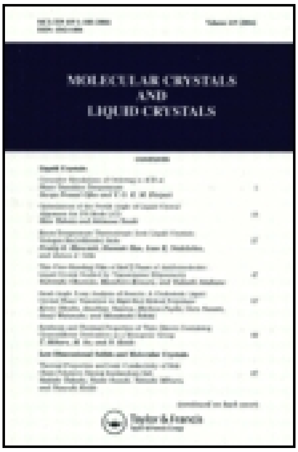


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Preparation of Self-Assembled Fullerene-Diaminododecane Multilayer Films on $(MeO)Si(CH_3)_2(CH_2)_4NH_2$-Modified Oxide Surfaces

Joon Shik Bae [a], Eung-Ryul Kim [a] & Haiwon Lee [a]

[a] Department of Chemistry, Hanyang University, Sungdong-ku, Seoul, 133-791, Korea

To cite this article: Joon Shik Bae , Eung-Ryul Kim & Haiwon Lee (1995): Preparation of Self-Assembled Fullerene-Diaminododecane Multilayer Films on $(MeO)Si(CH_3)_2(CH_2)_4NH_2$-Modified Oxide Surfaces, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 267:1, 139-144

To link to this article: http://dx.doi.org/10.1080/10587259508033985

Mol. Cryst. Liq. Cryst. 1995, Vol. 267, pp. 139–144
Reprints available directly from the publisher
Photocopying permitted by license only

PREPARATION OF SELF-ASSEMBLED FULLERENE-DIAMINODODECANE MULTILAYER FILMS ON $(MeO)Si(CH_3)_2(CH_2)_4NH_2$-MODIFIED OXIDE SURFACES

JOON SHIK BAE, EUNG-RYUL KIM, and HAIWON LEE
Department of Chemistry, Hanyang University,
Sungdong-ku, Seoul, 133-791, Korea

ABSTRACT Self-assembled fullerene-diaminododecane multilayer films were prepared on planar silicon wafer and quartz plate and on nonplanar fumed silica surfaces, and the growth of each layer and its uniformity was characterized by using FTIR, UV, contact angle measurement and ellipsometric measurement. It is suggested that fullerene-diaminododecane layers are not completely packed on oxide surfaces, but the growrh of each layer was confirmed.

INTRODUCTION

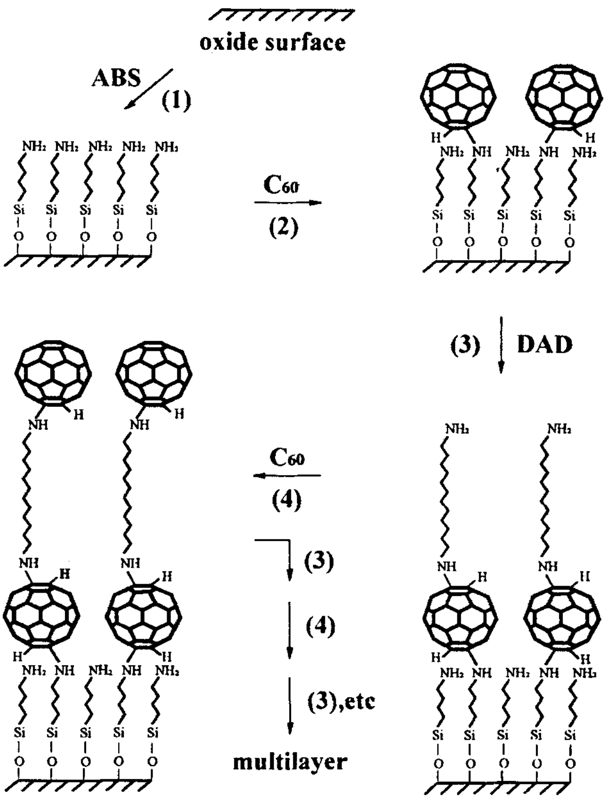
The current interests in controlling the designed microstructure of organic/inorganic materials to a few nanometers scale have been propagating in the scientific studies of molecular structure and molecular interactions on the various surfaces.[1-3] Among of various techniques for the preparation of ordered thin organic films, it is believed that classical Langmuir-Blodgett (LB)[4] and self-assembled (SA)[5] films could provide the desired control of molecular order at interfaces, and it is important to introduce appropriate functional groups in the molecular system with a high degree of control over the orientation of those groups. Covalently bound, self-assembled monolayer and multilayer films have a long-term stability in the presence of mechanical, chemical, and thermal stresses compared to LB films because of strong chemical bonds at the substrate-monolayer and monolayer-monolayer interfaces.[2,5]

Physically absorbed multilayer fullerene films via Langmuir-Blodgett (LB) technique, solution evaporation, and thermal evaporation of solid-phase fullerene have exhibited interesting properties with respect to optical response[6], electrical conductivity[7], and charge transport[8], chemical sensing activity[9]. Several groups have reported for the preparation of successful preparation of fullerene mono- and multilayers at the air-water interface by using LB method has been reported.[10-13]

In the recent years, several papers on the self-assembled fullerene films were reported. Two approachs were introduced towards fullerene self-assembly onto surface. One is to chemically modify the surface such as Si, ITO, and Au, with a reagent that undergoes a successive bond formation with a fullerene in solution,[14-16] and the other is to prepolymerize fullerene with amino groups of an appropriate compound and be followed by anchoring onto silicon surfaces.[9]

In the present study, we first report the novel self-assembled multilayer films of fullerene on planar silicon wafer, quartz plate, and on nonplanar silica surface. The process of growing fullerene-diaminododecane multilayers is shown in Scheme I.

Scheme I



EXPERIMENTAL

Materials. Fullerene, diaminododecane(DAD), ethanol, and toluene was purchased from Aldrich and 4-aminobutyldimethylmethoxysilane(ABS) was purchased from Hüls America Inc. All chemicals were used without further purification. Cab-O-Sil(fumed silica) L-90 (average particle diameter 24nm) was purchased from Cabot Corp.

Preparation and Chracterization of Self-assmbled Films In the first step, various substrates such as silicon wafer, quartz, and Cab-O-Sil (fumed silica) L-90 (average particle diameter 24nm) were soaked in 5mM toluene solution of 4-aminobutyldimethylmethoxysilane (ABS) for 24hs., producing a monolayer of covalently anchored amino groups. After copies washing with toluene, ABS-modified substrate was then soaked in 0.1mM benzene solution of C_{60} for 24hs. followed by rinsing with benzene thoroughly to remove residual physisorbed C_{60}, and then treated in 5mM ethanol solution of 1,12-diaminododecane (DAD) for another 24hs., rinsed with ethanol, then dried in vacuum. Multilayer films of C_{60}-DAD on ABS-modified surfaces were prepared by repeating these steps.

In a typical experiment, growth of multilayer C_{60}-DAD on ABS-modified various substrates are monitored by FT-IR, UV, ellipsometry, and contact angle mesurements before and after adsorption.

RESULTS AND DISCUSSION

Figure 1 shows the UV spectra of one and two layers of C_{60}-DAD on modified quartz plates (A,B), dried films of C_{60} on quartz (C), C_{60} in benzene solution (D), and C_{60} reacted with DAD in benzene solution for 6 hour (E). As reported in elsewhere[9,10,17], UV absorption maxima of C_{60} film cast on quartz are similar to that of C_{60} as shown in Table 1.

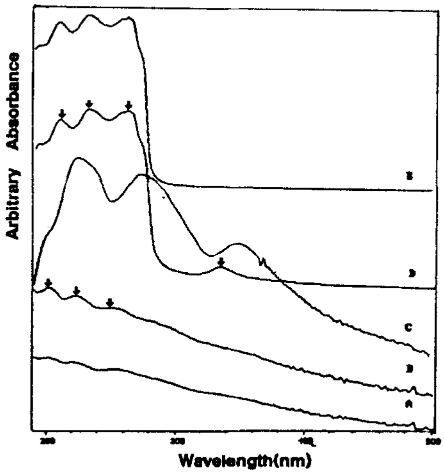


Figure 1 UV absorption spectra of fullerene C_{60}: (A) one layer of C_{60}-DAD on quartz plate; (B) two layer of C_{60}-DAD on quartz plate; (C) C_{60} film coated on quartz plate; (D) C_{60} in benzene solution; (E) C_{60} reacted with DAD in benzene solution for 6 hour

Table 1. UV absorption maxima λ_{max} of C_{60} in various states

States	λ_{max} (nm)			Ref.
hexane solution	213	257	329	17
Langmuir film on phenol aqueous solution			347	17
LB film	221	270	347	17
mixed LB film with icosanoic acid	220	265	340	11
vapor deposition film on NaCl(100)	221	270	347	18
vapor deposition film on MoS_2	220	280	340	19
vapor deposition film on Si(100)		263	339	20
film coated on quartz (this work)	216	264	339	
SA film on oxide surface (this work)	202	220	254	
C_{60} in benzene solution (this work)			334	
C_{60} reacted with DAD in benzene solution (this work)	210	232	262	

In Figure 1, the appearance of λ_{max} of self-assembled C_{60}-DAD films at 202 nm and the disappearance of λ_{max} of that films at longer wavelength region of 330-340 nm compared to those of other C_{60} at the same wavelength region were observed. This is due to the fact that according to N-H addition reactions across the C=C bonds in C_{60}, a single electron transfer proceeds the covalent bond formation and proton transfer as determined by UV/Vis and ESR spectroscopy.[21] It is supposed that numerous new bonds are formed at the expense of the π-bond of C_{60}, and we also suspect that only one or two surface amine units react per fullerene molecule as reported by Mirkin and coworkers.[14]

The relative hydrophilicity of the resulting fullerene-modified surface is confirmed via contact angle measurements. For example, ABS yields a relatively hydrophobic surface(θ=74°) and fullerene-modified surface also resulted in a hydrophobic surface(θ=73°). The film thickness of various multilayers was measured in order to investigate the uniformidity of C_{60}-DAD layers covalently bound to silicon wafer. The ellipsometric measurements were carried out on the basis of UV spectra and contact angle data, and we suggest that multilayer fullerene-diaminedodecane (C_{60}-DAD) films can be prepared on oxide surfaces.[22] Ellipsometric results indicate that the average layer thickness per C_{60}-DAD layer is about 9±2Å. Because the films absorbed onto ABS-modified silicon wafer do not exhibit an ideal growth of multilayer, we could not obtain adequate information for the exact layer thickness and surface coverage of fullerene per layer. It is thought that DAD molecules were considerably tilted to the each C_{60} layer and bonded to lateral sites of C_{60} molecules rather than to front site, so that the packing density of C_{60} layers is considerably low.

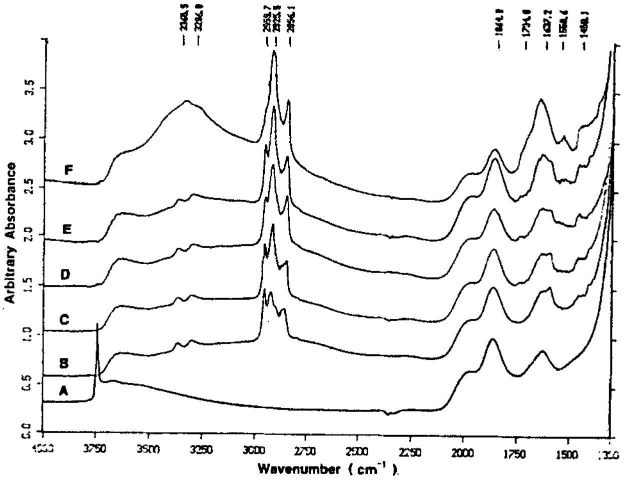


Figure 2 Infrared spectra of modified Cab-O-Sil: (A) pure Cab-O-Sil; (B)ABS-modified Cab-O-Sil; (C) C_{60} adsorbed on ABS-modified Cab-O-Sil; (D) 1 layer of C_{60}-DAD on ABS-modified Cab-O-Sil; (E) 2 layers of C_{60}- DAD; (F) 4 layers of C_{60}-DÅD

Infrared spectra of modified Cab-O-Sil was shown in Figure 2.[23] The spectrum A in Figure 2 is a typical infrared spectrum of dehydrated Cab-O-Sil, and shows the isolated hydroxyl groups bound to surface of Si atom at 3747cm^{-1}. The Si-O-Si combination and lattice vibrations at 1864 and 1635cm^{-1} are also appeared respectively. Reaction of dehydrated Cab-O-Sil with ABS results in complete reaction of the free silanol groups, this is known by the disappearance of that peak at 3747cm^{-1}, to give

ABS-modified surface. The two peaks at 3366 and 3302cm^{-1} are attributed to the primary amine of ABS, and broad band at 3600 - 3300cm^{-1} in the secondary amine which is formed by addition of a hydrogen in primary amine to double bond in C_{60} has been increased as growing the films. The peak at 2959cm^{-1} is also attributed to Si-CH_3 of ABS.

Two peaks in the C-H stretching region, especially those at 2925 and 2856cm^{-1}, are characteristic asymmetric and symmetric vibrations, and become prominent as C_{60}-DAD layers are grown. The covalently bound multilayers of C_{60} derivatives, C_{60}-DAD and C_{60}-ABS, show several major features in the C_{60} skeleton ring vibration region[6] at around 1651, 1554, and 1450cm^{-1}

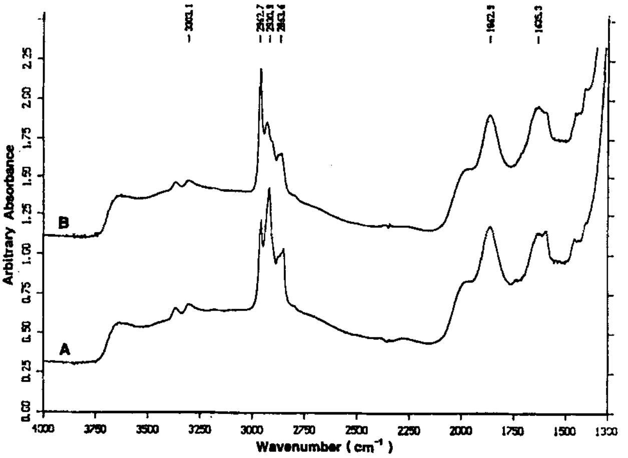


Figure 3 IR spectrum of modified Cab-O-Sil (a) 0.1 mM C_{60} adsorbed on ABS-modified Cab-O-Sil (b) 3.0 mM C_{60} adsorbed on ABS-modified Cab-O-Sil

Figure 3 shows that the formation of C_{60} layer depends on concentration of C_{60}, reaction time, reaction temperature than planar oxide substrate. When amine reacts with higher concentration at higher temperature in longer reaction time, the absorbance of secondary amine peak which means amine react with double bond of C_{60} was increased fairly. Especially, the new vibration mode of C-H streching which is formed by addition hydrogen in amine to double bond of C_{60} was appeared in 2962cm^{-1}.

CONCLUSION

It has been demonstared that self-assmbled multilayer films of fullerene-DAD on planar silicon and quartz plates, and on nonplanar Cab-O-Sil surface. The growth of each layer is confimed by using FTIR, UV and ellipsometry, however the uniformity and structural order is not clear yet. It is assumed that the coverage of monolayer is strongly dependent on the nataure of substrate and influenced the growth of following layers. The structural order of multilayer films is being under investigated.

ACKNOWLEDGEMENTS

This work was supported by a grant-in-aid from Korea Science and Engineering Foundation.

REFERENCES

1. J. D. Swalen, D. L. Allara, J. D. Andrade, E. A. Chandross, S. Garoff, J. Israelachvili, T. J. McCarthy, R. Murray, R. F. Pease, J. F. Rabolt, K. J. Wynne, and H. Yu, Langmuir, 3, 932 (1987)
2. H. Lee, L. J. Kepley, H. G. Hong, S. Akhter, and T. E. Mallouk, J. Phys. Chem., 92, 2597 (1988)
3. G. A. Ozin, Adv. Mater., 4, 612 (1992)
4. H. Fuchs, H. Ohst, and W. Prass, Adv. Mater., 3, 10 (1991)
5. A. Ulman, Adv. Mater., 2, 573 (1990)
6. B. Miller, J. M. Rosamilia, G. Dabbagh, R. Tycko, R. C. Haddon, A. J. Muller, W. Wilson, D. W. Murphy, and A. F. Hebard, J. Am. Chem. Soc., 113, 6291 (1991)
7. A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, Nature, 350, 600 (1991)
8. C. Jehoulet, Y. S. Obeng, Y. Kim, F. Zhou, and A. J. Bard, J. Am. Chem. Soc., 114, 4237 (1992)
9. D. Li and B. I. Swanson, Langmuir, 9, 3341 (1993)
10. J. Milliken, D. D. Dominguez, H. H. Nelson, and W. R. Barger, Chem. Mater., 4, 252 (1992)
11. T. Nakamura, H. Tachibana, M. Yumura, M. Matsumoto, R. Azumi, M. Tanaka, and Y. Kawabata, Langmuir, 8, 4 (1992)
12. L. Otavio, S. Bulhoes, Y. S. Obeng, and A. J. Bard, Chem. Mater., 5, 110 (1993)
13. N. C. Maliszewskyj, and P. A. Heiney, Langmuir, 9, 1439 (1993)
14. K. Chen, W. B. Caldwell, and C. A. Mirkin, J. Am. Chem. Soc., 115, 1194 (1993)
15. J. A. Chupa, S. Xu, R. F. Fischetti, R. M. Strongin, J. P. McCauley Jr, A. B. Smith Ⅲ, and J. K. Blasie, J. Am. Chem. Soc., 115, 4383 (1993)
16. W. B. Caldwell, K. Chen, C. A. Mirkin, and S. J. Babinec, Langmuir, 9, 1945 (1993)
17. Y. Tomioka, M. Ishibashi, H. Kajiyama, and Y. Taniguchi, Langmuir, 9, 32 (1993)
18. Y. Achiba, T. Nakagawa, Y. Matsui, S. Suzuki, H. Shiromaru, K. Yamauchi, K. Nishiyama, M. Kainosho, H. Hoshi, and T. Mitani, Chem. Lett., 1233 (1991)
19. M. Sakurai, H. Tada, K. Sakai, and K. Koma, A. Jpn. J. Appl. Phys., 30, L1892 (1991)
20. S. L. Ren, Y. Wang, A. M. Rao, E. McRae, J. M. Holden, T. Hager, K. Wang, W. Lee, H. F. Ni, J. Selegue, and P. C. Eklund, Appl. Phys. Lett., 59, 2678 (1991)
21. A. Hirsch, Q. Li, and F. Wudl, Angew. Chem. Int. Ed. Engl., 30, 1309 (1991)
22. The ellipsometric measurements were carried out in air at one angle of incidence (θ=70°). The thickness of each films was calculated automatically, using refractive index of organic layer (N_f=1.46-0i) and substrate optical constants as measured from a blank sample (N_s=3.732-0.151i).
23. H. G. Hong, D. D. Sackett, and T. E. Mallouk, Chem. Mater., 3, 521 (1991)