Control of Surface Energy using Bilayer Metallic Film Heterostructures

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Abstract – Surface energy is an important factor in determining the performance of application components in terms of preventing adhesion failure between thin films. In this regard, numerous attempts have been made to acquire the desired surface energy through chemical treatment or by using micro/nanostructures. However, such approaches are expected to provide extreme values of surface energy, which may not be suitable in achieving the enhanced performance of applications. In this study, we propose a method to control surface energy by using bilayer metallic film heterostructures. We measure the water contact angle of incompatible (Ni/Ag) and compatible (Zn/Ag) metal pairs under several experimental factors, including thickness, time, and temperature. Furthermore, we conduct Auger electron spectroscopy measurements to investigate the atomic concentration with respect to depth after the change in the water contact angle. The experimental results reveal that three parameters, namely, compatibility, film thickness, and environmental temperature, are major factors in controlling the water contact angle. Thus, we experimentally demonstrate that controlling these three parameters can provide the approximate desired water contact angle. This result is expected to aid in the performance enhancement of a wide range of application components, where control of surface energy is required.

1. Introduction

Surface energy is excess bonding energy due to an unbalanced set of interactions of the atoms at the topmost surface[1,2]. The past decade has witnessed that the surface energy of the material has been one of the most important factors in enhancing the performance of various multi-layer based applications to avoid any delamination failure at the interface[3-6]. In this regard, various works have been made to change the surface properties followed by the quantification of surface energy. To date, water contact angle measure-ment is considered as a simple and convenient method to quantify the wettability of the material surface where high(≥ 90

degrees) and low water contact angle indicates relatively high (hydrophilic) and low surface energy (hydrophobic), respectively[2]. Specifically, the water contact angle can be obtained by measuring the angle between the surface of a liquid and that of a target surface when ~2 μL of a stable droplet of de-ionized(DI) water is stabilized on the surface by attaining a thermodynamic equilibrium between inter-molecular interaction of water molecules and the surface energy. The water contact angle of the materials can be acquired by using various methods including Wilhelmy, captive drop, tilting method and contact area spreading on a substrate[1]. In the case of the surface certain roughness or texture, the water contact angle can be expressed with Wenzel and Cassie's equations where Wenzel's formula and Cassie's formula handles homogeneous and heterogeneous surfaces, respectively [7].

For the last few decades, enormous attempts have been made to acquire desired surface energy of the

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components in wide range of applications such as micro-channels in fuel cell[8], cell response[9], micro-gripping[10], electro-wetting on dielectric (EWOD) system [11] and thin-film based devices and nano-scale systems where the surface-to-volume increases signi-ficantly[12]. The strategies to attain the desired surface energy include surface texturing, post-treatment (plasma or ultraviolet ozone) and self-assembly monolayer (SAM). Note that such strategies can only provide the extreme cases of the surface energy either high or low which could be a bottleneck to prolong the performance maximi-zation of various systems.

Here, we report a method to control the surface energy by using bi-layer metallic film heterostructures as shown in Fig. 1. It was expected that change of the surface energy could be attributed to the diffused amount from the bottom layer toward the top-most surface[13]. Thus, with an optimized amount of the diffused amount, desired surface energy can be obtained. Considering that the compatibility of metal pairs, the thickness of the bottom layer and temperature could be a driving force to control the diffusion amount, various samples were prepared to investigate the effect of the aforementioned parameters on the surface energy. The experimental results revealed that these parameters are highly associated with the diffusion amount toward the surface and the surface energy. The outcome is expected to advance the development of micro and nano-scale systems with higher reliability and performances.

2. Experimental Details

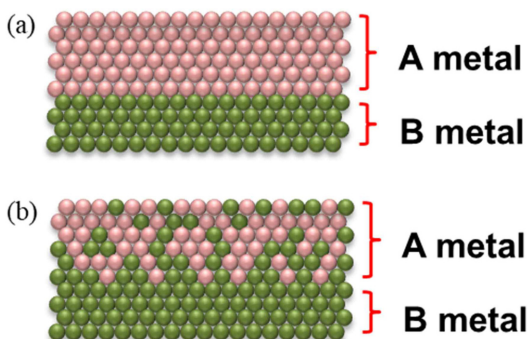The compatibility of materials is commonly categorized

Fig. 1. Schematic image of (a) before and (b) after the diffusion of metallic bi-layer heterostructures.

by quantifying the diffusion amount of the two materials in contact. Specifically, compatible materials are known to show diffusing into the other metal by at least a volume of 1% at room temperature. Partial compatibility of the materials can be classified as 0.1% to 1% of the diffused volume at room temperature[14]. Depending on this feature, compatibility can be categorized into 5 groups that are incompatible, partially incompatible, partially compatible, compatible, and identical. Classi-fication of material compatibility with respect to the diffused volume is presented in Table 1.

Based on the compatibility of metal pairs, nickel(Ni) and silver(Ag) for incompatible metal pair, and zinc (Zn) and silver(Ag) for compatible metal pair were chosen in this investigation. Incompatible metal pairs are assumed to have a relatively small diffusion at the interface between two metals and have a little change in the surface energy. In contrast, compatible metal pairs are assumed to have a relatively large amount of diffusion at the interface between the two metals and have changes in the surface energy. Among various pairs of metals, the reason for choosing incompatible nickel-silver(Ni/Ag) metal pairs and compatible zinc-silver (Zn/Ag) ones is that both nickel and zinc have different surface energy from that of silver. Hence, it is feasible to examine a drastic change of the water contact angle (WCA) when single and bi-layers are compared. In the case of the compatible metal pairs, bottom layers with different film thicknesses were prepared to investigate the effect of the bottom layer thickness. In this regard, specimens for incompatible and compatible pairs were set up as shown in Fig. 2(a) and (b).

Prior to sputter deposition, silicon(100) substrates were thoroughly cleaned with Acetone, Isopropyl alcohol and distilled water under the ultrasonic condition and dried with N_2 gas(99.99% purity). Films were deposited by RF magnetron sputtering using Ar gas. To obtain the

Table 1. Classification of material compatibility with respect to the volumetric solubility[14]

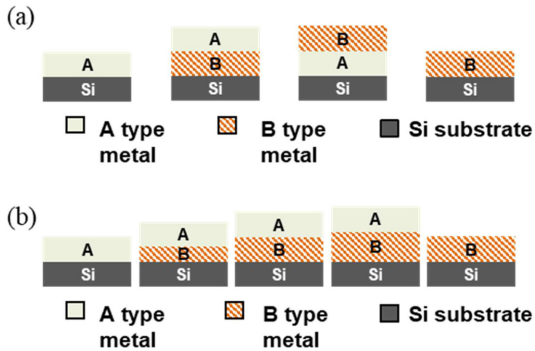| Classification	Solubility by volume
Incompatible	$\approx 0\%$
Partially incompatible	$\approx 0.1\ \%$
Partially compatible	0.1%~1%
Compatible	1%
Identical	100%

Fig. 2. A type single layer and A/B bilayer to investigate (a) the effect of B layer and vice versa for incompatible metal pairs (b) the effect of B layer thickness for compatible metal pairs on the surface energy change.

desired film thickness, sputtering time was controlled. However, all the sputter targets used in this experiment have different atomic bond energies, which result in different sputtering yields. Based on the sputtering time and film thickness measured by the atomic force microscope(AFM, Seiko SPA-400), the approximate sputtering yield of each target was calculated by a linear fit method. Note that Zn has a sputtering yield of 28 nm/min and Ag has that of 14 nm/min. Considering zinc and silver have the bonding energy values of 29 and 160.3 ± 3.4 kJ/mol[14], respectively, it is reasonable to claim that the bonding energy of the material can be associated with the sputtering yield. Furthermore, the surface roughness of all the deposited samples was expected to be in the level of a few nm ranges considering that the average surface roughness of Si substrate was ~0.1 nm. Thus, it can be stated that the effect of surface roughness on WCA change can be neglected.

To quantify the surface energy of the metallic bilayer heterostructures, the WCA method was utilized. To this end, ~2 μL of a stable DI water droplet was placed on samples by using a micro-pipette followed by capturing the droplet image through a CCD camera. By using photoshop software, the angle of each droplet was measured. With a different set of samples, WCA was measured under different time and temperature conditions to observe the effect of diffusion amount on the surface energy. Furthermore, Auger Electron Spectroscopy(AES) analysis was conducted to investigate the diffusion amount of the compatible metallic bilayer heterostructures.

3. Results and Discussion

The contact angles of incompatible Ni/Ag bi-layers and single layers were measured as-received and 8 hours after the deposition. Fig. 3 presents the results of WCA of Ni/Ag bilayers as received and 8 hours after the deposition stored at room temperature. The WCA of Ni and Ag were $69 \pm 3°$ and $86 \pm 2°$, respectively, which indicate comparatively higher surface energy of Ni than that of the Ag. For Ni/Ag or Ag/Ni bi-layers, both of them show a negligible change in the contact angle; $70 \pm 4°$ for Ni/Ag and $82 \pm 3°$ for Ag/Ni were observed. Almost no change in WCA is attributed to a relatively small diffused amount of Ag and Ni at the interface. Furthermore, the WCA results were measured to be consistent even after 48 hours stored at room temperature.

To investigate the WCA change for the compatible pairs of the metallic film, Zn and Ag were consecutively
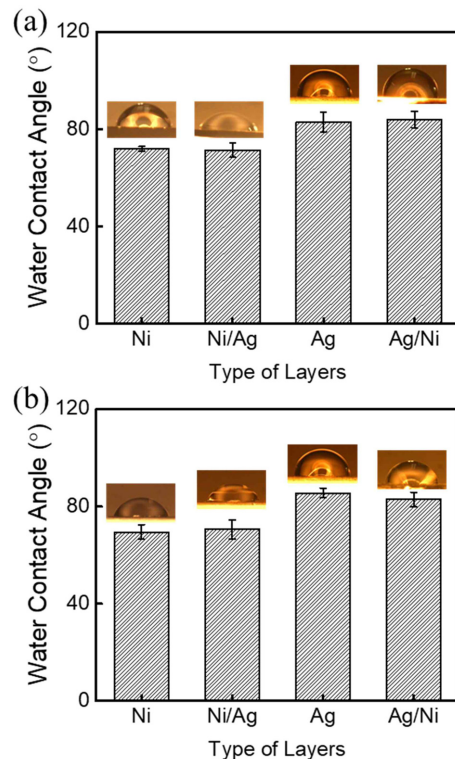

Fig. 3. Water contact angle (WCA) of single and incompatible metallic bilayer heterostructures measured (a) as-received and (b) 8 hours after the deposition. Inset optical images are the images of a water droplet on the given samples.
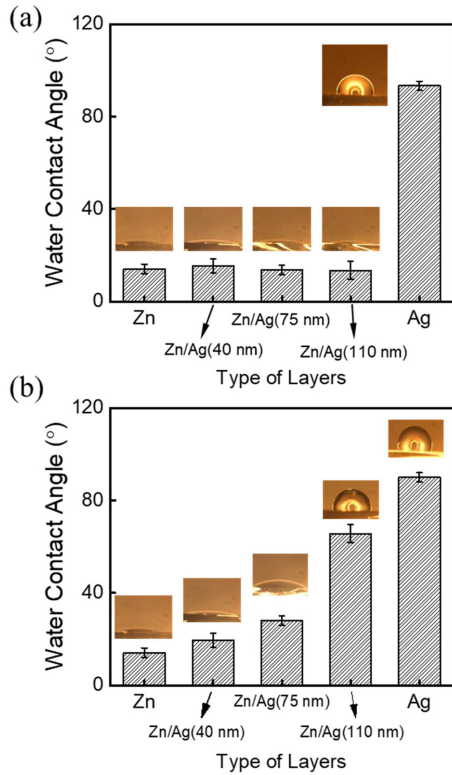
Fig. 4. Water contact angle (WCA) of compatible Zn/ Ag bilayer heterostructures with different thickness of bottom layers and single reference layers (a) as-received and (b) 48 hours after the sputtering.

which resulted in lowering the surface energy and increase of WCA.

To further investigate the effect of environmental temperature on the diffusion, a single layer of Zn(150 nm), and bi-layers of Zn(150 nm)/Ag(40 nm) and Zn(150 nm) /Ag(110 nm) samples were prepared. The samples were then stored in the oven at 80 °C for 40 minutes. The WCA were measured every 10 minutes. As presented in Fig 5, all the samples showed a quite similar WCA as low as 20° and showed a slight increase for the Zn/ Ag(40 nm). As for the Zn/Ag(110 nm), a significant increase of the WCA was observed from 20° to 90°, which is quite similar to that of Ag.

To acquire the composition of the materials with respect to the depth, Auger electron spectroscopy (AES) measurement was conducted. Note that atomic concentration at 0 minute of the sputtering time indicates the composition of the material at the sample surface. Two types of metallic bi-layer heterostructures that are Zn(150 nm)/Ag(40 nm) and Zn(150 nm)/Ag(110 nm) were prepared for the AES analysis. The measurements were made 48 hours after the deposition. Fig. 6(a) shows that almost no diffusion occurred for the Zn(150 nm)/Ag(40 nm). On the contrary, a large amount of Ag diffusion toward the surface had appeared which is consistent with the results of WCA.

According to the first Fick's law of diffusion, the number of materials passing through the unit area by the unit time is proportional to the first derivative concentration of the material. Based on the law, it is proper to assume that Zn(150 nm)/Ag(110 nm) exhibit an increase
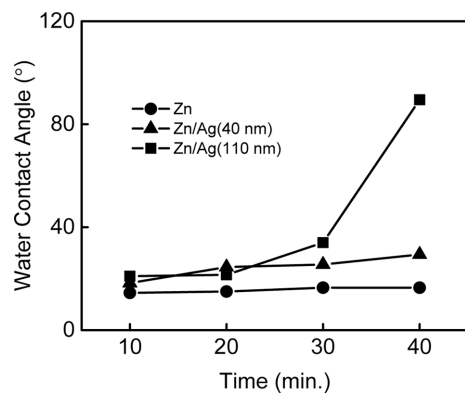
deposited on Si substrate. As shown in Fig. 4, the contact angles of single layers and compatible bi-layers with three different thicknesses of bottom layers were measured as received (Fig. 4(a)) and 48 hours after the deposition (Fig. 4(b)). The thicknesses of the Ag bottom layers were 40, 75 and 110 nm. As presented in Fig. 4(a), Zn(150 nm), Zn(150 nm)/Ag(40 nm), Zn(150 nm)/ Ag(75 nm) and Zn(150 nm)/Ag(110 nm) had similar WCA as that of as-received Zn. The WCA of these samples was measured to be ~13°. In the meantime, Ag showed WCA as high as $93 \pm 2°$. As can be seen in Fig. 4(b) where the measurement was conducted after 48-hours, it is interesting to note that a drastic change of WCA of the samples with Ag(75 nm) and Ag (110 nm). The WCA of Zn(150 nm)/Ag(75 nm) and Zn(150 nm)/Ag(110 nm) were $28 \pm 3°$ and $66 \pm 2°$, respectively. Thus, it can be noted that an increase of the underlying Ag layer thickness has aided in an increase of the diffused amount

Fig. 5. Water contact angle (WCA) change of Zn and Zn/Ag bi-layers which have different thicknesses of Ag layer stored in 80 °C for 40 minutes.
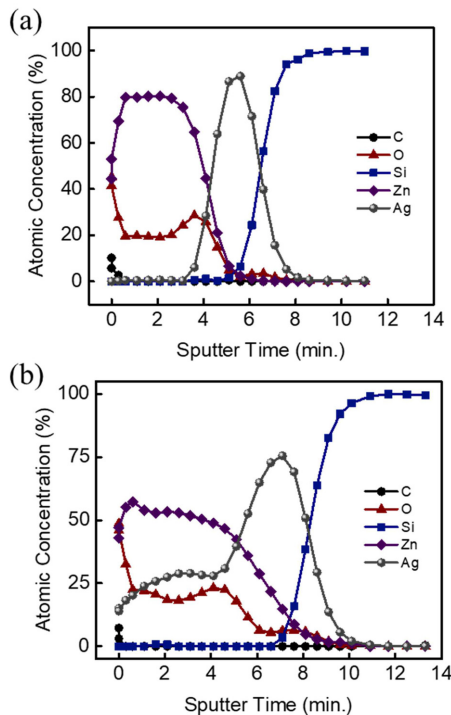
(a)

(b)

Fig. 6. AES data of (a) Zn(150 nm)/Ag(42 nm) and (b) Zn(150 nm)/Ag(110 nm) bilayer heterostructures.

in the diffused amount compared to that of the Zn(150 nm)/Ag(40 nm) bilayer. Furthermore, AES data demonstrate that there can be a critical thickness for bottom layers to diffuse and reach the surface.

4. Conclusions

There have been numerous works on developing hydrophobic or hydrophilic surfaces for a wide range of applications. However, particularly in fuel cell applications, the hydrophobic or hydrophilic surfaces act as poor conditions for exhausting water, which is a key factor in fuel cell efficiency[8]. Thus, it can be stated that control of the surface energy can be significant for applications where intermediate surface energy is needed. The proper surface energy, especially for micro or nano scale applications, can be accomplished by providing bilayers without changing any structures of the surface.

As addressed in the manuscript, the ultimate goal of our experiment is to control the surface energy by varying compatibility, thickness and temperature. These parameters were all considered to be critical factors for

obtaining a certain amount of diffusion. In this work, bilayer metallic film heterostructures with different compatibility were constructed by using the sputter deposition technique to control the surface energy. With the high compatibility of the metal pairs, the adequate thickness of the metallic film and relatively high temperature resulted in a drastic change of WCA. Specifically, the WCA of Zn/Ag compatible metal pairs was increased by ~4 times due to a large amount of diffusion at the interface. Furthermore, desired surface energy could be achieved with the proper thickness of the layers. On the contrary, almost no change in WCA was observed for the incompatible Ni/Ag bilayer metallic film heterostructures. This outcome is expected to aid in the performance maximization of small-scale applications where the adhesion property is significant[15].

Acknowledgements

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