Direct growth of copper nanowires on a substrate for boiling applications

Zhonghua Yao¹, Yen-Wen Lu², Satish G. Kandlikar¹

¹Microsystems Engineering Doctoral Program, Rochester Institute of Technology, Rochester, NY, USA
²Bio-Industrial Mechatronics Engineering, National Taiwan University, Taipei, Taiwan
E-mail: yenwenlu@ntu.edu.tw

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A new technique utilising electrochemical deposition with the assistance of porous alumina membranes as the fabrication template is developed to directly grow metallic nanowires on different substrates. To emphasise the nanowire application in boiling enhancement, Cu nanowire (CuNW) has been successfully fabricated on Si, Au and Cu substrates with improved thermal properties and mechanical reliability. Several process parameters to control the CuNW growth have been discussed. The nanowire structures applied in pool boiling enhancement are further investigated and significant enhancements are observed with all the surfaces with nanowire structures.

1. Introduction: Nanostructured materials have been widely applied in many fields, including optics, semiconductors and microelectromechanical systems (MEMS). Metallic nanowires (NW) have attracted considerable attention owing to their interesting electronic and physical properties [1–5]. Many fabrication methods, such as vapour–liquid–solid growth [6], thermal decomposition [7] and surfactant-assisted hydrothermal process [8] have been developed to create metallic NW arrays. Among them, the fabrication method with the assistance of porous membrane as a template is considered to be a convenient and versatile approach for NW preparation [9]. The templates can be porous polycarbonate membranes, nanochannel glasses and anodic aluminium oxide (AAO) membranes [10]. Especially, the AAO membrane, which possesses desirable characteristics, including tunable pore size, uniform structure and high thermal stability, has become a popular material in nanofabrication. The electrodeposition assisted by the utilisation of the AAO membrane template can create a variety of metallic [10–12], semiconductor [13, 14] and conductive polymer [15] NW arrays. Extensive research has been carried out on the applications of NW arrays in biomedical devices, optical sensing and electronic cooling [9]. However, the NW fabrication using the AAO templates has suffered limitations due to the requirement of a bonding layer commonly seen in the AAO membranes. In particular, a conductive thin film layer is usually needed on one side of the AAO membrane before the electrochemical deposition. An extra epoxy layer therefore is needed to bond the thin film layer on the AAO membrane to the substrate, which introduces an additional interfacial layer and becomes troublesome in practical applications. In the meantime, recent NW arrays have been greatly exploited in the boiling applications [16–18]. While this epoxy layer is inevitable in creating the NW arrays using the AAO templates, an additional thermal resistance is introduced. The thermal resistance of a typical epoxy adhesive containing boron nitride fillers is in the range of 0.7–1.6°C/W [19]. As the epoxy layer becomes thicker, its thermal resistance proportionately increases. The resistance furthermore increases as the temperature rises. The epoxy adhesive also traps air bubbles and forms voids, creating a non-uniform surface because of the high viscosity of the epoxy during its application. As a result, the epoxy layer becomes a major problem in the NW fabrication using the AAO template. In addition, when applying the epoxy on a large area, the difference in coefficient of thermal expansion (CTE) between the epoxy layer and NW array has to be taken into account, as it causes mismatch due to thermal stress at the interface and compromises mechanical reliability of the assembly. Hence, to address these issues, a new method is developed to directly deposit a metallic NW array on a plain substrate using the AAO template without any epoxy bonding layer. The mechanical reliability and flexibility of the NW arrays are therefore greatly enhanced. The interfacial thermal resistance between the NW array and substrate are eliminated, making the samples with the NW array capable of sustaining high temperatures for pool boiling application. With this method, the NWs can be fabricated onto various substrates; thus the selections of the substrate materials are flexible and the potential applications of the NW arrays are greatly broadened. For example, semiconducting substrates used for growing piezoelectric NWs are not preferred in many applications that require a flexible power source, such as an implantable biosensor. Using polymeric or plastic substrate instead of brittle metallic substrate for piezoelectric NW deposition in energy harvesting is advantageous [20].

2. Preparation of substrate materials: To examine the effect of substrate materials on the NW structures, three different substrates were employed for the NW deposition:

1. A (111) polished 4-inch silicon wafer was coated with a 500 nm-thick silver (Ag) layer by E-beam evaporation.
2. The 25 × 25 mm glass substrate was cut from a 75 × 25 mm glass slide coated with an 80 nm gold (Au) layer (BioGold®, Thermo Scientific).
3. The 20 × 20 × 3 mm copper substrate was customised by computer numerical control machine tools and mechanically polished.

All three types of substrates (i.e. Ag-silicon, Au-glass and Cu) were cleaned by acetone, isopropanol, deionised (DI) water rinse and dried at room temperature before use for the NW deposition. The substrates were also examined by atomic force microscopy (Veeco Dimension 3000) for the surface roughness measurement, as shown in Table 1.

3. Experimental: AAO membranes with a thickness of 60 μm and pore size of 200 nm (Anodisc, Whatman) were used as the templates for NW synthesis. To study the application of the metallic NW structure on pool boiling enhancement, Cu was chosen as the NW material because of its high thermal conductivity and mechanical reliability. For Cu nanowire (CuNW) directly grown on the Si substrate, a thin conductive film is still needed (e.g. Ag layer), and it is coated on the Si substrate instead of the AAO membrane. For the Au-glass and Cu substrates, no conductive thin film is needed, but the surfaces are polished for better surface contact. The AAO membrane was attached on the substrate before electro-chemical deposition (Fig. 1c). A liquid film of DI water was first applied between the AAO and substrate. Because of the hydrophilicity of the AAO membrane, the surface tension induced by the liquid film provided enough adhesion forces to attach the AAO membrane.
4. NW growth on different substrates: In recent years, extensive studies have been performed using various electrochemical methods and in situ scanning probe microscopy techniques to realise the electrochemical deposition mechanism of metallic materials on foreign substrates [22]. It is believed that the kinetics and mechanism of electrochemical deposition and the involved phase formation phenomena can be affected by electronic properties and surface homogeneities of the substrate materials. The electrochemical deposition inside the pores of the AAO membranes therefore relies not only on the deposition potential, but also on the surface condition of the substrates. Figs. 2a and b show the AAO template used in our experiment and the CuNW structures obtained. Although they have different heights, similar CuNW arrays are observed on different substrate materials. Since the NW structures are formed inside the pores of the AAO template, the NW are aligned vertically as the pores are. The as-deposited CuNW arrays on Ag-silicon, Au-glass and Cu substrates also have the same diameter of 200 nm as the pore size.

In addition, it is found that the NW arrays have different growth rates on different substrates under the same deposition conditions, as summarised in Table 1. Although there are many parameters, including the geometry and material property of the electrodes, which can affect the electrodeposition rates, the surface roughness of the substrates plays the most critical role [21]. The Ag-silicon has the smallest surface roughness of 5.2 nm and longest NW of 20–25 μm. The Au-glass has a larger surface roughness of 12 nm and shorter NW of 10–15 μm. Finally, the mechanically polished Cu substrate has the largest surface roughness of 400 nm and shortest NW of 5–10 μm. The Ag-silicon surfaces with the smallest surface roughness provide better surface contact with the AAO template than Au-glass and mechanically polished Cu substrate. As the rough topography usually has a higher requirement to ensure that the peaks of the roughened area are covered by an adequate coating material [23], copper ions (Cu^{2+}) take longer time to accumulate inside the pores for rough surfaces such as Cu substrates. Consequently, at a given synthesis condition, the NW growth rate varies and highly depends on the surface roughness of the substrate materials.

5. NW applications on boiling: By eliminating the epoxy layer, the NW structures can be readily employed in boiling application. An experimental setup shown in Fig. 3 was designed and built to allow testing of plain substrates and different substrates with CuNW arrays for the boiling performance [24]. Since copper is the most commonly used material in heat transfer and boiling applications, CuNW arrays deposited on the Cu substrates were selected

### Table 1 Deposition conditions for CuNW synthesis on different substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Surface roughness of the substrate (in RMS)</th>
<th>Deposition condition (potentiostat)</th>
<th>Average NW height (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-silicon (500 nm-thick Ag on 450 μm-thick silicon)</td>
<td>5.2</td>
<td>0.9 V for 900 s</td>
<td>20–25</td>
</tr>
<tr>
<td>Au-glass (80 nm-thick Au on 1.1 mm-thick glass)</td>
<td>12</td>
<td>0.9 V for 900 s</td>
<td>10–15</td>
</tr>
<tr>
<td>Cu (polished, 3 mm-thick copper)</td>
<td>400</td>
<td>0.9 V for 900 s</td>
<td>5–10</td>
</tr>
</tbody>
</table>
for testing heat transfer enhancement of water under pool boiling. The test samples were mounted on an insulated and sealed copper block. A 450 W capacity cartridge heater and a 100 W auxiliary heater served as the heating elements. The Cu substrate was machined to be $20 \times 20 \times 3$ mm and had a square channel 1 mm wide cut around the area of the heater. This was done to keep the heat transfer through the block one-dimensional, preventing any two-dimensional or fin effects from the highly conductive copper. A thermocouple hole was machined into the centre of the chip to measure the centre temperature. Three K-type thermocouples, each spaced 8 mm apart, were used to measure the temperature gradient through the tip of the heater. To measure the temperature gradient inside the chip, a 0.5 mm diameter hole was drilled through the side of the chip to place another thermocouple at 1.5 mm distance from the top. A LabVIEW virtual instrument was created to display temperatures, determine when the system reached a steady-state and to record the data. The heat flux was then calculated by 1D heat conduction equation. For each test, DI water was used to ensure it was free from contaminants. Water is chosen because of its well-known fluid properties and the minimal risk associated with handling the fluid. Prior to the test, the water was boiled sufficiently to eliminate any dissolved gases. The boiling system was allowed to reach steady-state before any data were collected. Periodically between the tests, more water was added to the pool to replenish the evaporated water vapour.

The boiling characteristic of testing samples is depicted in Fig. 4. The heat flux is based on the projected base area. The wall temperature was calculated as the temperature at the top surface of the test samples. The wall superheat was then obtained by subtracting the water saturation temperature from the wall temperature. Boiling on plain Cu substrate served as the primary control for comparing boiling performance. Two CuNW samples were tested and compared with the performance of plain Cu substrate. It is clear from Fig. 4 that higher heat flux can be dissipated through the substrates with the NW arrays compared to the plain substrate for a given wall superheat. For both samples with the NW arrays, the heat flux in most wall superheat regions was at least twice as much as that of plain surface, and the maximum heat flux was 160 W/cm² at 11.2 K wall superheat. Similar results on Si substrate with CuNW were also observed in our previous study [24], but the maximum heat flux value was only 134 W/cm² at 23 K superheat, suggesting that by changing the substrate material, the pool boiling performance of the NW structure can be further improved. The detailed mechanism was discussed elsewhere [16]. Basically, there are two major reasons for this enhancement: (i) the NW structures create a more active heat transfer area compared to a plain surface and (ii) the NW structure affects the mechanics of bubble dynamics in water pool boiling through the coupling effects of micro/nanoscale cavities. During the whole tests, no aging or peeling off was observed for the NW sample after repeated boiling, which confirms that the directly grown CuNW arrays possess high mechanical and thermal reliability. The testing results suggested that application of NW structures on the heater surface may greatly enhance pool boiling heat transfer.

To our best knowledge, this is the first pool boiling study using bulk substrates with directly grown NW without any interfacial layer. The heat flux for CuNW on Cu substrate during the testing reaches 164 W/cm² at 11 K wall superheat, which is among the highest values for pool boiling heat transfer with water. A comparison of recent studies on Cu nanostructures for pool boiling is summarised in Table 2. Our directly grown metallic NW has been shown to be advantageous in pool boiling heat transfer.

6. Conclusions: A simple and controllable method for directly growing metallic NW on plain surfaces using porous anodic aluminium oxide templates is provided. CuNW arrays are successfully fabricated on Ag-silicon, Au-glass and copper substrates, and this method can be further applied to a variety of substrates. The substrate with NW arrays demonstrates great enhancement in pool boiling heat transfer.

Table 2 Comparison of recent studies on substrate with Cu nanostructures on pool boiling heat transfer

<table>
<thead>
<tr>
<th>Material nanostructure</th>
<th>Working fluid</th>
<th>Surface characterisation</th>
<th>Boiling performance (W/cm² at K)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuNW attached on Si substrate with an epoxy layer</td>
<td>Water</td>
<td>200 nm in diameter, 50 μm in height</td>
<td>180–220 W/cm² at 30 K superheat</td>
<td>Chen et al. 2009 [16]</td>
</tr>
<tr>
<td>Cu nanorods created on Cu substrate by oblique-angle deposition</td>
<td>Water</td>
<td>50 nm in tip diameter, 450 nm in height</td>
<td>160 W/cm² at 15–20 K superheat</td>
<td>Li et al. 2008 [18]</td>
</tr>
<tr>
<td>CuNW bonded on Si substrate with an epoxy layer</td>
<td>FC-72</td>
<td>200 nm in diameter, 300 nm in pitch, 1–8 μm in height</td>
<td>19.5 W/cm² at 38 K superheat for 2 μm NW arrays</td>
<td>Im et al. 2010 [17]</td>
</tr>
<tr>
<td>CuNW directly deposited on Cu substrate using AAO templates</td>
<td>Water</td>
<td>200 nm in diameter, 5–10 μm in height</td>
<td>164 W/cm² at 11 K superheat</td>
<td>This work</td>
</tr>
</tbody>
</table>
transfer as compared to the bare substrate. The NW array without an intermediate epoxy layer proves to be beneficial in other applications, where larger area coverage of nanowires is desired.

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8 References