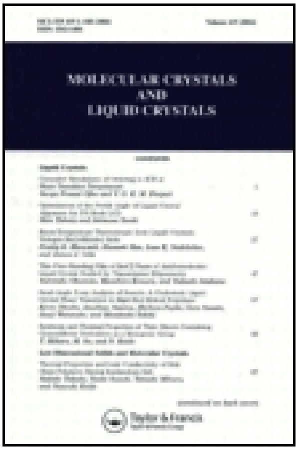

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Preparation and Characterization of Hydrophobic Modified Silica Film via Sol-Gel Process

Kyung Hwan Yoon [a] & Mahn Won Kim [a]

[a] Department of Physics, Korea Advanced Institute of Science and Technology, Daejon, 305-701, Korea

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Preparation and Characterization of Hydrophobic Modified Silica Film via Sol-Gel Process

KYUNG HWAN YOON and MAHN WON KIM

Department of Physics, Korea Advanced Institute of Science and Technology, Daejon 305-701, Korea

With controlling the amount of methyltrimethoxysilane (MTMS) in silica films via sol-gel process, the surface free energy of the films has been changed. The contact angle was measured to characterize the modified silica films. The surface free energy was determined, and correlated to the surface characteristic (hydrophobicity) of the films.

Keywords: silica thin film; hydrophobic; surface free energy; contact angle

INTRODUCTION

Organic modified silica coatings on various substrates have widely used in industry [1-2]. In these applications, surface characteristics (e.g. wettability and surface functional groups) are important to go to further processes (deposition of other materials, e.g. metal and polymer) or check to do their own functions (e.g. hydrophobicity in water repellant coating). We made silica films with different ratios of methyltrimethoxysilane in tetraethylorthosilicate. Contact angles were used for calculating surface free energy and correlating with surface characteristics of films.

EXPERIMENTAL

Methyltrimethoxysilane (MTMS, Aldrich, 95%), Tetraethylorthosilicate (TEOS, Acros, 98%), 2-propanol (IPA, Merck, 99.7%), 1-butanol (Aldrich, 99.5%), Hydrochloric acid (HCl, Junsei, 35%), Ammonium hydroxide (NH_4OH, Aldrich, 28-30%) and double distilled water were used without further purification. We used a 2-step acid-base method for preparing coating solutions [3]. The experimental procedure was as follows. First, mixed the following ratio, MTMS+TEOS : H_2O : IPA : HCl = 1 : 2 : 3.8 : 0.00073, then heated the solution for 90 min. at 60℃. Second, mixed 10 ml of the first solution with 1ml of 0.05 M NH_4OH. Finally, after aging for 1 day, diluted with 1-butanol. The solution was spin-coated on cleaned Si wafer. The coated sample was heated to 300℃. Contact angle was measured by Erma contact angle goniometer.

RESULTS AND DISCUSSION

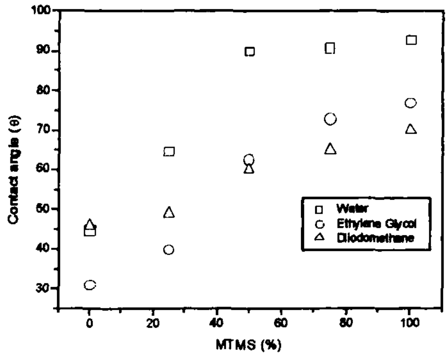

Figure 1. Contact angles for silica films

Fig.1 showed the contact angles of prepared silica films. The methyl group coverage of the film surface seemed not to be abruptly increased above 50 % MTMS because MTMS has three alkoxy groups that can be polymerized and unpolymerized functional groups (e.g. silanol and alkoxy groups) can be exposed on the film surface. Surface free energies of the films were calculated by water, ethylene glycol, and diiodomethane contact angles. Acid-base interaction theory[4] has been used to determine the surface free energy parameters, γ_s^{LW} (Lifshitz-van der Waals interactions comprising dispersion, orientation and induction forces), γ_s^+ (acidic term), and γ_s^- (basic term) in several studies on silica surfaces[5-7]. From the following equations, surface free energy parameters are calculated.

$$\gamma_s^{LW} = \gamma_D(1+\cos\theta_D)^2/4 \qquad (1)$$

$$\gamma_{EG}(1+\cos\theta_{EG}) = 2[(\gamma_s^{LW}\gamma_{EG}^{LW})^{1/2} + (\gamma_s^{+}\gamma_{EG}^{-})^{1/2} + (\gamma_s^{-}\gamma_{EG}^{+})^{1/2}] \qquad (2)$$

$$\gamma_W(1+\cos\theta_W) = 2[(\gamma_s^{LW}\gamma_W^{LW})^{1/2} + (\gamma_s^{+}\gamma_W^{-})^{1/2} + (\gamma_s^{-}\gamma_W^{+})^{1/2}] \qquad (3)$$

D, EG, and W denote diiodomethane, ethylene glycol, and water. The combination of the acidic and basic terms produce the acid-base component of the surface free energy, $\gamma_s^{AB} = 2\,(\gamma_s^{-}\gamma_s^{+})^{1/2}$.

Table 1. Surface tension components for hybrid films

sample	γ^{LW}(mN/m)	γ^{+}(mN/m)	γ^{-}(mN/m)	γ^{AB}(mN/m)	$\gamma = \gamma^{LW} + \gamma^{AB}$(mN/m)
0 %^{a}	36.5	0.50	38.71	6.22	42.69
25 %^{a}	34.8	0.53	16.6	5.93	40.73
50 %^{a}	28.6	0.29	2.97	1.86	30.46
75 %^{a}	25.7	0.005	5.39	0.33	26.03
100 %^{a}	22.9	0.003	5.53	0.26	23.16

a : MTMS fraction in MTMS/TEOS mixture. All surface energies are calculated from published data (*Langmuir*, 12, 1681 (1996))

In table 1, we knew that the basic term of total surface free energy was more sensitive than the acidic term of that. It is depicted graphically in Fig. 2.

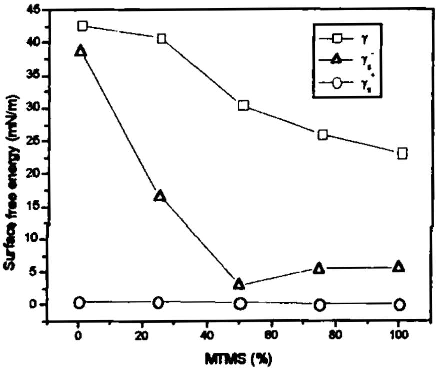

Figure 2. Surface energy components for modified silica films

It can be explained by two reasons: the increase of surface methyl group coverage and the interaction between probe liquids (water, diiodomethane, and ethylene glycol) and water-adsorbed silica surface. It is well agreed with literature data[8] that increasing the MTMS content decreases the surface silanol and alkoxy groups. The lone pair electron of oxygen in unpolymerized functional groups (e.g. silanol and alkoxy groups) is found to play an important role in determining the basic term. These functional groups seem to be considered as acidic (electron accepting) sites, but the adsorbed water molecules on the silica film surface cannot be excluded in this case[9]. Water molecules can form the hydrogen bond with the surface silanol and alkoxy groups[10]. So the basic (electron donating) term change in the surface free energy of the silica films is resulted from the interaction between the electron-donating water-adsorbed silica surface and probe liquids (water, diiodomethane, and ethylene glycol).

CONCLUSION

We made hydrophobic modified silica films via sol-gel process. From the contact angles of three different liquids (water, diiodomethane, and ethylene glycol) on silica surfaces, the surface free energy terms based on acid-base interactions were calculated. The decreasing basic terms can be explained by the increased methyltrimethoxysilane content and the interaction between the adsorbed water molecules and probe liquids.

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