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NANOSCALE SURFACE MODIFICATION TECHNIQUES FOR POOL BOILING ENHANCEMENT – A CRITICAL REVIEW AND FUTURE DIRECTIONS

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ABSTRACT

New discoveries presented in the last decade for enhancing boiling performance utilizing nanoscale structures on surfaces are critically examined in this paper. Since the mechanism for such a phenomenon is not fully understood, this review mainly focuses on the implementation of nanostructures on these surfaces as well as on the interpretation of underlying phenomena for changing the boiling performance. Design consideration and theoretical developments are also discussed followed by practical aspects of nanostructure manufacturing. The issues related to performance, ease of fabrication and reviewed durability (whenever available) are and recommendations are made for future research in this emerging area

NOMENCLATURE

- *r* surface roughness; the ratio of the total rough surface area (contact area) to the projected surface area (apparent area)
- θ_1 contact angle of the liquid on solid of species 1
- θ_w apparent contact angle of the liquid droplet on the nanostructured surface in Wenzel state.
- $\varphi_{\rm s}$ the ratio of the liquid contact area to the projected area
- θ_{CB} apparent contact angle of the liquid droplet on the nanostructured surface in Cassie-Baxter state

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1. INTRODUCTION

Pool boiling is an efficient mechanism for heat transfer due to the associated phase change process. With the demand for meeting high heat flux removal in excess of 10 MW/m² (1 kW/cm²) in electronic chip cooling application, further enhancements in pool boiling heat transfer are being investigated worldwide.

According to our current understanding, heat transfer during pool boiling is associated with three main mechanisms: transient conduction. microlayer evaporation. and microconvection, e.g. Meyers et al. [1]. These mechanisms are related to the in motion of liquid-vapor interface around a nucleating, growing and departing bubble on the heater surface. The shape of the interface influences the motion of the interface and has direct bearing on the three mechanisms. The region where the interface meets the heater surface is identified as the contact line region. The contact angle of the liquid-vapor interface at the contact line dictates the shape of the interface and the contact line motion, and associated heat transport processes.

The effects of contact angle on pool boiling heat transfer and critical heat flux (CHF) have been a topic of great interest in the boiling research. It is well known that the CHF decreases dramatically on hydrophobic surfaces, whereas hydrophilic surfaces exhibit higher heat transfer coefficients as well as higher CHF values [2, 3]. Recent advances on changing the surface energy of the heater surface have opened up new opportunities for enhancing the pool boiling heat transfer by changing the contact angle through the implementation of nanostructures on the heater surface.

This paper is divided into two parts. In the first part, an indepth review is presented on the effects of nanostructures on the pool boiling performance. This part is then followed by an extensive review of the nanostructure manufacturing techniques as well as their relative merits and disadvantages in making practical enhanced surfaces suitable in pool boiling application. Finally recommendations are made for future research to identify nanostructure characteristics that have direct bearing on pool boiling enhancement, and the manufacturing techniques to make these surfaces suitable in practical applications.

2. POOL BOILING HEAT TRANSFER ENHANCEMENT THROUGH NANOSTRUCTURES

The effect of contact angle on boiling incipience was first proposed by Davis and Anderson (1966) [4] in flow boiling. They included the static contact angle in their model to predict the onset of bubble nucleation. Cornwell [5] included the effect of contact angle hysteresis on bubble incipience and concluded that nucleation can begin at radii smaller than those predicted by the nucleation criteria using a static contact angle. Tehvar et al. [6] studied the changes in wetting characteristics of refrigerant R-113 caused by a porous plasma sprayed coating and its influence on the pool boiling characteristics. The pool boiling performance was studied as a function of number of active embryos and pore structure, both of which affected the wetting behavior of the surface. Shoji and Zhang [7] proposed that due to the contact angle hysteresis, a single contact angle for a liquid-vapor interface on a solid heater was not an appropriate measure of the surface wettability. Further, they emphasized that the contact angle hysteresis effects need to be taken into account while studying bubble dynamics.

O'Connor et al. [8] and Chang and You [9, 10] developed micro-porous and porous coatings of diamond, copper, and aluminum particles that could be applied as paint on a heater surface. These coatings increased the surface wettability. Heat transfer coefficient increased by a factor of up to 4.5 over a plain surface. Smaller micron-sized particles also improved the incipience behavior over particles larger than 10 μ m. The surface wettability and availability of nucleation cavities together contributed to the improved heat transfer characteristics.

Takata et al. [11, 12] developed a superhydrophilic surface by irradiating TiO_2 coated surface with UV light. The effects of contact angle were systematically studied in pool boiling of pure water on a sputtered TiO_2 surface. To quantify the interfacial heat transfer effects further, they also studied an evaporating droplet on a heater surface. Their results indicated that a highly hydrophilic surface promoted heat transfer in both cases. These studies pointed out that the surface wettability control effectively enhanced pool boiling heat transfer. Although contact angle control was accomplished through the UV irradiation, more practical control was desired in using this concept in practical devices. Thermal resistance of the coatings also poses as a limiting factor in porous coatings. Introduction of nanotubes and nanostructures significantly reduced the thermal resistance of the layer, and opened up a new era in enhancing pool boiling heat transfer.

2.1 Nanoporous Surface

Porous materials were applied extensively in enhancing pool boiling heat transfer. In his review article, Davis [13] outlined the development of porous materials along with their promise in numerous emerging applications. The early developments in nanostructures mainly focused on extending the microporous surface preparation techniques for preparing nanoporous surfaces. Vemuri and Kim [14] used a commercially-available nanoporous surface consisting of a 75 um thick layer made from aluminum oxide particles. The porous layer thickness was 70 µm and was glued to a 105 µm thick aluminum sheet using an epoxy with a thermal conductivity of 1.4 W/m-K. The special manufacturing technique (not described by the authors) yielded a nanoporous structure with pores of 50-250 nm diameters. The incipient superheat during pool boiling with FC-72 was reduced by 30 percent as compared to a plain untreated aluminum oxide surface. The boiling curve also showed improvement. However, the authors did not provide details on the wettability of the surface and the aging effects.

2.2 Nanotube Coatings (Carbon Nanotubes, TiO₂ Nanotubes and Others)

Following the groundbreaking discovery of carbon nanotubes by Iijima in 1991, several researchers saw its potential in increasing the wettability of a surface and in enhancing heat transfer in pool boiling application. In 2006, Launay et al. [15] developed a novel surface with microstructures containing carbon nanotubes grown on their surfaces to provide both microscale and nanoscale enhancements. The base surfaces consisted of plain and etched silicon, pin fins, and microchannels. The nanostructures were grown on a plain surface, sides of an array of pin fins, and over the top surfaces of microchannel side walls. The nanotubes were grown using a carbon nanotube (CNT) process with chemical vapor deposition (CVD) as described by Wei et al. [16]. The uncertainty in the heat flux measurements was between 5 and 30 percent depending on the heat flux level. Although significant performance enhancements of up to 100 percent were noted at lower heat fluxes, the results showed limited enhancements at higher heat fluxes. The poor thermal properties of the fluids used (PF5060) as well as the contact resistance between the substrate and the heater were cited as main reasons for the lower than expected performance. However, combining micro- and nanoscale features offers a unique method for enhancing the pool boiling heat transfer.

Ahn et al. [17] fabricated multiwall carbon nanotubes (MWCNT) on silicon substrates to create 9 to 25 µm tall carbon nanotube forests. The diameter of the vertically aligned MWCNT varied from 8-16 nm, with a random pitch between 8-16 nm. Two types of MWCNT, A and B, were obtained with 9 and 25 µm heights respectively. The heat transfer in pool boiling was augmented to the same degree in both cases over a plain silicon surface. However, the taller sample B resulted in a 28 percent improvement in CHF, as compared to 25 percent for Type A MWNCTs, over a plain silicon surface. The taller nanotubes seem to provide better pathways for liquid flow to the nucleation sites. The uncertainty in heat flux measurement was estimated to be around 8 percent at CHF. Additional results were provided by Ahn et al. [18] and Sathyamurthi et al. [19] in a subsequent paper on subcooled pool boiling. They also provided a mechanistic description for the enhancement in terms of the pinned contact line on CNT surfaces and a reduction in critical Taylor instability wavelength.

Ujereh et al. [20] performed experiments with different CNT array densities and area coverages on silicon and copper surfaces. In all cases, the incipience wall superheat was reduced along with heat transfer performance enhancements in pool boiling at lower heat fluxes. The CHF values were also improved in all these cases. The modified silicon surfaces exhibited higher enhancements, as the bare silicon surface was very smooth and had very few nucleation sites. The MWCNTs were approximately 50 nm in diameter and 20-30 µm long. The coverage on fully covered areas was estimated to be 30 $CNTs/\mu m^2$ in the primary (light) array and 60 $CNTs/\mu m^2$ in the dense region. Using a grid pattern based on the Taylor wavelength, estimated to be around 5 µm, resulted in a 60 percent performance improvement as compared to the fully covered (with MWCNT) sample. The island pattern on silicon with 250 µm circular regions at 1000 µm pitch resulted in a significantly lower performance with only 5 percent improvement. It was suggested to fully cover the region with MWCNT as manipulation of any macroscale area coverage was not seen as an effective way for improving the heat transfer performance. In addition, the CNT density was seen as playing a role in the wall superheat at boiling incipience.

Chen et al. [21] studied the pool boiling performance of superhydrophilic TiO₂ nanotube array (TNTA) covered surfaces with deionized water. The nanotubes were 150 nm in average diameter. The authors did not report the heights. The surfaces exhibited superhydrophobicity with a contact angle close to zero degrees, while the bare Ti surface resulted in a contact angle of 70°. Surfaces with TNTAs yielded approximately half the values of wall superheats during boiling at any given heat flux as compared to the bare Ti surface. The bubble generation mechanism was quite different with small diameter bubbles emerging at high frequency from the surfaces with TNTAs. While a large number of active nucleation sites were observed, there was no clear explanation provided for the enhancement mechanism.

A recent study by Singh et al. [22] under flow boiling conditions with carbon nanotube coated walls indicates that the

heat transfer performance was enhanced by 30-80 percent at lower heat fluxes. At higher heat fluxes, the improvement exhibited a complex behavior depending on the mass flux. More extensive studies are expected to emerge as researchers evaluate the enhancement performance of nanostructures under flow boiling conditions. Their application on the surfaces of microchannel walls also seems to be an interesting area.

2.3 Nanoparticle and Thin film Coating

Forrest et al. [23] developed nanostructured surfaces by employing Layer by Layer (LbL) assembly method. They conducted pool boiling experiments with various samples of different contact angles and found that the heat transfer performance increased with an increase in wettability of the surface. Heat transfer coefficient enhancements of up to 100 percent were found with hydrophilic samples. Thin-film coatings with fluorosilane had advancing contact angles of 140° to 160° and a receding contact angle of about 20°. The enhancement in CHF in these samples indicated that the receding angle is the important angle in determining the CHF behavior. This further confirms the applicability of the receding contact angle in the pool boiling CHF model presented by Kandlikar [3].

Wu et al. [24] in a recent paper reported the results of their pool boiling experiments on 1- μ m thick of titanium oxide (TiO₂) and silicon oxide (SiO₂) nanoparticle-coated surfaces. Their results also indicate that the hydrophilicity of titanium oxide surface provides higher heat transfer coefficient and CHF values.

Phan et al. [25] changed the surface wettability by coating a stainless steel surface with different processes. For hydrophobic surfaces, they discovered that bubbles could not coalesce with neighboring sites and that the wall condition deteriorated rapidly during boiling. For the hydrophilic coatings, the bubble departure diameter increased with a reduction in frequency. This observation was contrary to that reported by Chen et al. [21] for superhydrophilic surfaces. They believed that the dynamic contact angle played an important role and that the contact angle hysteresis was found to be an important parameter. They also developed a heat transfer model explaining the dependence of heat transfer coefficient on dynamic contact angles.

The next section provides a detailed review of the processes available for manufacturing nanostructured surfaces. The discussion focuses on the process flow and some of the fabrication considerations.

3. NANOSTRUCTURED SURFACE FABRICATION

It is known that both topological and chemical properties of the surfaces play a critical role in determining the surface wettability [26]. Since the heat transfer in pool boiling is highly related to the surface wettability, the fabrication techniques producing topological nanostructured surfaces and controlling the contact angle (or wettability) have the potential of enhancing the boiling heat transfer performance.

While the surfaces have nanostructures, the surface wettability must be realized by either of the two states: Wenzel or Cassie-Baxter states [27, 28], as shown in Figure 1. In Wenzel state, the liquid fills the cavities in between the nanostructures and completely wets the entire solid surface. The total actual solid-liquid contact area is greater than the apparent contact area (or projection area). The contact angle of the liquid on the surface is:

$$\cos \theta_w = r \cos \theta_I \tag{1}$$

where *r* is the surface roughness — the ratio of the total rough surface area (contact area) to the projected surface area (apparent area), θ_I is the contact angle of the liquid on solid (species 1), and θ_w was the apparent contact angle of the liquid droplet on the nanostructured surface in Wenzel state.

Equation (1) reveals that the nanostructures promote either wettability ($<90^{\circ}$, hydrophilic) or non-wettability ($>90^{\circ}$, hydrophobic), which depends on the chemical nature of the nanostructures – the deciding factor to wet the nano-cavity surfaces.

On the other hand, in Cassie-Baxter state, the air cavities repelled the liquid and alleviated on the nanostructured surface. The contact angle of a liquid droplet on the surface was understood:

$$\cos \theta_{CB} = 1 - \varphi_{\rm s} \left(\cos \theta_{\rm I} - 1 \right) \tag{2}$$

where φ_s is the ratio of the liquid contact area to the projected area, and θ_{CB} was the apparent contact angle of the liquid droplet on the nanostructured surface in Cassie-Baxter state. Since the nano-cavities are filled with air and their nano-cavity surface is hydrophobic, the overall contact angle (of the nanostructured surface) increases, compared to the one on a flat substrate with the same chemical composition.



Figure 1: Liquid sitting on nanostructured surfaces in (a) Wenzel state and (b) Cassie-Baxter state

Learning from Wenzel and Cassie-Baxter models, one approach to controlling the wettability and to producing a hydrophobic or hydrophilic surface would be to modify nanostructures (e.g. r or φ_s) or chemical wettability (e.g. θ_I) of the surfaces. Therefore, our next discussion focuses on the fabrication techniques creating nanostructures for altering the surface properties, along with chemistry approaches to make the surface either hydrophobic or hydrophilic. Traditional lithography techniques to fabricate the nanostructures are first introduced, followed by three types of fabrication techniques, including the use of porous materials, nanotubes, and nanoparticle as discussed earlier in the boiling section. A table for comparing the fabrication techniques is presented to summarize this section.

3.1 Nanostructured Surfaces by Using Lithography-Based Fabrication

The most straightforward approach to create tiny structures with excellent regularity and dimensional control would be a top-down approach using microelectromechanical systems (MEMS) fabrication techniques, such as lithography and etching processes. Hexagonal network-type silicon microstructures, patterned by deep reactive ion etching (DRIE), with nanoprotrusions (D=0.9 μ m), patterned by reactive ion etching (RIE), were fabricated and coated with a phydrophobic coating of plasma polymerized fluorocarbon (PPFC) [29]. Furthermore, utilizing photolithography and a modified DRIE process, whose intermediate steps of depositing and removing passivation layers are altered to create silicon nanotips on microscale patterns, has demonstrated hierarchical micro- and nanoscale structures [30].

Meanwhile, although photolithography is the primary method for creating microscale patterns, interference lithography (IL) is often employed for creating smaller features due to the fundamental limitation of photolithography in diffraction to nanoscale. This is very applicable for our applications [31-34]. For instance, by combing laser interference lithography with DRIE, a dense array of silicon nanostructures with a width of 50 nm and a height of 500 nm have been achieved for application to superhydrophobic surfaces [31]. By utilizing traditional photolithography for microscale patterns and IL technique for nanoscale patterns in sequence, a hierarchical structure of photoresist was achieved on a silicon substrate [33].

Photoresist was also patterned on a glass substrate using IL techniques and decorated with SnCl₂ nanoparticles through electroless plating. This resulted in hierarchical structured surfaces with both superhydrophobicity and iridescence. Similar example involves IL techniques and electroplating processes to create a nickel stamp, which embossed submicrometer periodic structures into the thermoplastic polymer (polystyrene) substrate [32]. A plasma-polymerized hexafluoropropene layer was then coated for introducing smaller periodic structures, resulting in the superhydrophobic property.

3.2 Nanostructured Surfaces by Using Nanoporous Material

(i) Nanoporous Material

Due to their simple fabrication process, nanoporous membranes of different materials have shown a promise in many emerging fields [13, 14]. Porous layers can be prepared either chemically or electrochemically while the latter one is typically applied [35, 36]. In the electrochemical method, single crystalline silicon is galvanostatically anodized in hydrofluoric acid (HF) solutions in an electrochemical setup. The silicon atoms locally dissolved with nanoscale pores formed in bulk. As a result, the single crystalline silicon was converted into an anodized porous film.

Using such an electrochemical technique, a threedimensional porous structure of metallic material has been demonstrated [37]. The electrochemical reactions promote the creation of quasi-static template and the formation of byproduct hydrogen gas, leading to a porous network and assisting the metallic deposition. Figure 2 shows typical images of Cu sample surfaces with porous structures after electrodepositon. The porous surfaces enhance boiling performance by providing an increased surface area, and increased number of active nucleation sites for boiling.



Figure 2: SEM images of Cu sample surfaces show porous structures after electrodepositon [37]

Porous films of alumina gel were used to produce an alumina film on glass plates with nanoscale roughness of flowerlike structures (R_a =50 nm). In conjunction with surface chemistry approach of introducing a TiO₂ layer and hydrolyzed fluoroalkylsilane (FAS) layer on the alumina film, the sample demonstrated the conversion of a superhydrophobic to superhydrophilic surface by UV irradiation [38].

(ii) Silicon Nanowire

The electrochemical approach to forming porous silicon membrane was applied to produce silicon nanowire (SiNW) [39-41]; electroless metal-particle-assisted etching is one of such approaches. The nanowires were prepared by immersing a silicon wafer into an aqueous solution of AgNO₃ and HF acid as an etchant. Ag⁺ reduces to Ag by oxidizing the silicon lattice, which HF subsequently etched. Initial reduction of Ag⁺ forms Ag nanoparticles, which defined the spatial region of the following oxidation and etching process. As the results, the unetched region formed nanowire arrays. The SiNW showed little crystallographic dependence and could be performed on crystalline or polycrystalline substrates.

Figure 3 shows the vertically aligned Si nanowires with 20-300 nm in diameter and 40-50 μ m in length used by Chen et al. for the boiling experiments [41].



Figure 3: (a) Top view of Si Nanowires, and (b) cross section of Si nanowires [41]

Similar silicon nanowire-etching processes are also developed and employed by other researchers with photolithography and wet-etching processes to form a hybrid-structured surface. Arrays of the silicon nanowires form on the surfaces of the micro-pyramid caves, defined by silicon wet-etching process. A silane layer is applied to enhance the overall surface hydrophobicity [42, 43]. Another recent study employs a similar approach with deep silicon dry etching and silver nanoparticle (Ag-NP)-assisted HF/H₂O₂ etching for silicon hierarchical-structured surfaces that demonstrates to possess good anti-sticking property and allow the droplet to bounce off freely [44].

Chen at al. reported in a recent study on pool boiling of saturated water on nanowires, made of Si or Cu via using this template-based fabrication technique [41]. They observed increases in the CHF and the heat transfer coefficients by more than 100%. In the same study, porous alumina membrane was used as a template for Cu nanowire synthesis. The Cu nanowire structures are approximately 200 nm in diameter and 40–50 μ m long and with a 50% filling ratio.

(iii) Nanoporous Template-Based Fabrication

Nanoporous materiasl can also be employed as a template to fabricate an array of one-dimensional rods or wires as the nanoscale pores can be filled with a variety of materials using different deposition techniques [45-47]. The nanopores of the templates can be uniform and dense, providing a means to synthesize nanoscale structures in a high yield. As prevalent emphasis has been made on production with low cost, high throughput, high volume and ease of manufacturing, nanoporous-template-based synthesis has been the method of choice for the fabrication of nanorod arrays [45].

The materials to fill these nanopores in the template can be the polymeric, inorganic, or metallic phase using dip filling, ion-encountering reaction, electroplating, chemical bath deposition (CBD), chemical vapor deposition (CVD), and physical vapor deposition (PVD) [41, 48-59]. A subsequent removal of the templates produces a porous network that is a replicate of the template. For instance, polystyrene (PS) has been employed with a porous alumina membrane as the template to realize a nanotube film [51, 52]. Polyacrylonitrile (PAN) synthesis, conjunction with an anodized aluminum oxide (AAO) porous membrane as the template, has been applied to produce aligned PAN nanofiber array and demonstrate superhydrophobicity [53].

3.3 Nanostructured Surfaces by Using Nanotubes and Nanowires

Other nanostructures of different geometry and materials are discussed, including carbon nanotubes, silicon nanowires, nanowires of the materials with photo-induced hydrophilic (PIH) effects, nanowires/fibers/tubes of other materials, and nanoparticles. Due to their excellent mechanical and electrical properties, as well as their potential application to engineering and technical fields, carbon nanotubes have been widely studied and are well developed. Therefore, only those applied to nanostructured materials for controlling surface wettability are discussed here. Followed by nanowires of the materials with PIH effect, such materials demonstrate their unique capability of wettability switch between hydrophobic and hydrophilic upon UV illumination. Other nanowire materials, such as metals, oxides and polymers are introduced with specific examples. Finally, the utilization of nanoparticles is examined.

(i) Carbon Nanotubes (CNT)

The remarkable properties of CNT give promise of different innovative applications [60-65]. The fabrication method of carbon nanotubes mainly relies on synthesis, which comprises of electric arc discharge, laser vaporization, and catalytic decomposition of hydrocarbons, often referred to as CVD [64]. Other fabrication methods include flame-based synthesis, electrolysis of molten halide salts, and cracking of liquid hydrocarbons. Although these various fabrication methods are available, the plasma enhanced chemical vapor deposition (PECVD) is the technique favored for producing aligned, individually-standing and size-controlled CNT [65]. A vertically aligned CNT forest (D=50nm, h=2µm) coated with hydrophobic polytetrafluoroethylene (PTFE) on a silicon surface demonstrates superhydrophobocity [66]. A CNT array grown by using a CVD system is deposited onto PAN-based carbon microfibers to form a hierarchical structured surface.

Making aligned CNTs hydrophobic or hydrophilic has been demonstrated by employing different techniques. For example, the combination of CNT and a temperature responsive polymer, which possesses a unique property of thermallyresponsive wettability, can achieve the capability of switching between hydrophilicity and hydropholicity [67]. Decorating the CNTs with the temperature responsive polymer, e.g. Poly(Nisopropylacrylamide) (PNIPAAm)) via surface-initiated atom transfer radical polymerization can provide the surface with the CNT array with responsive wettability [68].

Applying carbon nanotubes for enhancing the boiling performance has been studied by several groups [15-20]. The carbon nanotubes were grown using the CVD process and deposited onto the surface-micromachined structured surfaces to provide microscale and nanoscale enhancements [15].

Randomly-arranged MWCNT arrays were grown by using PECVD process with a calcined dendrimer as the precursor [20]. Arrays of the MWCNT (30 nm in diameter and 20-30 μ m in length) were applied on silicon and copper substrates to evaluate the nucleate boiling performance of FC-72. Another study was conducted to realize the effect of MWCNT coated onto the bottom walls of the microchannels while deionized (DI) water was used as working fluid [69]. It was found that the CHF can be enhanced at a low mass velocity due to the near-zero-contact-angle cavities formed by the mesh of CNT arrays and the increased heat transfer area. Ahn et al. employed CVD to synthesize vertical-aligned MWCNTs (D=8~16nm, H=9~25 μ m, P=9~16nm) in on silicon substrate and investigate their effects on saturated and subcooled pool boiling [17].



Figure 4: SEM image of MWCNTs synthesized on silicon wafer used in boiling experiment [17]

(ii) Nanotubes with Photo-Induced-Hydrophilic (PIH) effect for Wettability Conversation

Wang et al. reported in 1997 the phenomenon of "photoinduced hydrophilic (PIH) effect" when a titania (TiO₂) film was illuminated with UV light and the contact angle of water decreased to near 0° [70]. The TiO₂ film slowly became hydrophobic when stored in the dark [71].

TiO₂ nanotubes have been successfully produced by various methods, such as template based, hydrothermal, sol-gel methods and electrochemical anodization [72]. For example, electrochemical anodization was facilitated to form selforganized TiO₂ nanotube layers on titanium substrate [73]. The nanotube layer showed super-hydrophilic as-deposited while it super-hydrophobic modified with organic showed molecules, octadecylsilane (C₁₈H₃₇SiH₃), or (C₁₈H₃₇PO(OH)₂). octadecylphosphonic acid It also demonstrated a transition from super-hydrophobic to superhydrophilic upon UV illumination. Moreover, a vertically aligned TiO₂ nanotube (VATN) array as a hydrophobichydrophilic template was prepared in a similar fashion [74].

In addition, the PIH effect was investigated on other metal oxides, including ZnO, SnO₂, SrTiO₃, WO₃, and V₂O₅. Zinc oxide (ZnO) nanotips have been grown on various substrates by using sol-gel solutions or metal-organic chemical vapor deposition (MOCVD) [75-79]. A wettability transition on ZnO nanostructured surface was observed and examined using ultraviolet (UV) illumination and oxygen annealing [77-79].

(iii) Nanowire of Other Materials

Other deposition techniques, such as sputtering

deposition, chemical vapor deposition, thermal evaporation deposition, were applied to produce nanostructured surfaces [65, 80-82] of different metal, oxide and polymer materials. Another surface with hierarchical structure was made using photolithography for creating micropatterned epoxy replicas. It was then covered with n-hexatriacontane re-crystallized nanostructures via thermal deposition. The influence of crystallized nanostructures on the superhydrophobicity was investigated though examining the contact angle, contact angle hysteresis, droplet evaporation, propensity of air pocket formation, and adhesive forces [82]. In addition, nanotextures transparent trimethylmethoxysilane of (TMMOS, (CH₃)₃Si(OCH₃)) thin films were prepared by microwave plasma enhanced chemical vapor deposition (MPECVD) on glass, silicon, and polymer (e.g. polymethylmethacrylate (PMMA)) [80].

Meanwhile, cryptomelane nanowires were employed to construct a porous membrane exhibiting controlled wetting behavior ranging from superhydrophilic to superhydrophobic [83]. Stoichiometric solutions of potassium sulphate, potassium persulphate, and manganese sulphate monohydrate were hydrothermally applied on a substrate. The water was then removed to form a self-assembled nanowire membrane. In addition, aligned polyaniline nanofibres (D=10~40nm, H=70~360 nm) were prepared on a variety of substrates through a dilute electrochemical polymerization method. The as-deposited nanofibred surfaces present an excellent property of superhydrophobicity and become superhydrophobic once they are exposed to CHF₃ or CF₄ plasma [84].

In pool boiling application, an array of nanoscale copper rods in Fig. 5 was sputtering-deposited on a copper substrate. An oblique-angle deposition mechanism, where copper atoms were incident on the substrate at a large incidence angle, was proposed; it results in the formation of isolated nanorods due to the atomic shadowing effect during growth [81].

3.4 Nanostructured Surfaces by Using Nanoparticles

(i) Nanoparticle Assembly

Nanoparticles in liquid solutions as a colloid solution were spin-coated and processed onto a substrate to form a nanostructured surface. Titanium oxide (TiO₂), and silicon oxide (SiO₂), particles of 10 nm were coated on a copper substrate to form a hydrophilic surface to study the nucleate boiling and CHF of water and FC-72 dielectric liquid [24]. In addition, a Layer-by-Layer (LbL) deposition technique was employed to assemble multiple layers of polymer/SiO₂ nanoparticles onto nickel wire to augment nucleate boiling heat transfer [23]. The assembly method involved the deposition of a bi-layer in which the substrate was immersed first in a positively charged solution and then in a negatively-charged solution in a sequence. The solutions contained 24 nm diameter silica nanoparticles. The assembly of one layer of positively charged species and one layer of negatively charged species was referred to as a bi-layer. By repeating the process, multiple bi-layers were formed. Three different types of surface treatment, including hydrophilic, superhydrophilic, and hydrophobic coatings were applied. Superhydrophilic surfaces were prepared by an additional step. The samples were calcinated at 550 °C for 4 hours in a furnace. The hydrophobic surfaces were prepared by immersing the calcinated samples in a PTFE container with fluorosilane, and then placed in an oven at 140 °C. The effects of surface modification, both chemical constituency and surface morphology, were examined, showing that the boiling heat transfer coefficient increased while the wettability decreased and the contact angle increased. In addition, the thickness of the superhydrophilic coating enhanced CHF because the increasing number of nanoporous structures.



Figure 5: SEM image of the Cu nanorods after deposition; rod average diameter of 40–50nm and height of 450nm [81]

(ii) Nanoparticle-Mask Etching

In addition to being assembled onto surfaces, nanoparticles can be applied as the masking materials, in conjunction with various etching techniques, to create nanofeatures on the surfaces. A self-masking technique which utilizes nanoparticles as the etching masks, released from a dummy material (e.g. cover glass) during the etching process, are developed to form high-aspect-ratio nanopillar structures of polymer materials, including poly(monochloro-*p*-xylylene) (Parylene C), poly(dimethylsiloxane) (PDMS) and SU-8 photoresist [85].

3.5 Discussion

Various demonstrative examples of fabrication techniques for producing nanostructued surfaces with designed wettability have been surveyed and summarized in Table 1. The boundaries of classifying these techniques in this section are not entirely distinct as the new fabrication techniques and their combinations have evolved rapidly.

While these fabrication methods offer an exceptional strategy to produce structured surfaces and control the surface wettability, they have their cons and pros: some of them provide simple, scalable and cost-effective manufacturing means while some of the others are capable of creating nanostructures with good regularity and controllability.

Fabrication	Nanostructure diameter ¹	Density (or spacing)	Uniformity	Equipment requirement & cost	Durability	Boiling application	Ref. of nano- structured surface
Photolitho- graphy	D=0.9μm, H=1μm [29] D=200nm, H=40μm [30]	Precisely controlled; A wide range (low~high)	Excellent	Expensive (etcher, photolithography etc)	Robust		[29,30]
Interference lithography	D=50~200nm H=370nm~ several µm	Precisely controlled; A wide range (low~high)	Excellent	Expensive (etcher, laser lithographyetc)	Robust		[31-34]
Nanoporous surface	D=20~250nm H=70µm	Moderate to excellent controllability	Good	Less expensive	Moderate to Robust	[14]	[14,37]
Si-Nanowire (SiNW)	D=20~300nm H=400nm~50µm	Moderate to excellent controllability	Good	Less expensive to moderate to expensive	Moderate to Robust	[41]	[39,41-44].
Nanoporous template-based fabrication	D=20~200nm H= several μm	Moderate to excellent controllability	Good	Less expensive to moderate	Moderate to Robust	[41]	[41, 51-53]
Carbon Nanotube (CNT)	D=4.3~50nm, H=9~25µm, P=9~16nm	Moderate to excellent controllability	Good	Moderate to expensive (deposition system)	Moderate to Robust	[16-20, 22]	[16- 20,22,67,68]
Nanowire (NW) with PIH effect	D=150nm (TiO ₂) D=40~100nm; H=1.2μm (ZnO)	Moderate controllability	Good	Less expensive	Moderate to Robust	[21]	[21](TiO ₂) [75-79] (ZnO)
Other Nanowire (NW)	D=40~50nm H=450 nm (Cu) [81]	Varies	Varies	Special deposition equipment required	Moderate to Robust	[81]	[80,82,84]
Nanoparticle assembly	D=10~50 nm H=300 nm~1µm	Less controllability	Moderate to Good	Simple, less expensive	Moderate	[23,24]	[23,24]
Nanoparticle- masking	D=112 nm H=6.7 μm	Less controllability	Moderate to Good	Expensive (etcheretc)	Depends on material		[85]

¹ The dimension of the nanostructures varies from processes types and many process parameters. The values provided here are intended to give readers the numerical ranges that each fabrication technique can achieve.

 Table 1. Different nanostructured surface fabrication techniques and their applicability to boiling performance enhancement.

For instance, as top-down approaches, the lithographybased techniques can define features and spacing with high resolution and good controllability; the features can be further transferred to create complex and robust structures along with etching processes. They are compatible to today's silicon IC/MEMS processes. In contrast, as chemical synthesis, the formation of porous films, as well as the assembly of nanotubes, nanowires or nanopartilces are simple, scalable and cost-effective. The approaches can be applied to different metal, oxide or polymer materials. However, the large distribution of the shapes, sizes and spacing in the nanoparticles (and nanotubes, nanowires) are still challenging. In addition, the interface between the nanoparticles and substrate materials requires strong bonding strength to ensure durability.

Finally, to implement the nanostructured surfaces for pool boiling study involves considerations intertwined from many

aspects. Although the relationship between nanostructures and surface wettability can be deciphered by Wenzel and Cassie-Baxter models, how they individually and collectively play roles in bubble nucleation and heat transfer rate requires further detail examination. In addition, the high temperature and harsh environment caused by liquid or bubbles in practical aspects may cause the following problems: film delamination, particle damage and detachment. The choice of the fabrication techniques therefore becomes vital and should be made accordingly. It must be made not only from surface property (e.g. wettability and structure geometry) for heat transfer enhancement, but also from material durability and interfacial strength from reliability standpoint. Further evaluations in these aspects will be necessary.

4. SUMMARY OF POOL BOILING STUDIES USING NANOSTRUCTURES AND RECOMMENDATIONS FOR FUTURE RESEARCH

The nanostructures have received considerable attention in pool boiling application. The review presented in the earlier sections on the application of nanostructures in pool boiling indicates that the nanostructures are promising in enhancing the heat transfer performance. General findings may be summarized as follows:

- a) The wetting characteristics of a substrate can be varied by proper selection of the process and materials for creating nanostructured surfaces.
- b) For hydrophilic nanostructured surfaces, the pool boiling heat transfer coefficient as well as CHF values increase over the base untreated surface. The increase could be substantial, up to 100 percent or more depending on the type of the coating, coating height and its structure.
- c) The taller nanotubes perform better in both nucleate boiling and at CHF. The mechanism is not fully understood, but the availability of vapor embryos at lower heat fluxes and pathways for liquid flow through the nanostructures are believed to be the main reasons.
- d) Integrating macrostructures with nanostructures did not yield any beneficial results. This aspect needs further investigation. Specific geometries can benefit by macroscale manipulation of the surface as well.
- e) The nanostructured surfaces need to be optimized to provide higher heat transfer performance under pool boiling conditions for different fluids.
- f) The selection of the fabrication process is an important consideration from material, cost and reliability standpoints. Further studies are needed to evaluate aging properties of the nanostructured surfaces.
- g) The nanostructured surfaces can be implemented with designed wettability via different approaches. The lithography-based approaches can create the structures with controllability geometrical characteristics while the chemical synthesis approaches are simple, scalable and cost-effective.
- h) There is no clear understanding for the enhancement mechanisms with the nanostructured surfaces. This is an area where further research is needed.
- i) Pool boiling presents a harsh environment to the heater surface. High surface temperatures coupled with large interfacial velocities are detrimental to the nanostructures. A detailed durability testing of each new proposed nanostructures should be carried out with intermittent start-ups and shutdowns. In the preliminary evaluation, it is suggested that at least ten start-up, shut-down cycles, with each cycle consisting of a continuous run of at least four hours followed by a cool-down for twenty hours is suggested. The tested

heat fluxes should be at least 20-25 percent higher than the anticipated highest heat fluxes during operation. These numbers are derived from degassing considerations. The heat transfer performance should be evaluated as a function of aging of the nanostructures. SEM images of before and after testing cycles should be presented to confirm the durability of the surfaces.

j) Critical heat flux limits for each surface should be established. This limit should be developed in conjunction with the durability testing. Critical heat flux limits for the newly prepared samples as well as samples aged over different start-up/cool-down cycles should be established.

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