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Chemical Physics Letters 397 (2004) 17–20
CHEMICAL PHYSICS LETTERS
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Critical length of nanowires for hydrophobic behavior

Yu-Hung Cheng [a,*], Chung-Kuang Chou [b], Chih Chen [b], Syh-Yuh Cheng [a]

[a] *Material Research Laboratories, Industrial Technology Research Institute, Hsinchu 310, Taiwan, ROC*
[b] *Department of Materials Science and Engineering, National Chiao Tung University, Hsin Chu 300, Taiwan, ROC*

Received 20 July 2004; in final form 20 July 2004
Available online 12 September 2004

Abstract

This Letter investigates the wetting behavior on surface with well-controlled nanoscale structure. Water and water–alcohol droplets were brought to contact the surface electroplated by Ag nanowires. It is found that hydrophobic behavior becomes more pronounced as the length of the nanowires increases. A critical length of approximately 100 nm is observed, beyond which the contact angle approaches a steady value of 130°. In addition, the contact angle of water levels off around 160° when the length of the fluorine-coated Ag nanowires exceeds the critical value of 100 nm. The mechanism of the hydrophobic behavior on surface with nanoscale structure is proposed.

1. Introduction

When a liquid droplet is put onto a surface with a lower surface energy surface, the contact angle between the drop and the surface increases rapidly. Wenzel [1,2] and Cassie [3] reported this phenomenon decades ago, which becomes well-known now. In recent years, ultrahydrophobic surfaces, which are the surfaces with contact angles larger than 150°, drew lots of attention [4–8]. In these studies, surfaces not only with low surface tension but also with roughness on microscale or nanoscales were fabricated. Technical limitations of etching techniques restrict the surface structure to be controlled only in the micrometer scale [9]. Besides, a surface with lower surface tension could obtained by coating a thin layer of polymer fluorine or polymer silicone compounds [10]. Some researchers reported that the surface roughness and surface tension determined the contact angle [11]. However, only few studies have examined the relationship between surfaces with nanoscale structure and liquid contact angle [9]. The effect of nanoscale surface condition on wetting angle is still not clear. This study investigates how the surface in nanoscale affects the contact angle between a liquid droplet and the surface. Electroplating method was employed to obtain an array of well-aligned Ag nanowires and thus able to control the nanostructure on the surface and surface tension. The contact angles of various liquids with Ag nanowires of different lengths were measured.

2. Experiment

AAO was used as the template in the electroplating process [12]. The diameter of the channels and the spacing (*d*) between pores were around 200 and 80 nm, respectively. Firstly, an electrode was sputtered on the AAO surface, and silver nanowires were grown by electroplating inside the AAO channels at 25 °C. The electroplating solution contained silver nitride ($AgNO_3$, 58.9 mM) and acetic ammonium (CH_3COONH_4, 3.00 M). A DC voltage of 92 mV was applied to grow Ag nanowires at a fixed current of 0.4 mA. After the

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[*] Corresponding author.
E-mail address: yhcheng@itri.org.tw (Y.-H. Cheng).

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doi:10.1016/j.cplett.2004.08.063

deposition was complete, the AAO template was totally removed by 5 wt% sodium hydroxide (NaOH) solution at 60 °C. The nanowire arrays were cleaned in deionized water (DI water) for 15 min.

To investigate the surface properties of the Ag nanowires on the contact angle, a hydrophobic fluorine polymer film was deposited by plasma enhanced chemical vapor deposition (PECVD). Perfluorohexane (C_6F_{14}) was used as the precursor at 60 mTorr and at 13.56 MHz RF at 30 W. The measured deposition rate was 0.3 nm/s. It is worthy noting that the deposition also altered the spacing between the nanowires. A field emission scanning electron microscope (FE-SEM) was used for characterize the structure of the nanowires and the morphological change after the deposition of fluorine polymer film. Contact angles were measured by an instrument for measuring surface tension and contact angle.

3. Results and discussion

The Ag nanowire arrays were vertical to the Ag electrode after the removal of the AAO template by NaOH solution, as illustrated in Fig. 2. To investigate the effect of the nanowire length (L) on the contact angle, Ag nanowires with difference lengths were fabricated under various electroplating conditions. Two kinds of liquid droplets with different surface energy were used to examine the effect of surface energy on the contact angle. The surface tension of water was about 69.2 mN/m. Besides, water was mixed with alcohol to adjust the surface tension to be 58.4 mN/m.

Fluorine polymer film of thicknesses 10–50 nm was coated to tailor the surface properties of the Ag nanowires. Our results indicate that the contact angle increases as the length of Ag nanowires increase, and approaches to approximately 130° as the length of Ag nanowires is longer than 100 nm. Ultra-hydrophobic behavior was observed for Ag nanowires coated with fluorine polymer when the length of the nanowires was longer than 100 nm.

The Hydrophobic behavior of water on the Ag nanowires is shown in the Fig. 1a, in which a water droplet was placed on the surface of regular array of Ag nanowires. The enlarged schematic picture at the interface of the water droplet and nanowires is seen in Fig. 1b. The water fully wets the Ag electrode when the length of the nanowire is equal to critical length, L_c. When the length of the nanowire increases, the water cannot wet the surface of the nanowires and the electrode completely, and thus air is trapped in the gap among the nanowires. Therefore, the surface scale determines the air diffusion resistance. According to surface tension theory, a droplet on a rough surface seeks to minimize its size and its contact area for lowering its surface energy. This phenomenon is influenced by temperature, type of liquid and purity of the liquid in the droplet. When a liquid is dropped onto the surface of nanowire arrays, this system would exhibit the capillary characteristics. If cohesive force exceeds the adsorptive force, then the droplet curve between the nanowires would be concave, as seen in Figs. 1b and c. Liquid could not easily diffuse into the gap when contact angle (θ) exceeds 90°. However, the liquid could easily diffuse into the gap when the contact angle is lower than 90°. Eq. (1) represents the theoretical depth of the liquid that diffuses into the gap.

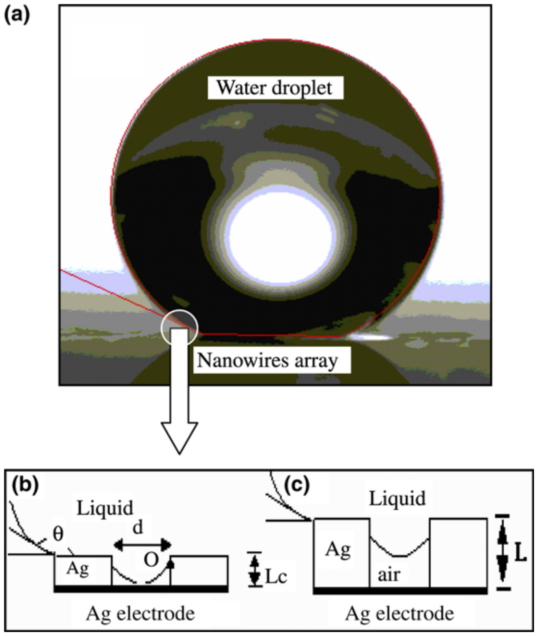

Fig. 1. Liquid droplet on the surface of nanowire arrays: (a) Optical photo of a water droplet on the Ag nanowire arrays. The schematic of the interface of the liquid and the Ag nanowire; (b) at the critical length (L_c); (c) at the length longer than L_c.

$$L = 2T\cos\theta\rho g d + \mathrm{d}L(P), \tag{1}$$

where T is the surface tension, g is acceleration of gravity, ρ is density of liquid, d is gap between Ag nanowires, a is diameter of nanowires, L is length of nanowires and P is the pressure in the gap between the nanowires.

If the capillary effect is used to predict the diffusion length, the modified term $\mathrm{d}L(P)$ must be added to the equation. Also, the reasons for the high contact angle include resistance to diffusion and low surface tension. The air confined in the nanostructure increases diffusion resistance as a layer of viscosity flow forms. Hence, both capillary and air resistance effect should be considered in this nanostructure system. Let the pressure in the confined volume be P. Then the pressure P in the gap between the nanowires becomes $P_i + P_o + \rho g L$ when a liquid droplet is placed on the nanowire arrays, where

P_i and P_o are the pressures exerted by the weight of the liquid and the pressure caused by a nanoscale effect. Besides, P_o is a function of L, d and T. Therefore,

$$P = P_\mathrm{i} + P_\mathrm{o} + \rho g, \tag{2}$$

$$P_\mathrm{o} = f(L, d, T). \tag{3}$$

The net force becomes zero at point O, as shown in the Fig. 1, i.e., the internal force, the absorption force, and the pressure force exactly balance. When the surface roughness is in nanoscale, the pressure between the nanowires would increase when the length of the nanowires is reduced. The effective contact area of this droplet on the nanowire arrays also declines as L decreases, as illustrated schematically in Figs. 1b and c.

Firstly, the water droplet on the surface of the Ag plate exhibited a contact angle of approximately 100°. In Cassie's theory[3], for the calculation of θ_c, let the characteristic scale named piller width a in Ref. [10] be the diameter of nanowires. Besides, let the L, d and θ_0 be 200, 80 nm and 100°, respectively. The theoretical contact angle is independent of the length of the nanowires. The calculated contact angle was approximately 125.4°. However, our experimental results shows that the contact angle was about 130° when using liquid with surface tension of 69.2 or 59.8 mN/m. The influences of L on the contact angle were elucidated using liquids with low surface tensions. The measured contact angles as a function of the length of the nanowires is shown in Fig. 2. As the length of the silver wires increases, the effective contact area of the liquid and the nanowires increases, resulting in the reduction of the contact angle. Thus the liquid almost wetted the surface.

However, air diffusion resistance between nanowires reduces as L falls below 100 nm. In this case, liquid can easily diffuse into the gap. The measured contact angle increases as L increases for both water and water–alcohol mixture. As seen in Fig. 2, the curves exhibit a critical length (L_c), beyond which the contact angle is a constant of approximately 130°. L_c is physically governed by the fully wetting of the droplet between the Ag electrode, as shown in Fig. 1b. The absorption force approaches to a constant gradually as L was increased. Nanowire arrays become fully hydrophobic because the droplet is only in contact with the top surface of the nanowires when L is equal to L_c. The contact area between droplet and nanowires decreases as the contact area would increase at the same time. The results can be explained by Cassie's theory. However, the result is not exactly as predicted by the theory. The real contact angle exceeds the theoretical angle by about 5°, which might be attributed to the nanoscale rough surface. It is speculated that the diffusion ability of the air confined between the nanowires is low because of the nanoscale surface. Hence, the contact angle deviates by 5° from theoretical value. Consequently, the contact angle increases as the length of the nanowires increases due to higher resistance of air diffusion.

The surface property and the spacing of the nanowires were modified by deposition of fluorine polymer, and their morphology evolution before and after the deposition is shown in Figs. 3a–d. Figs. 3a and b depict the cross-sectional and plan-view SEM images of the as-fabricated nanowires, respectively. After the deposition, a smooth fluorine polymer layer was formed on the

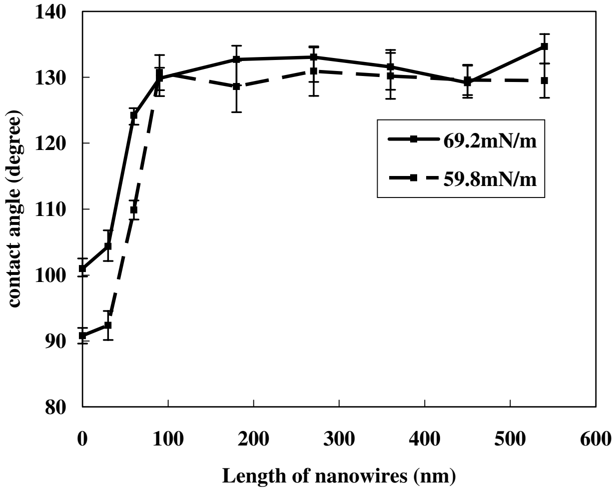

Fig. 2. Measured contact angle as a function of nanowire length for water and water–alcohol droplets.

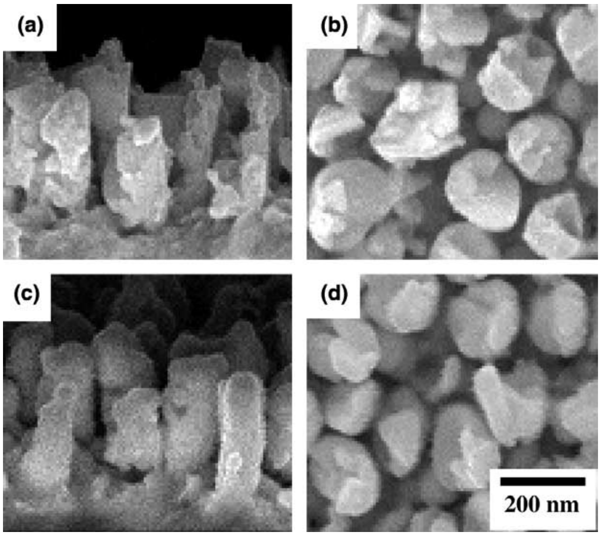

Fig. 3. Surface morphology of the Ag nanowires before and after the deposition of fluorine polymer: (a) SEM cross-sectional image of the nanowire arrays; (b) SEM plan-view image of the nanowire arrays; (c) SEM cross-sectional image of nanowire arrays coated with fluorine polymer; (d) SEM plan-view image of the nanowire arrays coated with fluorine polymer.

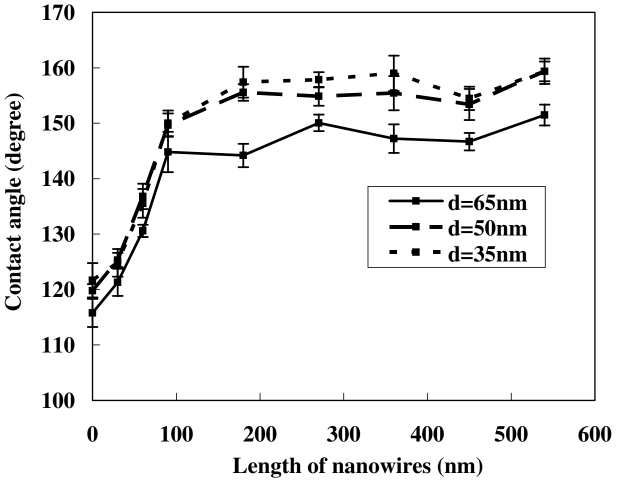

Fig. 4. Measured contact angle on fluorine-coated nanowires as a function of nanowire length for various nanowire gaps.

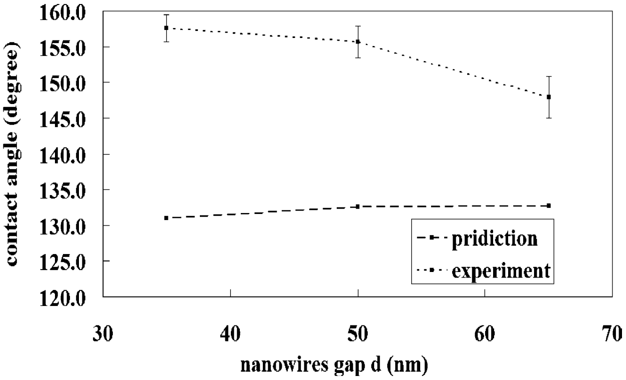

Fig. 5. Comparison between the theoretical and experimental results for an ultra-hydrophobic surface as a function of nanowire gaps.

nanowires. In the same time, the gap between the nanowires was reduced as the thickness of the deposited layer increased. The thicknesses of the fluorine polymer were 15, 50 and 45 nm, resulting in the gaps of 65, 50 and 35 nm, respectively. The surface energy of nanowire arrays was the same for the above three sets of nanowires, since the same deposition condition was used.

It is intriguing that there still exists a critical length of about 100 nm for the nanowires coated by fluorine polymer, as seen Fig. 4. Water droplets were employed to do the contact angle testing for the above three nanowires array with different gaps. The contact angle approaches to a constant as the length of the nanowires is greater than 100 nm. In addition, the contact angle increases with the decrease of gap between nanowires. It is inferred that when d becomes smaller, the effective contact area is reduced, causing the increasing the contact angle. The contact angle increases up to approximately 160° when L is greater than 100 nm and the gap is less than 50 nm.

Therefore, the discrepancy between the theoretical and experimental results could be clarified. As seen in Fig. 5, the predicted contact angle is approximately 130° for the three different gaps in Cassie's theory. However, the theoretical results deviate significantly from the experimental results. The average contact angle on a surface with a low surface energy surface reaches a steady value of 145°–160° when L exceeded 200 nm because the nanoscale effect impacts the contact angle seriously. The value of d was also shown to exhibit no relationship with the contact angle for Ag nanowires of various nanowires length.

4. Conclusions

Hydrophobic behavior has been studied on various nanoscale surfaces. The value of L_c was found to be around 100 nm for both Ag nanowires and the fluorine-coated nanowires. The contact angle of water approached a steady value of approximately 130° when the length of the Ag nanowires exceeded 100 nm; while it increased to about 160° for the fluorine-coated nanowires as L greater than 100 nm and d was less than 50 nm. Besides, the contact angle increased as the d value decreased. Liquid with high surface energy yielded a high contact angle.

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