Droplet Evaporation on Hot Superhydrophobic Microstructured Surface



Figure 1. (a) Image of water droplet on 120 °C superhydrophobic substrate. (a) Diagram of heat transfer from hot substrate to sessile water droplet.

As shown in Fig. 1 (a), when placed on the hot microstructured substrate, the droplet is in a Cassie-Baxter state [1] with the base interface contacting with the top surface of the micropillars on the substrate. Air cavities can be observed underneath the water droplet. Fig. 1 (b) shows the heat transfer from the heat source (hot plate) through the silicon substrate to the water droplet. Evaporation occurs at the liquid-vapor interface of the water droplet with heat and mass diffusing into the ambient air.

1. Energy balance model

An energy balance model can be developed for this heat and mass transfer process.

(1)

where *q*s the total energy transferred from the substrate; *q*temp is the energy required for the water temperature increase; *q*conv is the convective heat transfer from the water droplet to the ambient air; *q*rad is the radiation heat transfer from water droplet to the ambient air; *q*evap the heat released to the ambient air through evaporation.

(2)

(3)

(4)

(5)

where *c*p, , *T*w *V* and *h*fg are the specific heat capacity, density, temperature, volume and latent heat of the droplet water respectively; is the emissivity of the water droplet interface and is the Boltzmann constant; *S* is the liquid-vapor interface area and *h*conv is the natural convection heat transfer coefficient of the ambient air.

It can be estimated that at relative high temperature (*T* > 60°C) the is much larger than the summation of the three types of heat transfer [2]. Thus, in a quasi-steady state the heat transfer from the substrate to the water droplet is approximately equal to the heat released to the ambient air through evaporation.

(6)

2. Thermal circuit model



Figure 2. Thermal resistance network between the substrate and water droplet

Fig. 2 shows the thermal resistance network between the substrate and water droplet. Heat conducts from the substrate to the pillars and the vapor cavities. However, because of the large difference between the thermal conductivity of silicon pillars (100 Wm­-1K-1) [3] and water vapor (0.025 Wm­-1K-1) [4], thermal resistance of the vapor is much larger than that of the silicon pillars. As a result, heat primarily conducts from the pillar to the water droplet and the vapor cavities can be regarded as adiabatic parts.

Considering the periodicity of the pillar arrays, we can focus on one unit cell of the pillar array consisting of one pillar and one vapor cavity. The total thermal resistance in the unit pillar cell is expressed as:

(7)

Moreover, due to the small thermal conductivity of the vapor layer, the thermal resistance of the vapor layer *R*vapor is much larger (at least one order of magnitude) than the summation of constriction resistance *R*cons, silicon pillar resistance *R*pillar, silane resistance *R*silane and the spreading resistance *R*spr. Heat scarcely transfers through the vapor layer and the total thermal resistance in one unit cell can be simplified as:

(8)

The thermal resistance of the silicon substrate per unit cell is calculated as:

(9)

where *k*Si is the thermal conductivity of silicon, *p* is the width of the periodicity; *L*sub is the thickness of the silicon substrate.

The thermal resistance of the silicon micropillar is calculated as:

(10)

where *a* is the radius of the pillar; *L*sub is the height of the silicon pillar.

(11)

where *L*silane is the thickness of the silane coating layer and assuming to be 1nm [5], *k*silane is the thermal conductivity of silane.

(12)

where *k*w is the thermal conductivity of water.

*R*cons and *R*spr are the thermal constriction and spreading resistances which we will discuss in the next section.

3. Thermal constriction and spreading resistances

Thermal constriction or spreading resistances exist at the different cross-sectional region in the heat transfer process [6]. Constriction resistance exist when heat flows from a large cross-sectional area to a narrower one. And when heat flows from a small cross-sectional area to a wider one, there will be spreading resistance. The geometry structure feature of the pillar on the substrate determines that there will be cross-sectional area changes in the heat transfer process as shown in Fig. 3.



Figure 3. (a) Substrate and pillar in one unit cell. (b) Pillar and water layer in one unit cell. (c) Pillar

3.1. Constriction resistance

In one unit cell, the pillar can be regarded as a cylinder while the substrate and water layer are cuboids due to the periodicity. Previous researchers found that the constriction/spreading resistances are independent of the contact configuration shape as long as the ratio of the cross-section area is kept constant [7]. Thus, we can use an equivalent cylinder substrate and water layer to replace the cuboid ones without changing the results of constriction and spreading resistance. As shown in Fig. 3 (a) we use an equivalent cylinder with cross-section radius *b* and has the same cross-section area as the real cuboid substrate. We have the relation:

(13)

To calculate the constriction resistance caused be the cross-section decrease, we need first to get the temperature distribution in the unit substrate. Assuming the silicon substrate is homogeneous and heat transfer in the substrate is in a steady state, we will obtain the Laplace equation for the temperature in the substrate:

(14)

Since we employ the equivalent cylindrical substrate, the system can be set on a cylindrical coordinate as illuminated in Fig. 3 (a) and we will have the heat transfer equation with two spatial variables as follows:

(15)

The general solution of Eq. (14) has the form of:

(16)

where *U*(r) and *W*(z) are obtained by means of variable separation which satisfy:

(17a)

(17b)

Because of the periodicity of the unit cell, we assume that no heat transfer happens between two neighbor unit cell. As a result, we obtain an adiabatic boundary condition for the substrate heat transfer system.

(18)

where *b* is the radius of the substrate cylinder, *L*1 the thickness of the substrate, *T*h is the constant substrate bottom temperature controlled by the hot plate.

The temperature at the substrate bottom interface is kept as constant and without lost of generality we can set it to 0 when solving the equation. Thus, we obtain the second boundary condition:

(19)

As mentioned before, because the large thermal resistance of the vapor layer, heat flows primarily from the silicon pillar to the water. As a result, we can obtain an adiabatic boundary condition at the vapor-solid contact interface. Considering the small section area of the pillar, we assume there is a uniform heat flux distribution at the pillar substrate contact cross-sectional area. Thus, we obtain the third boundary condition for this heat transfer system:

(20)

where *f* is the heat flux through the cross-sectional area, *a* is the radius of the cylinder pillar.

Combining the three boundary conditions Eq. (18), (19), (20) with Eq. (16), we can obtain the solution:

(21)

where *J*0(*x*) and *J*1(*x*) are the first kind Bessel functions with order of 0 and 1 respectively, is the *n*-th root of *J*1(*x*)=0.

The minimum temperature at the cross-section area is:

(22a)

(22b)

The average temperature at the cross-section area is:

(23a)

(23b)

Now we can calculate the constriction resistance. The maximum constriction resistance can be obtained by the total thermal resistance in this system subtracts the silicon conductive resistance:

(24a)

(24b)

Also, the average constriction resistance can be obtained:

(25a)

(25b)

3.2. Spreading resistance

Spreading resistance exist at the cross-section area of pillar- water interface. Heat flows from the narrow pillar into the larger water surface. We assume there is a thermal boundary layer exist at the bottom of the droplet with thickness *L*2 [8]. As shown in Fig. 3 (b), we can set a cylindrical coordinate to analyze the heat transfer process. Also, we have the Laplace equation for the temperature in the water layer.

(26)

Similar to the constriction resistance, due to the small size of the micropillar, we assume there is uniform heat flux at the cross-section area of pillar- water contact interface. As a result, we have the first boundary condition:

(27)

Due to the internal flow inside the droplet, the temperature bulk water *T*b is at a relative constant temperature during the heat transfer process [9]. Thus, we have the second boundary:

(28)

where *h*w is the natural convective heat transfer coefficient of water.

Based on the no-slip boundary condition, the thin water layer is relative static to the pillar. Also, considering the periodicity of the unit cell, we can assume there is no heat transfer between the water layer in one unit cell with its neighbor water layer. Thus, we obtain the adiabatic boundary condition:

(29)

Combining the three boundary conditions Eq. (27), (28), (29) with Eq. (26), we can obtain the solution:

(30)

The maximum temperature at the water-pillar contact interface is:

(31a)

(31b)

The average temperature at the water-pillar contact interface is:

(32a)

(32b)

We know can calculate and the average spreading resistance. The spreading resistance can be obtained by the total thermal resistance in the heat transfer substrate the conductive thermal resistance. The maximum spreading resistance is calculated as:

(33a)

(33b)

Also, the average constriction resistance can be obtained:

(34a)

(34b)

4. Temperature distribution and water layer thickness

4.1 Temperature distribution in pillar

With the results of temperature distribution in the substrate and water layer, we now can calculate the temperature distribution inside the pillar. In cylindrical coordinate as shown in Fig. 3 (c), the heat transfer equation in the pillar expressed as:

(35)

The pillar side surface is surrounded by the vapor, which is adiabatic. Thus, we have the first boundary condition:

(36)

We know the temperature distribution on the water-pillar contact interface, which is described by Eq. (30). However, it is an infinite Bessel series form and difficult to compute as a boundary condition. To simplify the boundary condition described by Eq. (30), we use a quadratic function with similar value to replace it.

(37)

where *A* and *B* are two coefficients which can be obtained by fitting with Eq. (30).

At the pillar-substrate contact interface, we have also obtained the temperature distribution. Because of the large thermal conductivity of silicon, the temperature is almost uniform at that surface and we here use the average temperature as the boundary condition.

(38)

where *C* is a coefficient which can be calculated from Eq. (23).

Also, at the pillar-substrate contact interface we have the heat flux boundary condition:

(39)

Combining the four boundary conditions we can obtain the solution of Eq. (35):

(40)

Knowing the temperature at the top and bottom surface of the pillar, we can find the relation between the surface temperature with heat flux.

(41a)

(41b)

We now know that the difference of substrate bottom temperature *T*h and bulk water temperature *T*b is a function of pillar structure *a*, *b*, substrate thickness *L*1 water layer thickness *L*2 and heat flux *f*.

(42)

4.2. Water layer thickness

As we mentioned above, we assume there is thermal boundary layer at the bottom of the water droplet.

* Thickness of thermal boundary layer

Rayleigh number of the droplet is calculated as:

where *g* is the acceleration due to gravity (9.8 ms-2), is the volumetric thermal expansion coefficient (0.0007 K-1), is the kinematic viscosity (0.29410-6 m2s-1), *D* is the thermal diffusivity (0.16710-6 m2s-1), *d* is the diameter of the water droplet (0.001 m) and *T*s – *T*b is the maximum surface temperature difference of the droplet (10 K).

Marangoni number of the droplet is calculated as:

where is the dynamic viscosity (0.28210-3 Pa s), is the water surface tension. ( is about 0.17610-3Nm-1K-1)

(When *Ra* is small, there is no flow and heat transfer is purely by conduction; when it is large heat is transferred by natural convection. When *Ma* is small thermal diffusion dominates and there is no flow, but for large *Ma*, flow occurs, driven by the gradients in the surface tension.)

Large values of Rayleigh number and Marangoni number indicate that convection heat transfer is dominate in the droplet. The internal flow velocity driven by the buoyancy can be scaled as:

The internal flow velocity driven by Marangoni effect of the droplet can be scaled as:

The Reynolds number of the droplet internal flow is

As a result, we might regard the flow inside the droplet as laminar flow.

The laminar boundary layer can be estimated as:

where r is the radius of the water droplet

The thermal boundary layer can be estimated as:

where *Pr* is the Prandtl number of water droplet (1.9).

The water layer we choose should be thinner than the thermal boundary. To mitigate the influence of the internal flow on the heat transfer process in the water layer, we should have the water layer as thin as possible. Moreover, to make the temperature equation Eq. (30) in the water layer tenable, the thickness of the water layer *L*2 should be no less than () which is the same order but much less than the thermal boundary we obtained. Thus, we have *L*2 to be to simplify the calculation.

Here we have estimated the thickness of the thermal boundary layer. However, because of the simplicity in the scaling analysis, we can’t get the exact thickness of the thermal boundary layer. Here we use droplet contact radius as the characteristic length when scaling for the thermal boundary layer. However, in the real case, with the evaporation of the droplet, the characteristic length should be smaller than the initial contact radius. Thus, we might overestimate the thickness of the thermal boundary. When solving the temperature distribution equation, we have a minimum requirement of the water layer thickness, which should be no less than (5-10). Thus, we use the minimum thickness as the thermal boundary thickness, which is the order but less than what we estimated.

The reason why there is a certain requirement of the thickness of the water layer is that we have a constant temperature boundary condition. With the thickness, on that surface temperature is independent of *r*. But if r is too small, it is impossible to have a constant temperature surface when other conditions are kept unchanged.

5. Droplet evaporation model

As mentioned before heat transfer from substrate is equal to the heat release to the ambient via evaporation. The droplet evaporation equation based on the thermal circuit model is:

(35)

where *R*thermal is the total thermal resistance of all the pillar underneath the water droplet.

Since we obtain the thermal resistance in one unit cell, the thermal resistance underneath the water droplet can be calculated as:

(36)

where *r* is the contact radius of the water droplet on the substrate.

There are three different modes during the evaporation process: constant contact radius (CCR) mode, constant contact angle (CCA) mode and mixed mode. In the CCR mode with constant contact radius, we can calculate the droplet evaporation rate with the following equation:

(37)

where *r*c is the constant contact radius in the evaporation CCR mode.

When the droplet evaporation mode transfers from CCR mode to CCA mode, contact radius begins to decrease while the contact angle remains almost constant. The volume of the water droplet is very small after the CCR mode evaporation. Thus, we can use spherical cap assumption to calculate the volume based on the droplet contact radius *r*c and contact angle . The droplet volume at the transition moment from CCR mode to CCA mode is calculated as

(38)

During the CCR mode evaporation, volume of water droplet decreases from initial volume *V*0 to the transition volume *V*1. The evaporation rate is a constant during this process as illuminated by Eq. (37). Thus, we can calculate the evaporation time of the CCR mode:

(39)

The evaporation rate in the CCA mode can be calculate by the droplet volume equation:

(40)

Also, we can calculate the evaporation rate in the CCA mode through the thermal circuit equation:

(41)

Combining Eq. (40) and Eq. (41), we can obtain the expression of contact radius in the CCA mode:

(42)

Ignoring the mixed mode at the very end of the evaporation process, we then can obtain the evaporation time in the CCA mode:

(43)

The ratio of the CCR mode evaporation time and CCA mode evaporation time is:

(44)









