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ABSTRACT
Although the wettability of ultrafast laser-textured surfaces has been widely studied recently, most studies have only investigated the transition mechanism of surface wettability after laser irradiation with elapsed time. It is already known that the laser-textured copper surface experiences a wettability transition from hydrophilicity to hydrophobicity due to the occurrence of partial deoxidation from CuO to Cu₂O. This study investigates the surface wettability change of ultrafast (of the order of picoseconds) laser-textured copper surfaces treated with water baths of 50°C and 100°C. The pulse duration of the laser is 7 ps, the wavelength of the laser is 532 nm, and the fluence range is controlled at 1.27–2.97 J/cm². This simple treatment changes laser-textured surfaces from hydrophobic to hydrophilic ones. Detailed surface chemical analyses revealed that the formation of Cu(OH)₂ on top of the copper surfaces was attributed to the change in wettability.

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In recent years, various methods such as an etching process, electrochemistry, and chemical deposition have been developed to modify the surface wettability and roughness of different materials. Surface wettability needs to be controlled in applications such as self-cleaning, oil–water separation, antifogging, corrosion prevention, drag force reduction, liquid transportation, biodegradability, tribology, and pool boiling heat transfer. Not only ultrashort (femtosecond and picosecond) laser pulses but also nanosecond laser pulses have been recently used to perform surface modification. An ultrafast laser affords advantages including high resolution, precise ablation threshold, and minimal thermal damage for creating different patterns, with patterned structures showing only a small thermal deformation region; furthermore, an ultrafast laser can be used to form laser-induced periodic surface structures (LIPSSs) on various materials. In addition, the surface wettability and roughness can be changed after laser irradiation due to the chemical transition. Recently, many studies have used ultrafast laser surface texturing to change the surface wettability and roughness and have used ultrafast lasers to fabricate hydrophobic surfaces on different metals. For surface modification, a few studies have used ultrafast lasers to ablate tested surfaces and investigate the effect of heat transfer on laser-textured surfaces in pool boiling. Some studies have investigated the wettability transition for laser texturing surfaces. With the repeated low temperature annealing, Moze et al. found that Cu (II) oxide and hydroxide would transform into Cu (I) oxide and Cu metal. Thus, this led to the wettability change from hydrophilic toward hydrophobic. Ta et al. studied the change in the wettability of copper and brass and concluded that the wettability of textured surfaces changes from hydrophilic to superhydrophobic over time under ambient conditions because laser texturing induces partial deoxidation of oxides on the surface. Long et al. created various environments to discuss the transition wettability of a laser-structured copper surface and found that the surface adsorption of organic matter made initially hydrophilic copper surfaces to change to the hydrophobic ones. Chun et al. used low-temperature annealing and ethanol to accelerate the formation of a Cu₂O structure that made the surface highly hydrophobic; their...
results demonstrated that ultrafast laser-textured surfaces could be changed by certain treatments.

The present study used a deionized (DI) water bath as a simple treatment to change the wettability of ultrafast laser-textured copper surfaces. This can change initially hydrophobic surfaces into the hydrophilic ones. The surface characteristics were evaluated using different methods. The water droplet contact angle (WDCA) as measured from equisized water droplets (9 μl) by using a contact-angle goniometer (100SB, Sindatek Instruments Co., Ltd., Taiwan) was used to study the surface wettability of the copper substrates. The surface roughness and three-dimensional image of the tested copper surface were measured by laser scanning confocal microscopy (LSCM; VK-9710, Keyence, Japan). The surface morphology was analyzed by scanning electron microscopy (SEM; NOVA NANO SEM 450). The chemical composition was studied by Auger electron spectroscopy (AES); all kinetic energy data were calibrated with the Cu L\textsubscript{3}M\textsubscript{4,5}M\textsubscript{4,5} Auger peak kinetic energy of Cu (pure copper substrate) of 918.61 eV.

Copper samples (purity: 99.6%) with dimensions of 15 × 15 × 2 mm\textsuperscript{3} were polished mechanically using No. 2000 emery paper and cleaned ultrasonically with acetone for 30 min to remove the free oxide layer from the copper surfaces before laser irradiation. Figure 1(a) shows a schematic diagram of the ultrafast laser system. This system consisted of a picosecond (PS) laser source (ALTA-PS-532 W, Advanced Optowave Corporation, USA), an X-Y axis scanner (MS-II-14, Raylase AG, German), a piezoelectric transducer stage, a focusing lens, and a computer control system. The PS pulse laser had a pulse width of 7 ps with an operational uncertainty of ±2 ps and a wavelength of 532 nm. The laser scribing speed was fixed at 1000 mm/s with a repetition rate of 300 kHz. PS laser scanning was conducted line-by-line in the horizontal direction with a scanning interval being 10 μm, and the laser focusing diameter was approximately 20 μm. The laser fluence was controlled at 1.27, 2.12, and 2.97 J/cm\textsuperscript{2} to irradiate the tested copper surfaces, and it was obtained as pulse energy per area defined by the laser beam diameter in a focus. The environmental temperature was maintained at approximately 23 °C with a humidity of 55% during all experiments.

After laser irradiation, the copper surfaces were cleaned with ethanol and dried with a dry nitrogen stream to remove grease and some particles. As shown in Fig. 1(b), the as-prepared copper samples were dipped for 1 h into a DI water bath heated by a hot plate to various fluid temperatures. The DI water temperature was maintained at 50 °C or 100 °C. After 1-h treatment in the water bath, the copper substrate was removed from the solution and dried in a nitrogen stream.

Figure 2 shows the three-dimensional images and SEM images of the structures on a plain copper surface and a laser-textured copper surface (laser fluence: 1.27, 2.12, and 2.97 J/cm\textsuperscript{2}). The substrates showed ripple structures after laser irradiation, as shown in Fig. 3. The higher the energy density was, the more the removal of the material by the laser beam was. This, in turn, led to higher surface roughness, as presented in Table I.

Figure 4(a) shows the change in WDCA on laser-textured copper surfaces, which were exposed to the atmospheric air before...
FIG. 2. (a) LSCM image of the plain copper surface. (b) LSCM image of the laser-textured surface with a fluence of 1.27 J/cm$^2$. (c) LSCM image of the laser-textured surface with a fluence of 2.12 J/cm$^2$. (d) LSCM image of the laser-textured surface with a fluence of 2.97 J/cm$^2$.

water bath with different fluences of 1.27, 2.12, and 2.97 J/cm$^2$ for seven days; the WDCAs after 7 days are listed in Table I. The results indicated that all laser-textured surfaces showed hydrophobicity for different fluences after just one day. The initial wettability change was due to the partial deoxidation of the CuO surfaces (which was known as hydrophilicity) into hydrophobic Cu$_2$O surfaces when the tested samples were exposed to air.$^{34,35}$ After 7 days, the WDCA for a fluence of 1.27 J/cm$^2$ was $105^\circ$, which was the smallest among the three fluences tested. In contrast, the WDCA for a fluence of 2.97 J/cm$^2$ was $125^\circ$, which was the most hydrophobic. The results indicated that the higher the PS laser fluence was, the higher the WDCA was. The results in this study were similar to the results proposed by Gregorcic et al.$^{36}$ In their study, the stainless-steel surface was modified with the nanosecond laser of various fluences. Moreover, their results also revealed that, in the same interval of time, the higher laser fluence would cause the

FIG. 3. (a) and (b) SEM images of the laser-textured surface with a fluence of 2.97 J/cm$^2$. 

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surface to become more hydrophobic than a surface with lower laser fluence.

After all the laser-textured copper samples were exposed to air, the hydrophobicity of the surfaces was already developed and subsequently the water-bath treatment was performed. Figures 4(b) and 4(c) show the WDCA transition of the tested sample after the DI water bath (100 °C and 50 °C) treatment for 3.5 h. Clearly, all laser-textured copper surfaces showed hydrophilicity in the first 0.5 h after treatment in the water bath at 100 °C, as shown in Fig. 4(b). In particular, the copper substrates treated with a fluence of 2.97 J/cm² showed the highest hydrophilicity (WDCA ~ 57°). Samples treated with a fluence of 1.27 J/cm² soon become hydrophobic again (WDCA ~ 100°) after 1 h. On the contrary, the surface wettability of samples treated with a fluence of 2.97 J/cm² remained hydrophilic (WDCA ~ 85°) within 3.5 h. These results indicated that this water bath treatment (100 °C) could change the laser-textured surfaces from the original hydrophobic (laser irradiation after 7 days) to hydrophilic ones and the laser-textured copper surface with 2.97 J/cm² maintains the hydrophilicity effectively within 3.5 h. Furthermore, the difference in the WDCA increased as the laser fluence increased. On the contrary, the laser-textured copper substrates treated with laser fluences of 1.27 and 2.12 J/cm² and water bath treatment at a relatively low temperature of 50 °C soon recovered their initial hydrophobicity, as shown in Fig. 4(c). Compared with laser-textured surfaces treated in the high-temperature water bath (100 °C), those treated in the low-temperature water bath were more hydrophobic for all laser fluences.

To understand the mechanism of surface wettability transition, AES analyses were performed on laser-textured copper samples treated with a fluence of 2.97 J/cm² after DI water bath treatments at 50 °C and 100 °C. The Auger peak kinetic energy of Cu L₃M₄,5M₅,5 for the copper substrate is 918.61 eV and that of Cu L₃M₄,5M₅,5 for Cu(OH)₂ is 916.25 eV. These results indicated that the Cu LMM Auger peak enhanced after DI water bath treatments at both 50 °C and 100 °C, as shown in Fig. 5. Furthermore, the peak of Cu(OH)₂ increased dramatically after water bath treatment at 100 °C, whereas it increased only slightly after water bath treatment at 50 °C. As presented in Table II, the area ratio of Cu(OH)₂/Cu also increased with increasing water bath temperature, thereby resulting in the lower WDCA of the laser-textured copper surfaces. This implied that the surface wettability of copper surfaces changed with laser irradiation owing to the composition of Cu(OH)₂. After the laser-textured

| Types                                | Avg. Ra (nm) | WDCA (deg) |
|--------------------------------------|--------------|------------|
| Plain copper                         | 25           | 95–97      |
| Laser-textured copper surface (F = 1.27 J/cm²) | 44           | 100–105    |
| Laser-textured copper surface (F = 2.12 J/cm²) | 51           | 115–120    |
| Laser-textured copper surface (F = 2.97 J/cm²) | 56           | 120–125    |

FIG. 4. (a) WDCA of laser-textured copper surfaces treated with various fluences with elapsed time. (b) WDCA of laser-textured copper surfaces treated with various fluences with elapsed time after 100 °C water bath treatment. (c) WDCA of laser-textured copper surfaces treated with various fluences with elapsed time after 50 °C water bath treatment.
copper surfaces reacted with hot DI water, Cu(OH)$_2$ formed on top of the laser-structured copper surface, making the surface hydrophilic; furthermore, water bath treatment at 100 °C made the hydrophilicity last longer than in the case of water bath treatment at 50 °C. These results are identical to those obtained by Huang et al. They placed copper substrates into an aqueous solution of NaOH and (NH$_4$)$_2$S$_2$O$_8$ and found that Cu(OH)$_2$ nanoribbon arrays formed on the copper surface and made the surface hydrophilic. In addition, after hot water bath treatment, the surface morphology also changed, as shown in Fig. 6. Many microsized cubes appeared on the surfaces after hot water bath treatment. Furthermore, with increasing water temperature, clearer, larger, and more uniform microsized cubes were seen on the copper substrates. This indicated that these cubic structures were strongly associated with the formation of Cu(OH)$_2$ and the change in surface wettability. The obtained SEM images might differ slightly from those obtained in the previous study. The results indicated that these cubes are due to the formation of the CuO layer. In particular, these microsized cubes were associated with either Cu(OH)$_2$ or CuO, both of which make the surfaces hydrophilic.

In contrast, the results in this study were different from the results of Moze’s study. After pool boiling experiments, they did the chemical analyses on the laser-textured copper surfaces. Their results demonstrated that the surface chemical composition changed with a conversion of Cu(II) oxide (which represented CuO in this study) and hydroxide species into Cu(I) oxide (which represented Cu$_2$O in this study) and Cu metal species on the laser-textured copper surfaces. The reason for the different results was mainly due to the incipience of critical heat flux (CHF). They focused on the chemical transition on the laser-textured copper surface after the incipience of CHF. During the occurrence of CHF, the boiling phenomenon would transform from nucleate boiling toward film boiling, which represented the repeated occurrence of a vapor film. The temperature range of film boiling was 210 °C–230 °C and thus resulted in the effect of low-temperature annealing. This led to the partial deoxidation and the reduction of Cu(OH)$_2$. As a result, the laser-textured copper surface would become more hydrophobic after boiling experiments.

This study utilized the water bath process of 50 °C and 100 °C on the laser-textured copper surface. Both temperatures of water bath caused the formation of Cu(OH)$_2$, and water bath with higher temperature led to higher amounts of Cu(OH)$_2$. Furthermore, this method (water bath at 100 °C) was similar to the stage of nucleate boiling at lower wall superheat before the CHF phenomenon happened. After the process of water bath at different temperatures, the results of this investigation revealed that Cu(OH)$_2$ formed on the laser-textured copper surface and caused wettability transition of the surface from the hydrophobicity, which was already developed by being exposed to the atmospheric air, toward hydrophilicity.

### Table II. Normalized peak area of Cu L$_3$M$_{4,5}$M$_{4,5}$ Auger spectra at different water bath temperatures.

| Different treatments | Cu(OH)$_2$ | Cu | Cu(OH)$_2$/Cu |
|----------------------|-----------|---|--------------|
| Before water bath    | 0.452     | 0.347 | 1.303       |
| After 100 °C water bath | 3.876 | 1.206 | 3.214       |
| After 50 °C water bath | 0.509 | 0.305 | 1.669       |
In summary, this study proposes a simple method to change the wettability of ultrafast laser-structured copper surfaces. For the two evaluated conditions of water bath treatment (at 50 °C and 100 °C), it was observed that the fabricated laser-textured surfaces that were initially in a hydrophobic wetting state and exposed to atmospheric air during seven days changed to the hydrophilic state via the formation of Cu(OH)$_2$. Furthermore, the obtained results revealed that the temperature of the water bath played an important role in the chemical transition. A water bath at higher temperature leads to more formation of Cu(OH)$_2$. As a result, the more contents of Cu(OH)$_2$ on the copper surface make the laser-textured area more hydrophilic and effectively maintain its hydrophilicity for a longer period of time.

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