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Preparation and characterization of ultra-thin amphiphobic coatings on silicon wafers

Chun-Yueh Mou *, Wei-Li Yuan, Chih-Hsin Shih

Department of Chemical Engineering, Feng Chia University, 100, Wenhua Rd., Xitun Dist., Taichung 40724, Taiwan, ROC

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ABSTRACT

Fluorine-based amphiphobic coatings have been widely used in commercial domestic utensils and textiles to repel water and oil contaminants. However, few reports from the literature survey have discussed the effects on amphiphobicity of the nano- to micro-scale surface features of such a coating. In this research thin amphiphobic epoxy coatings based on a mixture of bisphenol A diglycidyl ether, tetraethylorthosilicate (TEOS), and a particular alkoxy silane with fluorinated side chains (F-silane) are deposited on silicon wafers. Film amphiphobicity is characterized by the measurement of water and oil contact angles of the coating. Film morphology is revealed in the scanned images using atomic force microscopy. The deposited films free of F-silane are about 10 nm thick. When a small amount of F-silane was firstly added, the water and oil contact angles of the deposited films jumped up to 107° and 69° respectively and then flattened out with increased F-silane. Water droplets gave an average plateau contact angle about 110°, while vegetable oil ones, 40°. It was noted that there is a dramatic decrease in the lyophobicity causing a reduction in contact angles. However, surface lyophobicity also depends on sub-microscopic surface structures. In addition, by increasing TEOS, it was shown that the formed silica sols or granules were helpful in enhancing the mechanical strength along with retaining the lyophobicity of the film.

1. Introduction

Functional coatings which render special properties such as antibacterial, self-cleaning, anti-glare, anti-UV, anti-IR, anticorrosive, antiferromagnetic, electromagnetic shielding, wear resistance, and thermal barrier have been applied to a variety of domestic and technological applications [1]. Among the many special functions, amphiphobicity is gaining more attention in lowering the surface wettability of a sample. Amphiphobicity includes both hydrophobicity and lyophobicity. Although many have studied hydrophobicity or even superhydrophobicity, such as the reversible switching between (super-) hydrophobicity and (super-) hydrophilicity of a surface by electro-, photo-, or thermal induction [2–6], only a few have reported on lipophobicity or amphiphobicity [7–12].

According to the theories of lotus effect, it is important to have two length scales in surface geometry to make an artificial surface rendering surface super-hydrophobicity [13]. On one hand, the commonly seen micro-sized papillae on the surface help trap air in between and a larger contact angle is predicted by the Cassie and Baxter equation [14–17]. On the other hand, the nano-structures over the micro-features also play an important role to provide reduced activation energy for the droplet receding process.

In order to create micro/nano-structures on a surface, several approaches have been taken. Li et al. used pyrolysis of metal phthalocyanines to form aligned carbon nanotube films [7]. Xie et al. used two polymers with different solubilities to form micro/nano-hierarchical papillae [10]. Similarly, binary structures have also been created by electrochemical deposition of copper on indium tin oxide substrates [18]. Electrochemical method has also been applied to growing variously shaped gold nano-structures [8]. In contrast to deposition, etching or corrosion has also been used to roughen the sample surface. For example, argon plasma has been used to etch a spin-coated monomer layer for subsequent polymerization into micro/nano-papillae [9]. Another technique is to establish low surface free energy by using polymers with fluorocarbon ends, side chains, or segments added to the hydrocarbon backbones in coating a substrate [19]. In addition to fluoro-alkanes, silane coupling agents are also a popular candidate to promote surface lyophobicity while enhancing the coating–substrate adhesion [20]. In most cases, no matter how the surface roughness is created, without fluorination or fluoro-compound, a lyophobic or amphiphobic surface cannot be obtained [7–10]. However, as technology advances towards nano-sized polymer films for industrial use, platforms to efficiently and accurately determine the mechanical properties of thin polymer films and coatings remain unavailable.

Currently, there are very few options for measuring properties of submicrometer-thick film coatings. Conventional mechanical testing devices usually do not have the sensitivity to measure forces applied to a thin polymer film in the low nanometer range [21]. Coating

* Corresponding author. Tel.: +886 4 24524650.
E-mail address: cymou165@gmail.com (C.-Y. Mou).

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thickness measurements and coating deposition characteristics on soft, smooth surfaces, such as silicon wafers, are especially hard to obtain using traditional scanning probe microscopy [22–24]. Our laboratory has previously been characterizing thin film depositions using traditional surface roughness measurement techniques such as Surfcorder (ET3000, Kosaka Laboratory, Japan) and scanning probe microscopy [25]. In this study, we explored several data analyzing techniques associated with atomic force microscopy (AFM) to examine the nanometer thickness and characteristics of amphiphobic coatings on silicon wafers.

In our work, silanes with fluorinated groups or side chains (F-silane) are used combined with epoxy and other film-forming chemicals in order for the fluorinated side chains to move to the surface during spin coating and thermal curing processes. We have shown that thin epoxy films, in the low nanometer range, with F-silane and silica particles can form on the silicon wafer to render an amphiphobic coating with desired hardness. Surface contact angles of water and oil were measured as indices of amphiphobicity.

2. Experimental details

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA, MW = 189, Chang Chun Group, Taiwan) was used to form epoxy films and its chemical structure is shown in Fig. 1. Crosslinker for epoxy (So-5110A) was purchased from Echo-Nanobio, Taiwan. The F-silane with fluorinated side chains (Si-1004L, Echo-Nanobio, Taiwan) is used as an amphiphobic coupling agent. Tetraethylorthosilicate (TEOS, 98%, Acros) was used as received for preparing silica particles in the films. Acetone, 1-butanol, and n-hexane (99%, 99%, and 95% respectively) are purchased from Acros and used as solvent without further purification. Silicon wafers (4″ in diameter, Tekstarter, Taiwan) are cleaned by the RCA cleaning method [26–29], and glass plates (2×5 cm^2, Shenshiu, Taiwan) are cleaned in acetone under ultrasonic oscillation for 30 min, rinsed by deionized water, and dried in oven for 30 min before used.

2.2. Film deposition procedures

A scheme of the amphiphobic film deposition process is given in Fig. 2. Using this method, epoxy-based amphiphobic coatings can be constructed on stainless steel plate, silicon wafer, or glass slide. Film precursor solutions of varied compositions including epoxy, F-silane, and TEOS are prepared and deposited on the substrate by spin coating at 2500 rpm for 20 s. In each deposition, only 1 drop precursor solution (0.02 ml) is used. Deposited films are cured in oven at 180 °C for 10 min. Crosslinked films are rinsed with deionized water and dried in oven at 60 °C for 30 min, followed by thickness, amphiphobicity, morphology, and hardness analyses.

To study the effects of F-silane on surface amphiphobicity, a set of films is deposited separately on silicon wafer at fixed epoxy and TEOS vol% but at different F-silane content from 0 to 13 vol%. The formulae with active ingredients are shown in series 1 of Table 1. Contact angles of water and oil droplets on the coatings are measured and plotted against F-silane vol%.

Since TEOS is able to react with F-silane and the surface oxide layer of the substrate, a series of films is prepared at fixed epoxy vol% but at different volumetric ratios of TEOS to F-silane, the formulae of which are shown in series 2 of Table 1. Film hardness is determined by pencil test (ASTM D 3363-05) and plotted against TEOS/F-silane ratio. During the analysis, a series of pencils (Lion Pencil, Taiwan) with hardness from 2B to 2H are used to scratch the film according to the procedures described in the cited document.

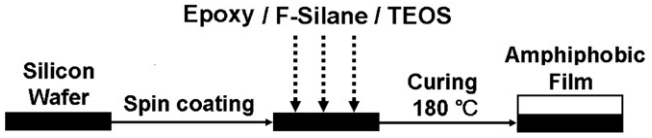

Fig. 2. Process for depositing amphiphobic coatings on silicon wafers. The coating formula is composed of epoxy resin as film matrix, crosslinker for curing, F-silane for amphiphobicity, and TEOS for film hardening.

2.3. Coating deposition analysis

Epoxy-based thin films are deposited by a spin coater (PM490, Pentad Scientific, Taiwan). Film samples are dried and cured in an oven (NTR-800, Grieve, USA). Surface morphology is examined with a NanoScope IV, multimode SPM from Veeco (Digital Instruments), operated in tapping mode. The cantilevers (spring constant 0.31–0.41 N/m) are purchased from Nanosensors, USA. AFM is a popular tool to characterize film surface structures on the nanoscopic scale [30,31]. Evaluation of the surface roughness in this report is based on scan areas of 5 μm × 5 μm. The roughness parameter used is the root-mean-square roughness *Rq*, the deviation from the mean height of surface, expressed mathematically as

$$Rq = \sqrt{\iint \left(h(x,y) - \overline{h}\right)^2 dxdy / \iint dxdy} \quad (1)$$

with the mean height of the surface as

$$\overline{h} = \iint h(x,y) dxdy / \iint dxdy \quad (2)$$

where $h(x,y)$ is the z data or pixel height collected by AFM [32]. Each *Rq* is obtained by taking average of 10 locations in the AFM images.

The phase image acquired together with the normal height one is a mapping of phase lag of the vibrated AFM probe from its driving bimorph before and after contacting the sample surface. Therefore, phase imaging is mostly used to distinguish between different components of a composite surface. In this work, the bare and coated silicon surface is imaged using this technique to show the distribution of epoxy films.

Rather than drawing a cross-sectional profile across the edge of a film on the substrate, the thickness of silane-free epoxy films is obtained by performing the histogram analysis of AFM images. Since the epoxy films without silane are not continuous, the difference between the peak values from the height histogram of image pixels can be used to calculate the step height or layer thickness in a statistical sense.

Amphiphobic properties are characterized by a contact angle meter (CA-D, Kyowa Interface Science, Japan). Contact angles of water and oil are measured at room temperature using 2 μl drops laid on the film via a syringe, which is placed 0.5 mm above. Determination of contact

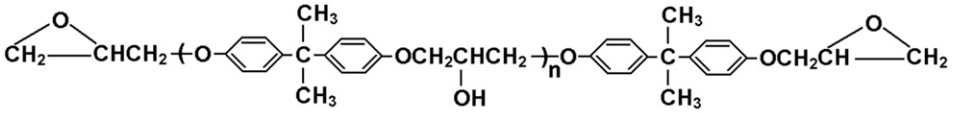

Fig. 1. Chemical structure of bisphenol A diglycidyl ether.