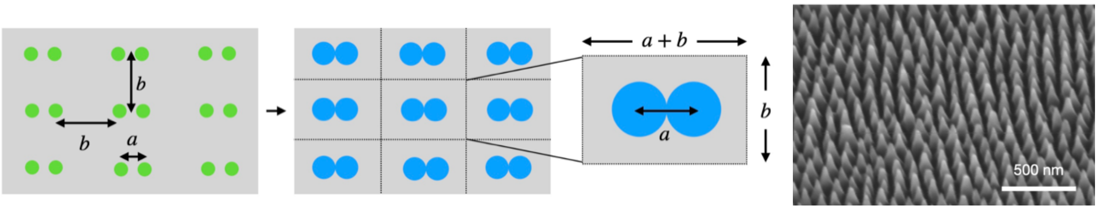

Figure 3. Schematic of the biphilic pattern geometry (left) and SEM image of the nanocones used in this study (right).

We then perform condensation experiments on the reference superhydrophobic nanocones and on the biphilic nanocones to evaluate their performances. The condensation droplets are detected by an image analysis algorithm from which we can extract the relevant data such as droplets size and position. The results will be described in the following part 4.

4．研究成果 (Research results)

We will now present the results on nucleation control and on biphilic antifogging surfaces.

(1) Understanding of nucleation control on flat surface

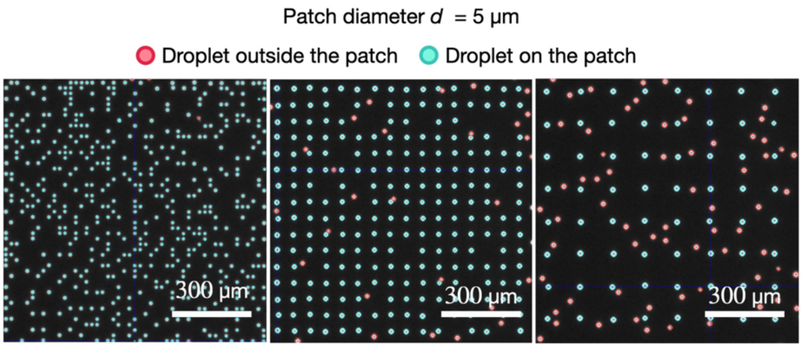

Figure 4. Images of the Matlab analysis. Droplets on the hydrophilic patch are marked blue, and droplets outside the patch are marked red. Scale bars represent 300 μm.

The result of the condensation control as a function of the pattern spacing p is described in the Figure 6. As we can see on the experimental data from Figure 5, when the spacing between the hydrophilic patches is to small, some patches remain dry while when the spacing is too large, all hydrophilic patches are wet but condensation droplets also appear on the hydrophobic area. This is visible as P_1 increases from 0.2 for a small spacing to 1 for a spacing larger than 100 μm. The number of uncontrolled droplets per patch P_2 increases as well when the grid is sparser. We understood that this phenomenon takes its origin in the change of local vapor supersaturation, using classical nucleation theory we proposed a model that can predict this behavior (plain curve on Figure 6). Importantly there is a nucleation-controlled region for spacing around 60 μm where droplets appear on all hydrophilic patches but not on the hydrophobic ones.

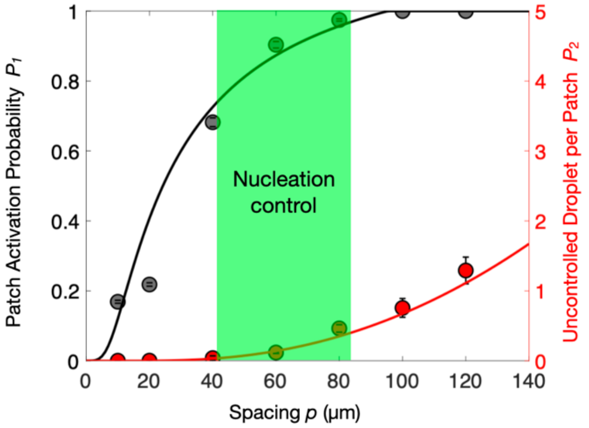

Figure 5. Patch activation probabilitiy P_1 and uncontrolled droplet per patch P_2 as a function of the spacing of the grid p.

(3) Biphilic antifogging surfaces

The condensation experiments conducted on biphilic nanocones revealed several facts. The first one is that the controlled previously performed on flat silicon wafer is also efficient on nanocones as seen on Figure 7 where pairs of droplets are formed only on the hydrophilic patterns. The second important point that we can note from the experiments is that despite the hydrophilic patch which increases the adhesion for sufficiently large spacing the droplets pair are always jumping upon coalescence.

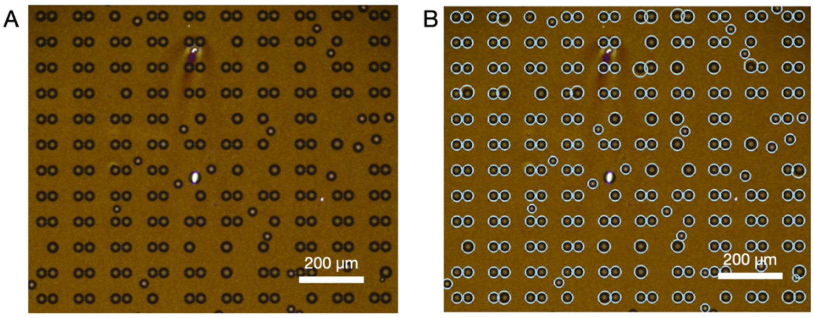

Figure 5. A microscopic image of biphilic jumping condensation **A** and its analysis **B**.

A direct comparison between the biphilic nanocones and the classic superhydrophobic nanocones (SHS) reveals the difference of drop size, size distribution and surface coverage over time, Figure 8.

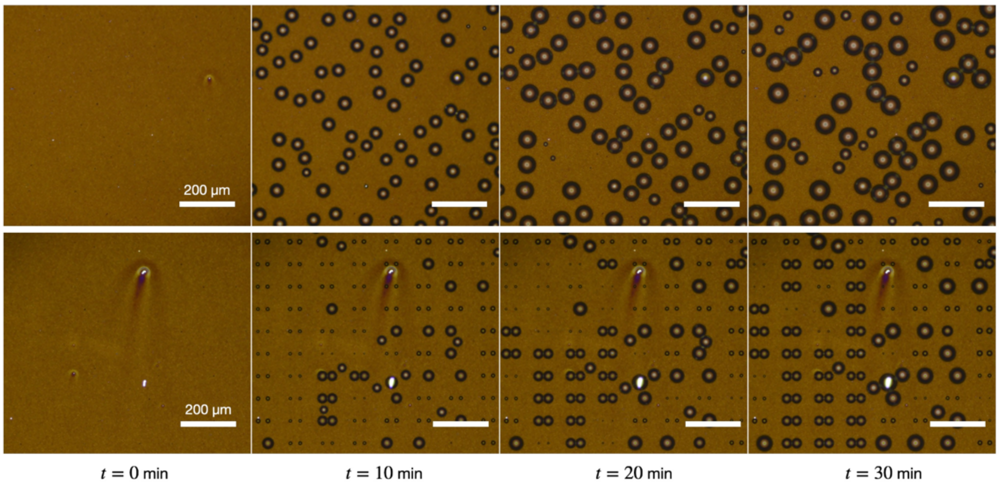

Figure 6 Comparison between homogeneous antifogging nanocones (top) and SHS (bottom). a = 35 µm, b = 80 µm, and d = 5 µm for the biphilic pattern. The humidity and temperature were 55.3±0.4% and 22.1±0.1 °C for SHS, and 58.2±0.3 % 22.1±0.1 °C for biphilic pattern. The surface temperature was set to around 10 °C so that the supersaturation will be around 1.25

The quantitative analysis of the images with a custom-made Matlab code reveals that our surfaces outperform the current best antifogging surface for several important metrics. First, the surface covered by the condensation is reduced in the case of the biphilic surface which is beneficial for optical applications (Figure 8). Second, the average droplet volume is reduced by a factor 5 when compared to the best current antifogging surface (hydrophobic nanocones), Figure 8.

Finally, we demonstrated that the surface coverage and mean droplet volume can be controlled by tuning the biphilic design parameters.

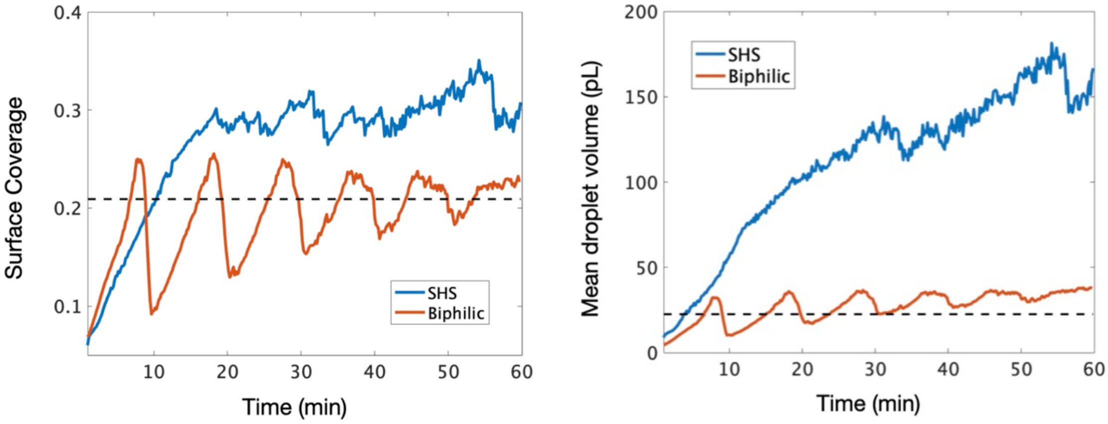

Figure 7. Evolution of the Surface coverage (left) and mean droplet volume (right) with time for the best superhydrophobic surface (in blue) and the biphilic nanocones (in red). Our design outperforms the current state-of-the-art.

Our results constitute the new reference for antifogging surfaces. This is also a very promising design for antifrosting applications; indeed, one of the frosting mechanisms is frost propagation from a frosted droplet to the neighboring supercooled condensation droplets on the surface. The frost propagation mostly depends on the interdroplet distance and the droplet volume, both parameters that we can control.

５．主な発表論文等

〔雑誌論文〕　計0件

〔学会発表〕　計5件（うち招待講演　2件／うち国際学会　1件）

１．発表者名
Hiroki Yachida

２．発表標題
Improved antifogging surface with paired biphilic pattern

３．学会等名
第61回日本伝熱シンポジウム

４．発表年
2024年

１．発表者名
Hiroki Yachida

２．発表標題
Condensation Control on Antifogging Surfaces

３．学会等名
熱工学コンファレンス2023

４．発表年
2023年

１．発表者名
Hiroki Yachida

２．発表標題
Condensation control on antifogging surfaces

３．学会等名
第60回日本伝熱シンポジウム

４．発表年
2023年

１．発表者名
Timothee Mouterde

２．発表標題
Non-wetting states and condensation

３．学会等名
IUTAM Symposium on Dynamics and Interface Phenomena of Bubbles and Droplets at Multiple Scales（招待講演）（国際学会）

４．発表年
2023年

１．発表者名 Timothee Mouterde
２．発表標題 Towards advanced antifogging surfaces
３．学会等名 Toronto 5th UT2 - MAC Student Workshop 2024（招待講演）
４．発表年 2024年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関