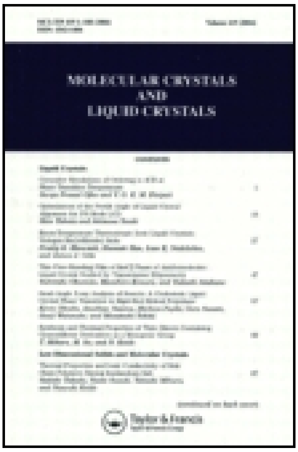

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Force Curve Measurement of Self-assembled Organic Monolayers Bound Covalently on Silicon (111)

Harald Graaf [a], Masato Ara [a] & Hirokazu Tada [a]
[a] Institute for Molecular Science, Okazaki National Research Institutes, Myodaiji, Okazaki, 444-8585, Japan

To cite this article: Harald Graaf, Masato Ara & Hirokazu Tada (2002): Force Curve Measurement of Self-assembled Organic Monolayers Bound Covalently on Silicon (111), Molecular Crystals and Liquid Crystals, 377:1, 33-36

To link to this article: http://dx.doi.org/10.1080/713738482

Mol. Cryst. Liq. Cryst., Vol. 377, pp. 33-36
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290088474

Force Curve Measurement of Self-assembled Organic Monolayers Bound Covalently on Silicon (111)

HARALD GRAAF, MASATO ARA and HIROKAZU TADA*

*Institute for Molecular Science, Okazaki National Research Institutes,
Myodaiji, Okazaki 444-8585, Japan*

Self-assembled monolayers of alkyl chains were prepared on silicon (111) surfaces. The surface was characterized by atomic force microscopy (AFM). Atomically flat terraces were observed in topographic images of the films with contact mode AFM, indicating the formation of highly ordered monolayers. Force curve measurements showed that the adhesion force between organic films and gold coated cantilever was much stronger comparing to the force on hydrogen terminated surfaces.

Keywords: self-assembled monolayer (SAM); silicon (111); force curve

INTRODUCTION

Covalently bond alkyl and aryl monolayers on hydrogen-terminated silicon surfaces have been studied because of their potential applications such as passivation of silicon surface.[1] Compared to the well-known self-assembled monolayers formed by thiols on gold or by silanes on siliconoxid, the covalent Si-C bond, which can be easily formed by a reaction, e.g. induced by heat or light, of an 1-alkene and a hydrogen-terminated silicon surface[2] , showed higher thermal stability [3] as well as a higher chemical stability [1] ,[4]. This high stability allows different chemical modifications by known reactions for various kind of applications like bioreactive monolayers[5] or for stabilization of the silicon surface[6].

In the present paper, we prepared monolayers of alkenes on Si(111) by heating treatment and observed the surface with atomic force microscope (AFM), Measuring the force curve as well as the topographic image of the prepared sample opens a way to study monolayers formed on the silicon surface and indicates the quality of the formed SAM.

EXPERIMENTAL

Silicon (111), medium n-doped (1-10 Ωcm) and p-doped (8.4 Ωcm) were hydrogen terminated according to the literature.[7] The H-terminated substrates were transferred directly into the dodecene. After placing the substrate into the solution it was heated up to 433 K under continuous argon bubbling for 24 hours. After 24 hours the solution were cooled down to room temperature. The samples were removed from the solution and cleaned by rinsing with petrolether, ethanol and dichloromethane.

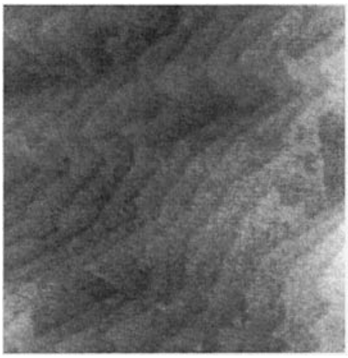

FIGURE 1 hydrogen terminated p-type silicon (2 x 2 μm)

Topographic images and force curves of freshly prepared H-terminated and monolayer covered silicon were examined by AFM (JSPM-1300, Jeol, Japan) under ambient conditions. Silicon nitride coated cantilevers (NT-MDT, spring constants 0.6 and 4.5 Nm^{-1}) were used.

RESULTS AND DISCUSSION

For all prepared samples (H-terminated silicon as well as alkene covered silicon), clear steps with a step height of about 0.33 nm were found by measuring the topographic images (see Figure 1).

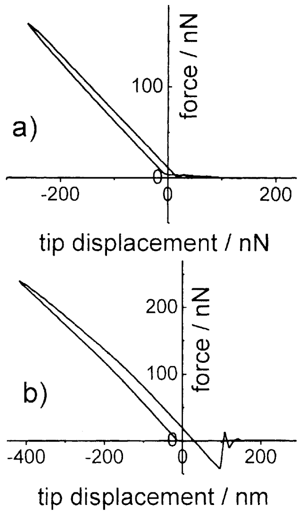

FIGURE 2 Force curves measured on hydrogen-terminated silicon (a) and dodecene SAM (b)

Figure 2 shows the different force curves measured on hydrogen-terminated silicon as well as on a dodecene (C12) monolayers. In all cases during the approach of the cantilever only a very small change in the force was seen until the tip contact the sample. This indicates that there is neither a strong interaction between substrate and tip nor more than a rather small amount of condensed water from the air is on the surface of the sample, which can form different capillary bridges between the tip and the sample. During retract the hydrogen-terminated silicon showed also only a very small adhesion.[8] On the other hand the adhesion of the monolayer is quiet high. Compared to the H-terminated substrate, the monolayer is softer and the tip can move a little bit into the film during the approach, which leads to more van der Waals interactions between tip and substrate. This increase in the amount of van-der-Waals interactions leads to a higher force, which is necessary to retract the tip from the monolayer.

For SAMs prepared of different alkenes (octene, decene, dodecene, octadecene) the adhesion force showed no dependence of the chain length

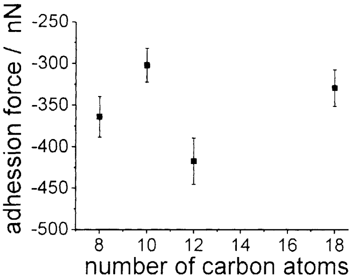

FIGURE 3 Adhesion forces of SAMs prepared of alkenes with different chainlengths

(see Figure 3). This indicates that the attractive interaction between the monolayer and the tip is dominated by the top carbon atoms of the alkenes in the film. At maximum only the top 8 carbon atoms showed can interact with the tip. This can be understood, if the tip can only reach a depth of 8 carbon atoms while extending through the film.

In summary, the force curves of SAMs prepared by different alkenes covalently bound to silicon (111) in comparison to hydrogen-terminated silicon were evaluated. The stronger adhesion force for monolayers compared to H-terminated silicon can be understood by the softness of the SAMs. Different chain lengths of the molecules ($C \geq 8$) in the SAM showed no influence on the adhesion force, which indicates that the tip can penetrate into only the top carbon atoms (maximum 8 atoms).

REFERENCES:

[1] M.R. Linford, P. Fenter, P.M. Eisenberger, C.E.D. Chidsey, J.Am.Chem.Soc. **117** 3145 (1995)
[2] J.M. Buriak, Chem.Commun. 1051(1999)
[3] M.M. Sung, J. Kluth, O.W. Yauw, R. Maboudian, Langmuir **13** 6164 (1997)
[4] A.B. Sieval, A.L. Demirel, J.W.M. Nissink, M.R. Linford, J.H. van der Maas, W.H. de Jeu, H. Zuilhof, E.J.R. Sudhoelter, Langmuir **14** 1759 (1998)
[5] P. Wagner, S. Nock, J.A. Spudich, W.D. Volkmuth, S. Chu, R.L. Cicero, C.P. Wade, M.R. Linford, C.E.D. Chidsey, J.Struct.Biol. **119** 189 (1997)
[6] A. Bansai, N.S. Lewis, J.Phys.Chem.B **102** 4058 (1998)
[7] C.P. Wade, C.E.D., Chidsey, Appl.Phys.Lett. 71 1679 (1997)
[8] A.L. Weisenhorn, P.K. Hansma, T.R. Albrecht, C.F. Quate, Appl.Phys.Lett. **54** 2651 (1989)