Effect of fluoropolymer spots on pool boiling heat transfer

V Yu Vladimirov¹, S Ya Khmel¹, A I Safonov¹, V V Semionov¹, E A Chinnov¹
¹ Kutateladze Institute of Thermophysics, Russian Academy of Sciences, 1 Ac. Lavrentyev Ave., Novosibirsk, 630090, Russia

e-mail: victor.lipps@gmail.com

Abstract. In this paper, the investigation of pool boiling heat transfer on biphilic micro/nanostructured surfaces is presented. An array of micrococoons from silicon oxide nanowires was synthesized on the surface of a copper heater using the gas-jet electron beam plasma chemical vapor deposition method. The biphilic properties of the surface were achieved by applying fluoropolymer spots by hot wire chemical vapor deposition. Technology of creating biphilic surfaces was developed and boiling curves were obtained for used samples. The advantages of using a biphilic surface to enhance heat transfer were demonstrated in comparison with a smooth surface and a micro-nanostructured surface without local hydrophobic fluoropolymer regions. This technology can be applied to enhance boiling heat transfer.

1. Introduction
As a result of the growing power of various microelectronic devices with a simultaneous tendency towards their miniaturization, there is a need to develop more efficient cooling systems, in particular, using intensive heat transfer during boiling. There are various ways to intensify boiling heat transfer. One of the most promising methods is creating biphilic micro/nanostructured surfaces. Micro/nanostructuring has already demonstrated the ability to influence heat transfer through various effects such as changes in the density of evaporation centers, wettability, etc. [1, 2]. Arrays of oriented nanowires made of silicon, copper, and other materials are used to enhance boiling heat transfer. Such nanostructures make it possible to increase both the critical heat flux and the heat transfer coefficient in comparison with a smooth surface. The application of two-scale structuring (at the micro and nanoscale) can have an even greater effect on boiling heat transfer [2, 3].

On the other hand, there are works devoted to numerical simulation [4] and experimental study [5] of biphilic surfaces for heat transfer enhancement, which demonstrate the prospects of their use. In this case, biphilic topography is understood as the creation of local hydrophobic regions that could play the role of highly efficient evaporation centers. It is assumed that good wettability on the rest of the surface will prevent the early development of the heat transfer crisis, which is typical for conventional completely hydrophobic surfaces. Besides, the creation of local hydrophobic regions, which can work as centers of evaporation, can facilitate the organization of liquid and vapor flows, which is also a factor that significantly increases the boiling efficiency even with an average decrease in the thermal conductivity of the sample [6].

In this work, it was planned to use biphilic surfaces produced in several stages. As the first step, creating micro/nanostructured surfaces was suggested. In this case, micro/nanostructuring is the synthesis of SiOx nanowires by the gas-jet electron beam plasma chemical vapor deposition method [7, 8]. SiOx was chosen as a material for synthesis due to its high chemical stability. This method...
allows for creating surfaces of various morphologies at relatively low temperatures. In this work, it was assumed to create an array of micrococoons - tin catalyst particles placed on the surface and overgrown from all sides with SiOx nanowires. Such structures have shown themselves to be the most stable to fracture during boiling since they have better adhesion in comparison with other investigated structures [9], which is an important factor for determining the practical applicability of the technology.

After creating an array of micrococoons, a fluoropolymer, which was chosen because of its high hydrophobicity, was deposited locally on the surface by the hot wire chemical vapor deposition (HW CVD) method.

2. Experimental setup and methods
In this work, biphilic surfaces were formed on a micro/nanostructured surface. Arrays of micrococoons made of silicon oxide nanowires were used as the micro/nanostructured surface. These arrays were synthesized on a copper substrate (copper heater) with a tungsten sublayer. First, tin particles were deposited on the surface, previously coated with tungsten, which acted as a growth catalyst. The synthesis of silicon oxide nanowires was carried out by the gas-jet electron beam plasma chemical vapor deposition method on particles of the tin catalyst [7-10]. As a result, an array of micrococoons was formed on the surface.

Then a layer of fluoropolymer was deposited on such a surface by HW CVD. As is known, the fluoropolymer is a highly hydrophobic material. The method is described in detail in the paper [11]. The deposition process parameters were as follows: activator wires temperature 580°C; the precursor gas pressure 0.5-0.05 Torr; the distance activator-substrate 30-50 mm; substrate temperature 30 °C; and deposition time 90-180 minutes. The parameters were selected so that fluoropolymer coatings with a thickness of about 1 μm were formed on a smooth flat surface. On micro/nanostructures with a developed surface area, the thickness of the fluoropolymer coating was less. The fluoropolymer was deposited through a mask with a hole diameter of 100 μm and a distance between the hole centers of 500 μm for forming local regions (spots). The mask was set at two distances of about 200 μm and about 10 μm. In the first case, the maximum preservation of the micro/nanostructured surface was achieved. In the second case, the number of radicals that could penetrate the gap between the mask and the substrate in the area of the geometric shadow was minimized.

The characterization of the samples was carried out using JEOL JSM-6700F scanning electron microscope equipped with energy dispersive X-ray spectrometers (EDS) for element analysis. The water contact angle was measured using a KRUSS DSA-100 device.

Pool boiling experiments on biphilic surfaces, created by the above-described method were carried out using a cylindrical installation with a working zone diameter of 50 mm and a height of about 70 mm. The lower part was made in the form of a Teflon washer, into which the sample was pressed. The metal wall played the role of a stabilizing heater to maintain the saturation temperature. The liquid level was maintained approximately 30 mm above the washer. Distilled degassed water was used as a working liquid. Atmospheric pressure was maintained by a small steam vent.

The calibration accuracy of the used thermocouples was 0.1°C. A NI-9214 controller was used to collect the data. Two Gwinstek GPO-743035 were used as power sources for the experimental sample and the stabilizing heater.

The error in determining the heat flux was less than 5% at fluxes over 40 W/cm² and less than 2% at fluxes over 80 W/cm². A detailed description of the setup and measurement technique is contained in [10].

3. Experimental results and discussion
Initially, fluoropolymer coatings were deposited by the HW CVD method through the mask, which was located 200 μm above the surface of a heater with arrays of micrococoons made of silicon oxide nanowires. The deposition process parameters were as follows: the precursor gas pressure – 0.5 Torr; the distance activator-substrate – 50 mm; deposition time – 90 minutes. On the surface obtained, the
circular fluoropolymer spots were not detected either visually or using an optical microscope. Figure 1 shows SEM images of an array of micrococoons of silicon oxide nanowires before and after deposition of the fluoropolymer coating.

**Figure 1.** Comparison of the morphology of nanomodified surfaces before and after deposition of the fluoropolymer through the mask.

The figure clearly shows that the micrococoons were covered with a layer of fluoropolymer. However, the surface morphology at different points of the sample practically did not change. The elemental composition of the sample surface in the center and at a distance of 250 μm also practically did not change. Contact angle measurements showed that the surface was hydrophobic. Therefore, it can be assumed that the fluoropolymer coating was continuous, despite the deposition through the mask. Apparently, the reason for this circumstance lies in the mean free path of active radicals that form the fluoropolymer coating. In the HW CVD method, radicals are formed from a precursor gas on the activator wire grid, move to the deposition surface and form a fluoropolymer film on it. Estimates showed that this length was 20 μm. Thus, the distance of 200 μm between the mask and the substrate surface was sufficient for active radicals to freely penetrate under the mask, distribute over the heater surface, and form a continuous fluoropolymer coating. In this case, the coating was not uniform in thickness, it was thicker in the areas corresponding to the holes in the mask and thinner in other areas.

To change this situation and form local regions (spots) with a fluoropolymer coating, the deposition parameters were changed. At first, the distance between the mask and the substrate was minimized to about 10 μm; secondly, the pressure of the precursor gas was reduced to 0.05 Torr. The remaining parameters of the deposition process were as follows: the distance between the activator and the substrate – 30 mm; deposition time – 180 minutes. As a result of these changes, the mean free path increased by a factor of 10, and deposition with a flow of active radicals close to free molecular flow was realized. Therefore, the penetration of radicals under the mask into the area of the geometric shadow was sharply reduced. Analysis of the morphology of the obtained coatings showed the correctness of the decisions made. Figure 2 shows images of local regions (spots) with a diameter of 100 μm, coated with the fluoropolymer. These spots are well observed using optical (Figure 2b) and scanning electron microscopes (Figure 2a, 2c).

Morphology analysis of the coating showed that there is no fluoropolymer in the space between the spots. Elemental analysis of the obtained coatings using EDS also confirms that the composition of the spots corresponds to the fluoropolymer. Figure 3 shows the surface mapping images for various elements.
Figure 2. Local regions (spots) covered with the fluoropolymer: SEM images (a, c) and optical microscope image (b).

Figure 3. Elemental composition mapping of the biphilic coating surface of the heater obtained using the mask: (a) - fluorine, (b) - carbon, (c) - silicon.

In the region of the spots, fluorine and carbon (components of the fluoropolymer) are clearly recorded (Figure 3a, 3b), and in the space between the spots, silicon dominates (Figure 3c).

The experiments were carried out using three surfaces, whose brief description is given in Table 1. Surface #1 is an array of micrococoons of silicon oxide nanowires, a common micro/nanostructured surface (Figure 1a). Fluoropolymer was not applied to it. It was used as a reference surface to determine the contribution of micro/nanostructures to heat transfer enhancement. The fluoropolymer was deposited onto surface #2 over the micro/nanostructures in a continuous non-uniform layer due to the too large distance between the surface and the mask (200 μm). On surface #3, after micro/nanostructuring, local areas covered with fluoropolymer (10 μm gap) were created.

The boiling curves, obtained from the pool boiling heat transfer experiments on the test surfaces are shown in Figure 4. The experiment on surface #1 showed no significant difference from a smooth copper surface. The well-known Rohsenow correlation [12] was used as a reference for a copper surface. Three experiments were performed on surface #2. The first experiment (#2(1)) showed worse heat transfer than that for a smooth surface, which is associated with high hydrophobicity due to a continuous fluoropolymer layer. One bubble (vapor layer) was formed above the surface. This bubble detached at a low frequency and worsened heat transfer. In the second experiment (#2(2)), a higher heat transfer efficiency was achieved compared to experiment #2(1). The best result was achieved in the third experiment (#2(3)). This effect is apparently associated with the gradual destruction of the fluoropolymer film: the fluoropolymer was preserved in the regions of the greatest thickness of the film (where the holes of the mask were located) and was destroyed in the course of experiments on the rest of the surface. This is confirmed by measurements of contact angles, which showed a decrease in the hydrophobicity of surface #2 (Figure 5). Thus, in the course of a series of experiments, surface #2 reached a biphilic state due to self-organization with partial destruction. This conclusion is also
confirmed by the experiment on initially biphilic surface #3, where local fluoropolymer spots were obtained. The boiling curve for this sample was close to results #2(3).

**Table 1.** Brief description of experimental samples

| #  | Texture type                          | Hydrophobic coverage | Size of hydrophobic zones | Distances between zones | Mask              |
|----|--------------------------------------|----------------------|---------------------------|-------------------------|-------------------|
| 1  | Micrococoons covered with nanowires  | no                   | no                        | no                      | no                |
| 2  | Micrococoons covered with nanowires  | Continuous          | -                         | -                       | Yes, gap 200 μm   |
|    |                                      | non-uniform deposition |                          |                          |                   |
| 3  | Micrococoons covered with nanowires  | Locally deposition   | Circle with a diameter of 0.1 mm | 0.5 mm Hydrophobic area 3% | Yes, gap 10 μm   |

![Figure 4. Boiling curves for samples #1 - #3 and Rohsenow correlation for the smooth copper surface](image)

**Figure 4.** Boiling curves for samples #1 - #3 and Rohsenow correlation for the smooth copper surface

![Figure 5. Contact angles on surface # 2 after the first experiment (a) and after the third experiment (b).](image)

**Figure 5.** Contact angles on surface #2 after the first experiment (a) and after the third experiment (b).
Conclusions
As a result of this work, the technology of local deposition of a fluoropolymer on micro/nanostructured samples was developed to create biphilic surfaces.

In the course of developing the technology, heating elements with different surfaces were created: micro/nanostructured, micro/nanostructured with a continuous inhomogeneous layer of fluoropolymer, and micro/nanostructured bifilic with local areas with fluoropolymer.

The bifilic micro/nanostructured surface with local hydrophobic regions showed noticeably higher heat transfer efficiency compared to a smooth copper surface and a micro/nanostructured surface without fluoropolymer.

The surface with a continuous non-uniform layer of fluoropolymer showed gradual destruction of the fluoropolymer in the regions of the smallest film thickness during boiling. At the same time, the efficiency of heat transfer approached the data for the bifilic surface.

This technology can be applied to enhance boiling heat transfer.

Acknowledgements
The study was carried out under state contract with IT SB RAS.

References
[1] Surtaev A, Serdyukov V and Pavlenko A 2016 Nanotechnologies Russ 11 696
[2] Liang G, Mudawar I 2019 Int. J. Heat Mass Transfer 128 892
[3] Wen R, Ma X, Lee Y-C and Yang R 2018 Joule 2 2307
[4] Gong S, Cheng P 2015 International Journal of Heat and Mass Transfer 80 206
[5] Betz A R et al 2013 International Journal of Heat and Mass Transfer 57 733
[6] Rahman M M, Pollack J, McCarthy M 2015 Scientific reports 5 1
[7] Khmel S Ya, Baranov E A, Zaikovskii A V, Zamchyi A O, Maximovskiy E A, Gulyaev D V, Zhuravlev K S 2016 Phys Status Solidi A 213 1774
[8] Khmel S Ya, Baranov E A, Zamchyi A O, Maximovskiy E A, Gulyaev D V, Zhuravlev K S 2016 Phys Status Solidi A 213 1790
[9] Chinnov E A, Shatskiy E N, Khmel S Ya, Baranov E A, Zamchyi A O, Semionov V V, Kabov O A 2017 IOP Conf. Series: Journal of Physics: Conf. Series 925 012033
[10] Khmel S, Baranov E, Vladimirov V, Safonov A, Chinnov E 2021 Heat Transfer Engineering 43
[11] Safonov A I, Sulyaeva V S, Gatapova E Ya, Starinskiy S V, Timoshenko N I, Kabov O A 2018 Thin Solid Films 653 165
[12] Rohsenow W M 1951 MIT Division of Industrial Cooperation, Cambridge, Massachusetts, Technical Report No 5 (Heat Transfer Laboratory)