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Effect of treatment temperature on surface wettability of methylcyclosiloxane layer formed by chemical vapor deposition

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ABSTRACT

The surface wettability of the native Si oxide surfaces were tuned by chemical adsorption of 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS) molecules through thermal CVD method at different temperature. Water contact angle measurements revealed that the water contact angles of the TMCTS-modified Si oxide surfaces at the temperature of 333–373 K were found to be in the range of 92 ± 2–$102 \pm 2^\circ$. The advancing and receding water contact angle of the surface prepared at 333 K were found to be $97 \pm 2/92 \pm 2^\circ$, showing low contact angle hysteresis surface. The water contact angles of the surfaces prepared at the temperature of 373–413 K increased with an increase in the treatment temperature. When the treatment temperature was more than 423 K, the water contact angles of TMCTS-modified surfaces were found to become more than 150°, showing superhydrophobic surface. AFM study revealed that the surface roughness of the TMCTS-modified surface increased with an increase in the treatment temperature. This geometric morphology enhanced the surface hydrophobicity. The surface roughness could be fabricated due to the hydrolysis/condensation reactions in the gas phase during CVD process. The effect of the treatment temperature on the reactivity of the TMCTS molecules were also investigated using a thermogravimetric analyzer.

1. Introduction

Control of surface wettability is very important in various practical applications such as window coating, self-cleaning surfaces, microfluidics, corrosion resistance of engineering metals, and micro/nanoelectromechanical systems [1–3]. In the fields of the surface wettability, in particular, the superhydrophobic surface, which shows a static water droplet contact angle of more than 150°, has been major subject of extensive research. To fabricate a superhydrophobic surface, the introduction of both roughness and low surface energy to the surface is essential. Many surfaces in nature such as the lotus leaf and water strider's legs create their superhydrophobic properties from a hierarchical surface texture over-coated with hydrophobic functional groups [4,5]. These features inherent in nature can guide us to create superhydrophobic surfaces using a variety of methods [6–11]. However, the presence of the minute surface texture on the superhydrophobic surface leads to the faults such as poor optical clarity, poor resistance of abrasion, and poor long-term durability [12].

Recently, contact angle hysteresis that are a difference between the advancing (θ_A) and the receding (θ_R) contact angles have attracted much attention [13,14] because on the surface with low or negligible contact angle hysteresis the water droplet can move easily and do not come to rest. This is the practical definition of "water repellency": on the water repellent surfaces the water droplets are not pinned, independent of the water contact angle [13,15]. Such low or negligible-hysteresis surfaces have been prepared on SiO_x surface and oxidized Al surfaces using various silane coupling agents such as $(Me_3SiO)_3SiCH_2CH_2Si(Me)_2Cl$, $(Me_3SiO)_2SiMeCH_2CH_2Si(Me)_2Cl$ (θ_A and θ_R values reported for water were estimated to be ~104°/103°, and ~106°/105°, respectively) [15], and $(CF_3(CF_2)_5CH_2CH_2Si(CH_3)_2O)_2SiCH_3H$ ((θ_A and θ_R for water values reported were estimated to be ~110°/109°) [14]. It has been reported that the molecular level smoothness and flexibility, i.e., liquid-like structure, on the surfaces contributed to the formation of the surface with the low or negligible contact angle hysteresis [15]. This means that it is not easy to prepare such a low or negligible-hysteresis surfaces on the engineering materials

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because the engineering material surfaces are not the molecular level smoothness. Thus, it is very important to develop a technology to fabricate low or negligible-hysteresis surface on the engineering materials. Fabrication of superhydrophobic surfaces showing low or negligible-hysteresis is considered to be a means for this.

1,3,5,7-Tetramethylcyclotetrasiloxane (TMCTS) is one of the silane coupling agents having Si-H groups and has attracted much attention due to its wide potential in the high functionalization of powders [16] and solid substrates [17]. The methylcyclosiloxanes are immobilized on the various metal oxide surfaces through covalent bonds which are formed by condensation between the surface OH groups and Si-OH groups resulting from the hydrolysis of a part of the Si-H groups. Tada et al., has investigated the correlations between wetting and structure in methylsiloxane layers on oxides surface formed by chemical vapor deposition (CVD) and liquid phase deposition (LPD) from the TMCTS [17]. They revealed that a methylcyclosiloxane monolayer having a static contact angle of $97.4 \pm 1.3^\circ$ was formed by CVD and the LPD method produced methylcyclosiloxane multilayers showing a contact angle of $86.6 \pm 4.9^\circ$. However, they have not estimated the contact angle hysteresis of the hydrophobic surfaces covered with methylsiloxane molecules. In contrast, Hozumi et al. have successfully prepared ultaralyophobic surface on Al- and Ti-coated Si substrate (aluminum and titanium surfaces) by thermal CVD method at 353 K using he TMCTS as a raw material [13]. The θ_A and θ_R values of the aluminum and titanium surfaces were estimated to be 104°/102°, and 102°/99°, respectively, showing essentially negligible contact angle hysteresis. In addition, Hozumi et al. found that by increasing the CVD treatment temperature from 353 to 453 K, the hydrophobicity of the aluminum and titanium surfaces was enhanced because of the change in the surface morphology, resulting in the formation of the superhydrophobic surface. From these results, the TMCTS is considered to be an effective starting material to form ultralyophobic surface by thermal CVD. However, the details of the effect of the treatment temperature on the wettability of the methylsiloxane-covered surfaces has not yet been reported. Thus, it is crucial to reveal the correlation between surface wettability including dynamic contact angle and process conditions in the CVD process using the TMCTS as a raw material.

In this paper, we report on the effect of the treatment temperature on the wettability of the methylsiloxane-covered surfaces prepared by thermal CVD using methylcyclosiloxane as a raw materials. In addition, the effect of the treatment temperature on the reactivity of the TMCTS molecules were also investigated using a thermogravimetric analyzer.

2. Experimental procedures

2.1. Materials and surface modification procedure

1,3,5,7-Tetramethylcyclotetrasiloxane (TMCTS: $C_4H_{16}O_4Si_4$) was used as received without additional purification. *n*-type Si (100) wafer ($10 \times 10 \times 0.5$ mm) or glass ($10 \times 10 \times 1$ mm) was used as substrates. They were ultrasocnically cleaned for 5 min in acetone, ethanol, and ultrapure water in that order and were then dried with inert nitrogen gas. Next, UV/O_3 cleaning was performed on the cleaned substrate for 30 min at atmospheric pressure using a photo surface processor (Senlights. Co.: PL16-110). After the UV/O_3 cleaning, the substrate surface showed a water contact angle of less than 5°. After this UV/O_3 cleaning, each sample was immediately placed with a glass vessel containing 200 μl of TMCTS into a 100 cm^3 PFA block digestion vessel in a nitrogen atmosphere with less than 15% relative humidity. The vessel was sealed with a lid and was then heated for 72 h in an electric oven maintained at 333–443 K. After each sample preparation, each sample was ultrasonically cleaned in acetone, ethanol, and ultrapure water for 5 min and were dried with inert nitrogen gas.

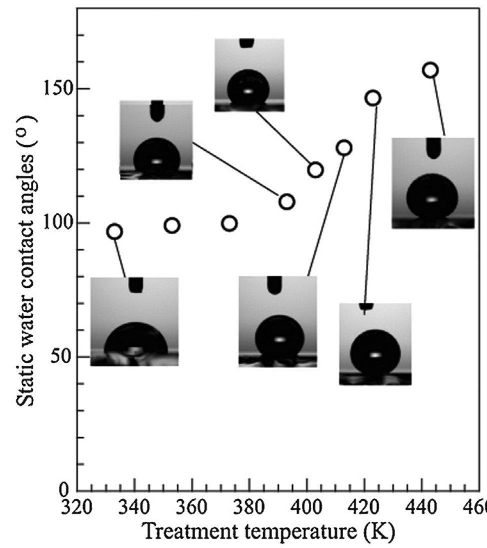

Fig. 1. Static water contact angles of the TMCTS-modified surfaces as a function of treatment temperature.

2.2. Characterization

Static water contact angles after surface modification were estimated using a contact angle meter (Kyowa Interface Science, DM-501) based on a sessile drop measuring method with a water drop volume of 5 μl. The measurements were conducted in air at 298 K. The water contact angles were measured at different five points and were averaged. The dynamic water contact angles of the SAM-modified surfaces were determined using ultrapure water that was added and withdrawn from the drop, respectively. Their measurements were conducted in air at room temperature. Surface morphologies were acquired with an atomic force microscope (AFM; Nanocute + Nanonavi II, SII nanotechnology, Co.,) using a Si probe (SII, SI-DF40, force constant 49 N/m) with a response frequency of 343 kHz. The root mean square (RMS) roughnesses of the sample surfaces after surface modification were estimated with an AFM. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a JEOL JPS-9010MC using a monochromatic Mg Kα X-ray source (1253.6 eV) to investigate the chemical bonding states and atomic concentration of the thin film. The emission current and anode voltage were operated at 25 mA and 10 kV, respectively. The binding energy was calibrated using C 1s peak (284.6 eV) of the hydrocarbon (-CH_x). The relevant fitting curves were analyzed by Gaussian line shape and Shirley background subtraction. Information on chemical bonding of the samples was obtained by FT-IR (IR Prestige-21, Shimadzu Co.). Spectra were recorded within the range of 400–4000 cm^{-1} with 256 scans at a resolution of 4 cm^{-1}. Thermogravimetric analysis (TGA) was performed by using a thermogravimetric analyzer (DTG-60H, Shimadzu Co.). The system was operated in the dynamic mode in the temperature range of 298–523 K at a heating rate of 10 K/min. All the experiments were carried out under an aerated atmosphere.

3. Results and discussion

Static water contact angles of the TMCTS-modified surfaces as a function of treatment temperature are shown in Fig. 1. Inset shown in Fig. 1 exhibit the water droplet behavior on the modified surfaces. At the temperature of 333–373 K, the water contact angles