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 experimental studies reported in the literature on the boiling phenomena on nanostructures, and implementation of nanostructures on various substrates. The paper also focuses on the interpretation of underlying phenomena for enhancing the boiling performance. The main influencing parameter in controlling is seen as the change in the surface energy of the boiling surface, which is characterized by the contact angle of the liquid and vapor phase interface at the heating surface. The nanostructures are seen to alter the contact angle. Design consideration and theoretical developments are also discussed, followed by practical aspects of nanostructure manufacturing. The issues related to performance, ease of fabrication, and durability (whenever available) are reviewed and recommendations are made for future research in this emerging area.

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.

Additionally, in the past decade, a significant number of studies showed that the utilization of nanofluids—nanoparticles suspended in colloid solutions—improved the CHF and heat transfer performance in pool boiling [4–8]. Recently, Kim et al. [8] found the main mechanism of CHF enhancement using nanofluids was because some nanoparticles were deposited...
on the heater surface to form a porous layer during boiling. This layer changed the surface wettability, and improved the CHF as well as the boiling performance. The finding validates the importance of the surface wettability and the utilization of nanostructures on the heater surface as an effective major approach to improve heat transfer in pool boiling.

This paper is divided into two parts. In the first part, an in-depth 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.

**POOL BOILING HEAT TRANSFER ENHANCEMENT THROUGH NANOSTRUCTURES**

The effect of contact angle on boiling incipience was first proposed by Davis and Anderson [9] in flow boiling. They included the static contact angle in their model to predict the onset of bubble nucleation. Cornwell [10] 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. Tehver et al. [11] 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 [12] 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 and You [13] and Chang and You [14, 15] developed microporous 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 micrometer-sized particles also improved the incipience behavior over particles larger than 10 μm. The surface wettability and availability of nucleation cavities together contributed to the improved heat transfer characteristics.

Takata et al. [16, 17] developed a superhydrophilic surface by irradiating TiO2 coated surface with ultraviolet (UV) light. The effects of contact angle were systematically studied in pool boiling of pure water on a sputtered TiO2 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 wetting 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.

**Nanoporous Surface**

Porous materials were applied extensively in enhancing pool boiling heat transfer. In his review article, Davis [18] 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 [19] used a commercially available nanoporous surface consisting of a 75-μm-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 diameter. The incipient superheat during pool boiling with FC-72 was reduced by 30% 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.

**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. [20] 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. [21]. The uncertainty in the heat flux measurements was between 5 and 30%, depending on the heat flux level. Although significant performance enhancements of up to 100% were noted at lower heat fluxes, the results showed limited enhancements at higher heat fluxes. The poor thermal properties of the fluids used (PF5060) and 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. [22] 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 to 16 nm, with a random pitch between 8 and 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% improvement in CHF, as compared to 25% 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% at CHF. Additional results were provided by Ahn et al. [23] and Sathyamurthi et al. [24] 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. [25] performed experiments with different CNT array densities and area coverage 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/μm² in the primary (light) array and 60 CNTs/μm² in the dense region. Using a grid pattern based on the Taylor wavelength, estimated to be around 5 μm, resulted in a 60% 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% 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. [26] studied the pool boiling performance of superhydrophobic 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. [27] under flow boiling conditions with carbon nanotube-coated walls indicates that the heat transfer performance was enhanced by 30–80% 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.

Nanoparticle and Thin Film Coating

Forrest et al. [28] developed nanostructured surfaces by employing a 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% 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. [29] in a recent paper reported the results of their pool boiling experiments on 1-μm-thick 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. [30] 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. [26] for superhydrophobic 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.

**NANOSTRUCTURED SURFACE FABRICATION**

It is known that both topological and chemical properties of the surfaces play a critical role in determining the surface wettability [31]. 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 [32, 33], as shown in Figure 1. In the Wenzel state [32], 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:

$$\cos \theta_w = r \cos \theta_1$$  (1)

where $r$ is the surface roughness—the ratio of the total rough surface area (contact area) to the projected surface area (apparent area), $\theta_1$ is the contact angle of the liquid on solid (species 1), and $\theta_w$ is the apparent contact angle of the liquid droplet on the nanostructured surface in the 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 nanocavity surfaces.

On the other hand, in the Cassie–Baxter state [33], the cavities are filled with air, which repels and alleviates the liquid on the nanostructured surface. The contact angle of a liquid droplet is:

$$\cos \theta_{CB} = 1 - \phi_s (\cos \theta_1 - 1)$$  (2)

where $\phi_s$ is the ratio of the liquid contact area to the projected droplet area and $\theta_{CB}$ is the apparent contact angle of the liquid droplet on the nanostructured surface in Cassie–Baxter state. Since the nanocavities are filled with air and their nanocavity 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.

Learning from the 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 $\phi_s$) or chemical wettability (e.g., $\theta_1$) 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 nanoparticles as discussed earlier in the boiling section. It is noted that the boundaries of classifying these techniques are not entirely distinct, as the new fabrication techniques and their combinations have evolved rapidly. Finally, a table for comparing the fabrication techniques is presented to summarize this section.

### 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 nanoproductions, patterned by reactive ion etching (RIE), were fabricated and coated with a hydrophobic coating of plasma-polymerized fluorocarbon (PPFC) [34]. 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 [35].

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 [36–39]. 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 has been achieved for application to superhydrophobic surfaces [36]. 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 [38].

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 [37]. A plasma-polymerized hexafluoropropene layer was then coated for introducing smaller periodic structures, resulting in the superhydrophobic property.

![Figure 1](image-url) Liquid sitting on nanostructured surfaces in (a) the Wenzel state and (b) the Cassie–Baxter state. (Figure provided in color online)
Nanostructured Surfaces by Using Nanoporous Material

Nanoporous Material

Due to their simple fabrication process, nanoporous membranes of different materials have shown their promising applications in many emerging fields [18, 19]. Porous layers can be prepared either chemically or electrochemically. Silicon porous structures, for instance, are commonly applied today, since they were first reported in 1950s [40–44]. Using electrochemical methods, single crystalline silicon can be galvanostatically anodized in hydrofluoric acid (HF) solutions. The silicon atoms are locally dissolved with nanoscale pores formed in bulk; the single crystalline silicon is then converted into an anodized porous film. By employing this anodization approach, the silicon chips with submicron roughness in Figure 2a were prepared and investigated for the boiling heat transfer in FC-72. The results showed considerable enhancement in the nucleate boiling heat transfer coefficients compared to the untreated silicon surface [44].

In addition, porous films of alumina gel were used to produce an alumina film on glass plates with nanoscale roughness of flowerlike structures (Ra = 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 [45].

Three-dimensional (3D) porous structures of other different metallic materials have been made using electrochemical techniques [46]. A well-ordered 3D porous copper surface layer with nanostructured porosity is obtained by using a simple electrochemical deposition method with in-situ grown dynamic gas bubble templates [46]. The electrochemical reactions promote the creation of quasi-static template and the formation of by-product hydrogen gas, leading to a porous network and assisting the metallic deposition. Figure 2b shows typical images of Cu sample surfaces with porous structures after electrodeposition. The porous surfaces enhance boiling performance by providing an increased surface area, and increased number of active nucleation sites for boiling.

Silicon Nanowire

Silicon has shown novel electrochemical properties in solutions containing hydrofluoric acid (HF); electroless metal-particle-assisted etching is one of the approaches that utilize the unique silicon electrochemical property to produce silicon nanowire (SiNW) [47–49]. 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 3a and b illustrate the SiNWs with desirable axial crystallographic orientations prepared by this electroless metal-particle-assisted etching technique. The as-synthesized SiNW arrays, which possesses the significant characteristics of reflection suppression over the visible light spectral range, are demonstrated to incorporate with a silicon solar cell as efficient antireflection coatings [49].

Similar silicon nanowire-etching processes have also been developed and employed by other researchers with photolithography and wet-etching processes to form a hybrid-structured surface [50, 51]. Arrays of the silicon nanowires are formed on the surfaces of the micro-pyramid caves, which are earlier defined by silicon wet-etching process. The structures are shown in Figures 3c and d. A silane layer is applied to enhance the overall surface hydrophobicity. Another recent study employs a similar approach with deep silicon dry
etching and silver nanoparticle (Ag-NP)-assisted HF/H₂O₂ etching for creating silicon hierarchical-structured surfaces, as shown in Figures 3e and f. The surface demonstrates a good antisticking property and allows the droplet to bounce off freely [52].

Chen et al. [49] 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. 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 µm long, with a 50% filling ratio.

Nanoporous Template-Based Fabrication

Nanoporous materials have also been 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 [53–55]. 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 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 [53].

The materials to fill these nanopores in the template can be the polymeric, inorganic, or metallic phase using dip filling.

Figure 3 (a, b) SEM images of silicon nanowires (SiNW) [48]: (a) SiNW arrays are formed by immersing p-type (111) single-crystalline silicon substrate into an aqueous HF/AgNO₃ solution; (b) SiNW arrays are prepared from a polycrystalline silicon substrate. (c, d) SEM images at different magnifications for hierarchical structures created on silicon substrates: The microscale pyramids are made by KOH etching and the nanoscale structures are made by Au-assisted HF/H₂O₂ etching [50]. (e, f) Images of a rough surface with fine nanostructures, which possess good antisticking property and allow water droplets to bounce off freely [52]: (e) optical image; (f) SEM image.
Nanostructured Surfaces by Using Nanotubes and Nanowires

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 applications to engineering and technical fields, carbon nanotubes have been widely studied and well developed in a variety of aspects. Only those applied as nanostructured materials for controlling surface wettability are discussed here. Nanowires of the materials with PIH effect are followed. Such materials demonstrate their unique capability of switching the wettability between hydrophobic and hydrophilic due to UV illumination. Other nanowire materials, such as metals, oxides, and polymers, are discussed with specific examples. Finally, the utilization of nanoparticles is examined.

Carbon Nanotubes (CNT)

The remarkable properties of CNT give promise of different innovative applications [68–74]. The fabrication method of carbon nanotubes mainly relies on synthesis, which comprises electric arc discharge, laser vaporization, and catalytic decomposition of hydrocarbons, often referred to as CVD [72]. Other fabrication methods include flame-based synthesis, electrolysis of molten halide salts, and cracking of liquid hydrocarbons. Among these fabrication methods, plasma-enhanced chemical vapor deposition (PECVD) is the technique favored for producing aligned, individually standing and size-controlled CNT. Meanwhile, the wettability of a single CNT has been studied extensively—the CNTs can maintain the wettability for the liquids with moderate surface tension (<180 m N⁻¹). Materials with a low surface tension can wet the CNT surface with a contact angle less than 90°. Therefore, by controlling the CNT arrangement and the surface chemistry, the wettability of the CNT-coated surfaces can be controlled [75].

For instance, a vertically aligned CNT forest in Figure 5a coated with hydrophobic polytetrafluoroethylene (PTFE) on a silicon surface shows superhydrophobicity [73]. Additionally, in Figure 5b, a continuous forest of CNTs grown and deposited on the PAN-based carbon fiber forms a micro/nano hierarchical structured surface, in which the CNTs reduce the area fraction of a water droplet in contact with the carbon surface and the two-tier structure induces superhydrophobicity [74].

The aligned CNTs can be further applied to making surfaces hydrophilic. The combination of CNT and a temperature-responsive polymer, which possesses a unique property of thermally responsive wettability, can switch the surfaces between hydrophilicity and hydrophobicity [75, 76]. The temperature-responsive polymer (e.g., poly(N-isopropylacrylamide) or PNIPAAm) is deposited on the CNTs via surface-initiated atom transfer radical polymerization (SI-ATRP). A spreading behavior of a water droplet on a repeated cycling of the temperature from 25 to 40°C with a quick recovery process is observed as shown in Figure 5d.

In the applications of enhancing the boiling performance, carbon nanotubes have been adapted by several groups [20–23, 25, 77]. The carbon nanotubes in Figure 5e were grown using the CVD process and deposited onto the surface-nanomachined silicon structures to provide microscale and nanoscale enhancements [20]. Randomly arranged MWCNT arrays were grown by using a PECVD process with a calcined dendrimer as the precursor [25]. Arrays of the MWCNT in Figure 5f with different densities and area coverage 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 a working fluid [78]. 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. [23] employed CVD to synthesize the vertically aligned MWCNTs in Figure 4g on silicon substrate and investigated their effects on saturated and subcooled pool boiling.

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

Wang et al. [79] reported in 1997 the phenomenon of “photo-induced hydrophilic (PIH) effect” in a titania (TiO$_2$) film. As depicted in Figure 5a, these TiO$_2$ thin films became hydrophilic when illuminated with UV light, and slowly returned to the initial hydrophobic state when irradiated by visible light (VIS) [79–81]. Not only can TiO$_2$ be made in thin films; nanoscale tubular structures of TiO$_2$ are successfully demonstrated by various methods, such as template-based, hydrothermal, sol–gel methods, and electrochemical anodization [82]. For example, electrochemical anodization was facilitated to form self-organized TiO$_2$ nanotube layers in Figure 5b on a titanium substrate [83]. The nanotube layer showed as super-hydrophilic as deposited, while it showed as super-hydrophobic when modified with self-assembly mono-layers (SAM)—octadecylsilane (C$_{18}$H$_{37}$SiH$_3$) as silane-SAM or octadecylphosphonic acid (C$_{18}$H$_{37}$PO(OH)$_2$) as acid-SAM. It also demonstrated a transition from super-hydrophobic to super-hydrophilic upon UV illumination, as shown in Figure 5c. Moreover, a vertically aligned TiO$_2$ nanotube array as a hydrophobic–hydrophilic template was prepared in a similar fashion [84].

In addition, the PIH effect was investigated on other metal oxides, including ZnO, SnO$_2$, SrTiO$_3$, WO$_3$, and V$_2$O$_5$. Zinc oxide (ZnO) nanotips have been grown on various substrates by using sol-gel solutions or metal-organic chemical vapor deposition (MOCVD) [85–89]. A wettability transition on ZnO nanostructured surfaces was observed and examined using UV illumination, oxygen annealing, or other means [87–89].

Nanowire of Other Materials

Other deposition techniques, such as sputtering deposition, chemical vapor deposition, and thermal evaporation deposition, were applied to produce nanostructured surfaces [74, 90–92] for different metal, oxide, and polymer materials. Another surface with a hierarchical structure was made using photolithography for creating micropatterned epoxy replicas. It
was then covered with n-hexatriacontane recrystallized nanostructures via thermal deposition. The influence of crystallized nanostructures on the super-hydrophobicity was investigated though examining the contact angle, contact-angle hysteresis, droplet evaporation, propensity for air pocket formation, and adhesive forces [92]. In addition, nanotextures of transparent trimethylmethoxysilane (TMMOS, \((\mathrm{CH}_3)\_3\mathrm{Si(OCH}_3)\)) thin films were prepared by microwave plasma-enhanced chemical vapor deposition (MPECVD) on glass, silicon, and polymer (e.g., polymethylmethacrylate [PMMA]) [90].

On the other hand, controllable wettability ranging from super-hydrophilic to super-hydrophobic was obtained in a nanowires membrane made of cryptomelane [93]. Stoichiometric solutions of potassium sulphate, potassium persulfate and manganese sulfate monohydrate were hydrothermally applied on a substrate. The water was then removed to form a self-assembled nanowire membrane. In addition, aligned polyaniline nanofibers were prepared on a variety of substrates through a dilute electrochemical polymerization method. The as-deposited nanofibered surfaces present an excellent property of super-hydrophobicity and become super-hydrophobic once they are exposed to CHF$_3$ or CF$_4$ plasma [94].

In pool boiling application, an array of nanoscale copper rods in Figure 6 was sputter-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 [91].

**Nanostructured Surfaces by Using Nanoparticles**

**Nanoparticle Assembly**

Nanoparticles in liquid as a colloid solution were spin-coated and processed onto a substrate to form a nanostructured surface. Titanium oxide (TiO$_2$) and silicon oxide (SiO$_2$) particles of 10 nm diameter 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 [29]. In addition, a layer-by-layer (LbL) deposition technique was employed to assemble multiple layers of polymer/SiO$_2$ nanoparticles onto nickel wire to augment nucleate boiling heat transfer [28]. The assembly method involved the deposition of a bilayer in which the substrate was immersed first in a positively charged solution and then in a negatively charged solution in a sequence [95]. 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 bilayer. By repeating the process, multiple bilayers were formed, and their surface morphology is shown in Figure 7b. Three different types of surface treatment, including hydrophilic, super-hydrophilic, and hydrophobic coatings, were applied. Super-hydrophilic surfaces were prepared by an additional step. The samples were calcinated at 550°C for 4 h 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 of the increasing number of nanoporous structures.

**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 nanostructures on the surfaces. A self-masking technique that utilizes nanoparticles as the etching masks, released from a dummy material (e.g., cover glass) during the etching process, is 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 [96].

**DISCUSSION**

To implement the nanostructured surfaces for pool boiling study involves considerations intertwined from many aspects. On one hand, the nanostructures introduce surface irregularity and increase bubble nucleation sites, which can enhance the heat transfer performance. On the other hand, based on the Wenzel and Cassie–Baxter models, nanostructures change surface contact angles and wettability, which also control the hydrodynamic behavior of bubbles on the substrate surface interfaces, leading to the initiation of critical heat flux condition [3]. Thus, the roles of these nanostructures and surface wettability in changing bubble nucleation and heat transfer rate individually and collectively require further examination.

On the other hand, from a fabrication prospect, demonstrative examples of the techniques to produce nanostructured surfaces with designed wettability have been surveyed. Table 1 shows a performance comparison of the techniques in terms of structure geometry characteristics (e.g., size, density, and uniformity), equipment requirement, material durability, and their application in boiling. While these fabrication methods offer an exceptional strategy to produce structured surfaces and control the surface wettability, they have their pros and cons. Some of them provide simple, scalable, and cost-effective manufacturing means; some of the others are capable of creating nanostructures with good regularity and controllability; some require expensive tools. They all can only partially address the need for improving the heat transfer performance in boiling applications.

For instance, as top-down approaches, the lithography-based techniques can define features and spacing with high resolution and good controllability. This capability allows us to study geometrical effects of the surfaces on boiling phenomena by precisely producing designed nanostructures. This is different from other related studies in earlier literature, which focus on surface roughness parameters (e.g., average surface roughness $R_a$, rms roughness $R_q$, peak-to-mean surface roughness $R_p$). Additionally, the lithography-based techniques are compatible to today’s silicon IC/MEMS processes, permitting their applications to be integrated with silicon devices.

The fabrication techniques using nanoporous materials, which can result in structures with reasonably controllable dimensions and density, seem appealing and advantageous over other high-temperature substrates. They are cost-effective and scalable.

The structured surfaces made with nanotubes (and nanowires) and nanoparticles are mostly based on chemical synthesis or self-assembly, which are also 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 nanotubes and nanoparticles is still challenging. Moreover, in some cases, the interfacial strength between the nanoparticles and substrate materials may not be strong enough to sustain the harsh environment caused by liquid or bubbles at high temperature during boiling in practical aspects, causing film delamination, particle damage, and detachment.

In addition to the fabrication techniques, the material choice of the nanostructures is also important; the materials must be mechanically strong and capable of enduring the high temperature and harsh environment during pooling. Based on the material cost, mechanical and thermal properties, and manufacturability, a list of the materials is included in Table 2. Silicon has the highest material cost per unit area, but is often preferable due to its excellent mechanical strength and thermal conductivity as well as its well-established micro/nanofabrication tools. Metal materials also have excellent mechanical and thermal properties, which allow the applications in boiling. On the other hand, ceramic and polymer materials suffer poor thermal conductivity, or mechanical properties may become less favorable.
As Figure 2 illustrates, this section presents the application of nanostructures in pool boiling, providing general findings and summarizing nanostructure behaviors, with emphasis on nucleate and pool boiling. For nucleate boiling, nanostructured surfaces increase the heat transfer coefficient and CHF values compared to untreated surfaces. The increase is significant, with CHF enhancement up to 100% or more in some cases. The mechanism behind this enhancement is not fully understood but is attributed to the availability of vapor embryos at lower heat fluxes and at CHF. The mechanism is not fully understood, but the increase could be substantial, up to 100% or more depending on the type of the surface, coating, coating height and its structure.

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

<table>
<thead>
<tr>
<th>Fabrication</th>
<th>Nanostructure diameter</th>
<th>Density (or spacing)</th>
<th>Uniformity</th>
<th>Equipment requirement &amp; cost</th>
<th>Durability and interfacial strength</th>
<th>Boiling application</th>
<th>Ref. of nanostructured surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolithography</td>
<td>D = 0.9 µm, H = 1 µm</td>
<td>Precisely controlled; A wide range (low–high)</td>
<td>Excellent</td>
<td>Expensive (etcher, photolithography . . . etc)</td>
<td>Robust</td>
<td></td>
<td>[29,30]</td>
</tr>
<tr>
<td>Interference lithography</td>
<td>D = 50–200 nm, H = 370 nm–several µm</td>
<td>Precisely controlled; A wide range (low–high)</td>
<td>Excellent</td>
<td>Expensive (etcher, laser lithography . . . etc)</td>
<td>Robust</td>
<td></td>
<td>[31–34]</td>
</tr>
<tr>
<td>Nanoporous surface</td>
<td>D = 20–250 nm H = 70 µm</td>
<td>Moderate to excellent controllability</td>
<td>Good</td>
<td>Less expensive</td>
<td>Moderate to Robust</td>
<td>[14]</td>
<td></td>
</tr>
<tr>
<td>Si-Nanowire (SiNW)</td>
<td>D = 20–300 nm H = 400 nm–50 µm</td>
<td>Moderate to excellent controllability</td>
<td>Good</td>
<td>Less expensive to moderate</td>
<td>Moderate to Robust</td>
<td>[41]</td>
<td>[39, 41–44]</td>
</tr>
<tr>
<td>Nanoporous template-based fabrication</td>
<td>D = 20–200 nm H = several µm</td>
<td>Moderate to excellent controllability</td>
<td>Good</td>
<td>Less expensive to moderate</td>
<td>Moderate to Robust</td>
<td>[41]</td>
<td>[41, 51–53]</td>
</tr>
<tr>
<td>Carbon Nanotube (CNT)</td>
<td>D = 4.3–50 nm, H = 9–25 µm, P = 9–16 nm</td>
<td>Moderate to excellent controllability</td>
<td>Good</td>
<td>Moderate to expensive (deposition system)</td>
<td>Moderate to Robust</td>
<td>[16–20, 22]</td>
<td>[16–20, 22, 67, 68]</td>
</tr>
<tr>
<td>Nanowire (NW) with PIH effect</td>
<td>D = 150 nm (TiO2)</td>
<td>Moderate controllability</td>
<td>Good</td>
<td>Less expensive</td>
<td>Moderate to Robust</td>
<td>[21]</td>
<td>[21][TiO2] [75–79] (ZnO)</td>
</tr>
<tr>
<td>Other Nanowire (NW)</td>
<td>D = 40–50 nm H = 450 nm (Cu)</td>
<td>Varies</td>
<td>Varies</td>
<td>Special deposition equipment required</td>
<td>Moderate to Robust</td>
<td>[81]</td>
<td>[80, 82, 84]</td>
</tr>
<tr>
<td>Nanoparticle assembly</td>
<td>D = 10–50 nm H = 300 nm–1 µm</td>
<td>Less controllability</td>
<td>Moderate to Good</td>
<td>Simple, less expensive</td>
<td>Moderate to Robust</td>
<td>[23, 24]</td>
<td>[23, 24]</td>
</tr>
<tr>
<td>Nanoparticle masking</td>
<td>D = 112 nm H = 6.7 µm</td>
<td>Less controllability</td>
<td>Moderate to Good</td>
<td>Expensive (etcher . . . etc)</td>
<td>Depends on material</td>
<td></td>
<td>[85]</td>
</tr>
</tbody>
</table>

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

Among the various fabrications and materials available to create the nanostructured surfaces with controllable wettability, a proper combination becomes vital and should be made accordingly to meet our need in boiling applications. The choice must be made not only for surface property (e.g., wettability and structure geometry) for heat transfer enhancement, but also for material durability and interfacial strength from reliability standpoint. Further evaluations in these aspects will be necessary.

Table 2 Material choice for nanostructured surface and their applicability for boiling performance enhancement

<table>
<thead>
<tr>
<th>Material</th>
<th>Cost</th>
<th>Mechanical strength</th>
<th>Thermal conductivity</th>
<th>Manufacturability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>High</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Lithography, or nanoporous material, or nanowire (NW), or nanoparticle assembly</td>
</tr>
<tr>
<td>Metal</td>
<td>Medium</td>
<td>Excellent</td>
<td>Excellent</td>
<td></td>
</tr>
<tr>
<td>Ceramic</td>
<td>Medium</td>
<td>Excellent</td>
<td>Poor</td>
<td></td>
</tr>
<tr>
<td>Polymer</td>
<td>Low</td>
<td>Poor–good</td>
<td>Poor–good</td>
<td></td>
</tr>
</tbody>
</table>

**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 nanostructures are promising in enhancing the heat transfer performance. General findings may be summarized as follows:

1. The wetting characteristics of a substrate can be varied by proper selection of the process and materials for creating nanostructured surfaces.
2. For hydrophilic nanostructured surfaces, the pool boiling heat transfer coefficient and the CHF values increase over the base untreated surface. The increase could be substantial, up to 100% or more depending on the type of the coating, coating height and its structure.
3. 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.

4. Integrating macrostructures with nanostructures did not yield any beneficial results. This aspect needs further investigation. Specific geometries can benefit from macroscale manipulation of the surface as well.

5. The nanostructured surfaces need to be optimized to provide higher heat transfer performance under pool boiling conditions for different fluids.

6. 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.

7. 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.

8. There is no clear understanding for the enhancement mechanisms with the nanostructured surfaces. This is an area where further research is needed.

9. 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 nanostructure should be carried out with intermittent startups and shutdowns. In the preliminary evaluation, it is suggested that there be at least 10 startup, shutdown cycles, with each cycle consisting of a continuous run of at least 4 h followed by a cool-down for 20 h. The tested heat fluxes should be at least 20–25% 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. Scanning electron microscopy (SEM) images of before and after testing cycles should be presented to confirm the durability of the surfaces.

10. 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 startup/cool-down cycles should be established.

**NOMENCLATURE**

- $D$: diameter of nanoscale features
- $L$: length of nanoscale features
- $P$: pitch between nanoscale features
- $r$: surface roughness; the ratio of the total rough surface area (contact area) to the projected surface area (apparent area)
- $R_a$: average surface roughness
- $R_q$: root-mean-square values of surface roughness
- $R_p$: peak-to-mean surface roughness

**Greek Symbols**

- $\theta_l$: contact angle of the liquid on solid of species 1
- $\theta_w$: apparent contact angle of the liquid droplet on the nanostructured surface in Wenzel state
- $\theta_C$: the ratio of the liquid contact area to the projected area
- $\theta_{CB}$: apparent contact angle of the liquid droplet on the nanostructured surface in Cassie–Baxter state

**REFERENCES**


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