Research Article Adv. Mat. Lett. 2011, **2**(5), 345-348 ADVANCED MATERIALS *Letters*

www.vbripress.com, www.amlett.com, DOI: 10.5185/amlett.2011.9101am2011 Published online by the VBRI press in 2011

Formation process of two-dimensional crystalline film of vacuum-evaporated n-alkane: a molecular dynamics simulation

Hong-zhen Li[1*], Zhao-xiang Wang[2], Dong-hua Jing[3], Xiang-he Kong[1], Ke-zhu Yan[1]

[1]*College of Physics and Engineering, Qufu Normal University, Qufu 273165, China*
[2]*Laboratory for Renewable Energy, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*
[3]*Xingtan College, Qufu Normal University, Qufu 273100, China*

[*]Corresponding author. E-mail: hongzhenli09@163.com

Received: 26 April 2011, Revised: 22 July 2011 and Accepted: 26 July 2011

ABSTRACT

The formation of two-dimensional crystalline film of *n*-pentadecane ($C_{15}H_{32}$) on a flat substrate with attractive forces similar to that of the metals or graphite substrate is investigated with molecular dynamics simulation. By controlling the deposition rate of the molecules, we observed the behavior in adsorption and conformational change of single molecule and the growing process of the *n*-pentadecane film. Two distinct sub-processes are recognized in the formation of the crystalline film, the formation of the molecular clusters and the coalescence of the molecular clusters. It is found that the conformational changes are gentle when only or few molecules are deposited on the substrate. However, this change becomes drastic as more molecules are gathered together. The accelerated conformational variation is attributed to the no-bonding molecular interaction. Copyright © 2011 VBRI press.

Keywords: *n*-alkane, two-dimensional film, substrate, molecular dynamics simulation, evaporation, single molecule, adsorption, conformation.

Hong-zhen Li is currently a Lecturer in college of physics and engineering, Qufu Normal University. He received his Ph.D. degree from Yamaguchi University, Japan. He formerly worked as a postdoctoral fellow in Japan Advanced Institute of Science and Technology for about three years, and as a partnership researcher in National Institutes of Natural Science, Japan for one year. His major research interests include: Computational physics, Low-dimensional physics (mainly in thin films, surface and interface physics), and Biophysics.

Xianghe Kong, Male, born in 1960, PhD, Professor. Dr. Kong obtained his Bachelor and PhD degrees in Qufu Normal University and Anhui Institute of Optics & Fine Mechanics, Chinese Academy Sciences in 1982 and 2004 respectively. From 1982 to present, he worked at Qufu Normal University. Dr. Kong's research interests focus on molecular or ionic interaction, molecular spectroscopy, mass spectrometry, REMPI of cluster and molecule, and environmental pollutants online monitoring technique. Dr. Kong has published more than 100 papers. Up to now, There are 30 students for M.S. graduated in his group.

Ke-zhu Yan, male, a native of Yanzhou, Shandong province, China. He is currently a professor in college of physics and engineering, Qufu Normal University. He received his Ph.D. degree from Shanghai University in 2000. His major research interests include: computational physics, quantum statistics and quantum optics.

Introduction

With the discovery of new functions of the organic macromolecules, such as the catalytic, the electric, the biological and the medical function in recent years, the organic macromolecular compounds are investigated extensively. Their applications have been widely extended, from the only use as insulator in the past to the utilization of the conducting polymer, the polymer membrane for separation, the medical polymer materials, the polymer catalyst etc. at present. The organic compounds when used as electronics material are often in forms of thin films. However, the study on the formation process of the organic film was hindered due to the complexity of the structure of the macromolecular materials. The *n*-alkanes have simple molecular structures but show various aggregation forms.

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Therefore, research on the formation of the *n*-alkane thin films will lay important foundation for the preparation of organic electronic materials and membranes of living bodies [**1-6**].

Although many authors have studied the *n*-alkane films, the previous investigations are mainly focused on the properties (such as mechanics, thermodynamics, optics, and electric properties) of the films. An understanding to how the molecules are deposited and how the film grows still remains unavailable. Actually the interactions among the deposited molecules and between the molecule and the substrate have important impacts on the formation process, the structure of the film and its physical properties. Some primary explanations have been proposed for the deposition of the *n*-alkane films. Nevertheless, these explanations were based on postulations to the experimental observations and often disagree with each other. [**7-10**]. Therefore it is necessary to find out the formation mechanism of two-dimensional film. This work is to investigate the behavior in adsorption, the conformational change of the molecules on the substrate and the growing process of the *n*-pentadecane film.

Model and simulation method

Molecular model

The molecule is assumed to be composed of CH_2 and CH_3 groups. These groups interact with each other via bonded potentials (*e.g*. bond stretching, bond-angle bending, and dihedral-angle distortion) and non-bonded van der Waals potential. The atomic force field used in the simulation consists of, (i) the C-C bond-stretching potential

$$U_{stretch}(l) = \frac{1}{2} k_b (l - l_0)^2 \qquad (1)$$

Where l is for the C-C bond length and l_0 is its equilibrium value, (ii) the potential for the bending of C-C-C bond angle θ

$$U_{bend}(\theta) = \frac{1}{2} k_\theta (\cos\theta - \cos\theta_0)^2 \qquad (2)$$

Where θ_0 is the equilibrium bond angle, (iii) the torsion potential

$$U_{torsion}(\phi) = k_\phi \sum_{n=0}^{5} a_n \cos^n \phi \qquad (3)$$

where Φ is the dihedral angle formed by four consecutive carbon atoms, and (iv) the 6-12 Lennard-Jones potential between united atoms separated by more than three bonds along the chain and between the atoms in different chains,

$$U_{LJ}(r) = \begin{cases} 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\} (r < r_c) \\ 0 \ (r > r_c) \end{cases} \qquad (4)$$

where r is the distance between the atoms, and r_c is the cut-off distance chosen to be 2.5σ. In all presentations in this work, the length and the energy are expressed by the following reduced units: the unit length σ = 0.38 nm, the unit energy ε = 500 J/mol. Values of all the parameters used in our simulation are the same as those used in our previous papers [**11, 12**].

Substrate model

It has been experimentally found that some anomalous change of molecular orientation takes place in films on a glass substrate. Here we consider a flat substrate without atomistic scale structures. Hence the substrate potential only depends on the distance r from the evaporated molecule to the substrate surface. Here we adopt the following conventional form given by Steele **[13**]:

$$\phi_{sub}(r) = \frac{2\pi q\sigma^2}{\mathrm{A}} \left\{ \frac{2}{5}\left(\frac{\sigma}{r}\right)^{10} - \left(\frac{\sigma}{r}\right)^{4} - \frac{\sigma}{3d}\left(\frac{\sigma}{r + 0.61d}\right)^{3} \right\} \qquad (5)$$

By setting the parameters in eq.5, the substrate has the depth of the potential minimum of about 11ε, the degree of total attraction of an n-alkane crystal when {001} is the substrate surface. This is also a reasonable value for highly attractive substrate such as metals and graphite [**14, 15**].

Evaporation source and substrate position

The molecules used in the present study are vacuum-evaporated n-pentadecane, $C_{15}H_{32}$. The evaporating source consists of 400 molecules. In order to prepare an isotropic melt source, the initial crystalline sample was melted at a low temperature ramping rate and allowed to relax at 550K, a little lower than the evaporation temperature. Setting the source at the temperature of 550K is to avoid the snowflake evaporation. The relaxing time of the source is about 10ns.

The substrate is fixed 100 angstroms away from the top of the evaporation source. A very weak attractive wall is fixed at the bottom of the evaporation source to prevent the molecules from escaping to the opposite side. The illustration is shown in the following.

In order to investigate the behavior of the molecule on the substrate and the growing process of the two-dimensional film in detail, the increase of the molecule number is required at a stable rate. In this work, the time interval of deposition of the molecule onto the substrate is about 10ps. In order to shorten the waiting time of crystallization of molecules on the substrate, the

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temperature of the substrate is set at 200K (the undercooling ΔT = Tm -T c is about 80K).

Results and discussion

Different adsorption processes and slow conformational change of single molecule

The details of the molecular adsorption vary with the conformation, the velocity, and the orientation of the chain axis of the molecule on the substrate. Bow and elbow are the typical forms of molecules on the substrate (**Fig.1**)

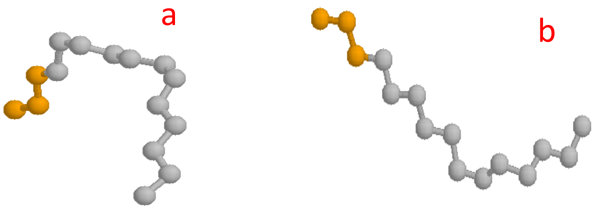

Fig. 1. The typical forms of molecules on a substrate (a) bow, (b) elbow.

when a single molecule is deposited on the substrate, even at temperatures of 200K (the undercooling ΔT = T_m-Tc = 80K is relatively high), the conformational change of the chain is still very slow. It is hard to change the molecule to the *all trans* form. We did not find *all trans* form single molecule, and *all trans* form cluster which consisted of few molecules for a relaxation time of about 800ps. When there are only few molecules on the substrate, they all maintain the bow or elbow conformation.

Stage of multi molecular clusters

During the film growing process (from the adsorption of the first molecule to the formation of the whole two-dimensional crystalline film), the formation of the film experienced a stage of multi molecular clusters. In the stage, with the increase of number of the deposited molecule, both the number of the clusters and size of the clusters increase (compare **Fig. 2** (**a**) and (**b**). It is interesting, however, that the molecular clusters do not coalescence if no more molecules are added, even if the clusters are relaxed for as long as 1000ps (**Fig. 2** (**b**)).

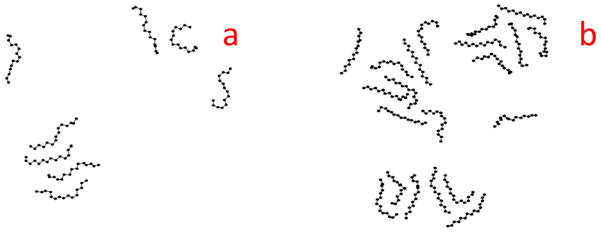

Fig. 2. Typical clusters containing (**a**) 8 and (**b**) 21 molecules and their growths.

Formation of whole film and dramatic conformational change of large cluster

As more molecules are deposited on the substrate, the formation process enters a new stage of growth: the clusters aggregate to form a two-dimensional crystalline film. In the stage, when add molecules, it does not result in the increase of cluster numbers. Rather the size of the clusters increases with increasing molecules (compare **Fig. 3** (**a**) and (**b**)). Finally the large clusters join together to form a well-crystallized film (**Fig. 3** (**b**), (**c**) and (**d**)).

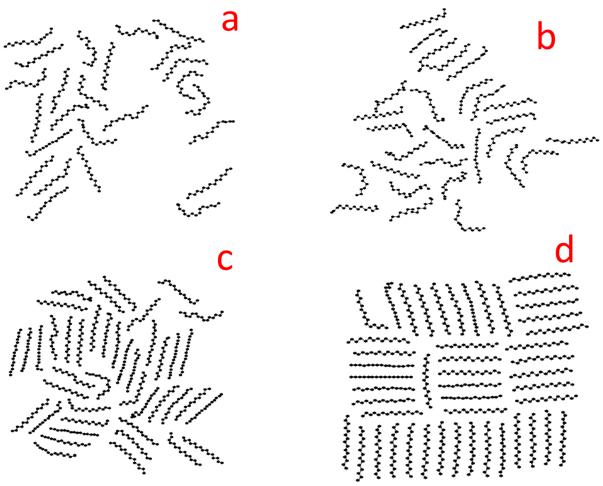

Fig. 3. The coalescence of clusters. (**a**) 25 molecules, (**b**) 28 molecules, (**c**) 43 molecules, (**d**) 48 molecules.

Comparison of the conformational evolution of molecules in **Fig. 3** (**c**) with that of the single molecule in **Fig. 1**, an obvious feature is found. The molecules in large clusters have drastic conformational change. For example, although it takes *ca*. 500 ps to relax from **Fig. 2** (**a**) to Fig. **3** (**b**), the conformational change is not obvious. However, the conformational change is so dramatic that the film in **Fig. 3** (**c**) can be regarded as a crystalline state, though the relaxation time is less than 200 ps from **Fig. 3** (**b**) to (**c**). Actually a two-dimensional crystalline film of *n*-pentadecane has been completed in **Fig. 3** (**d**). The conformation of the molecules is an almost perfect all trans form.

Conclusion

The formation of two-dimensional *n*-pentadecane crystalline film was studied by molecular dynamics simulation. By controlling the deposition rate of the molecules at a uniform time interval of 10ps, the behavior of single molecule on the substrate and the growing process of the film with the increase of the molecule are clarified. Two distinct stages are recognized during the formation of a two-dimensional *n*-pentadecane crystalline film. Firstly the deposited molecules gather to form clusters. At this stage, the number of clusters does not increase with increasing molecule numbers. In the second stage, the numbers of the clusters decrease as more molecules are deposited on the substrate; actually it is the coalescence of molecular clusters, which forms larger cluster. We also notice that the change of conformation to *trans* form is very slow when there are only few molecules on the substrate. However, the variation of the conformation becomes dramatic when one molecule is surrounded by other molecules in large cluster (the second stage). The molecular

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interaction is supposed to be responsible for the accelerated conformational change of the molecules.

Acknowledgements

This work is supported by the Scientific Research Starting Foundation of Qufu Normal University, and by Shan-dong Nature science Foundation (No. ZR2011AQ016). HZL appreciates the helpful discussion with Prof. T. Yamamoto at Yamaguchi University, Japan.

Reference

1. Santhanamoorthi, N.; Kolandaivel, P.; L. Adler-Abramovich, Gazit, E.; Filipek, S.; Viswanathan, S.; Strzelczyk, A.; Renugopalakrishnan, V. *Adv. Mat. Lett.* **2011**, *2(2)*, 100. **DOI**: 10.5185/amlett.2010.12223
2. Dhakate, S.R.; Aoki, T.; Ogasawara T. *Adv. Mat. Lett.* **2011**, *2(2)*, 106. **DOI**: 10.5185/amlett.2010.12189
3. Patrykiejew, A.; Sokołowski, S.; Ilnyskyi, J.; Sokołowska, Z. *J. Chem. Phys.* **2010**, *132*, 244704. **DOI**: 10.1063/1.3456263
4. Li, Z.L.; Djohari, H.; Dormidontova, Elena E. *J. Chem. Phys.* **2010**, *133*, 184904. **DOI**: 10.1063/1.3498781
5. Sharma, Chhavi.; Gautam, Sneh,; Dinda, A.K.; Mishra, N.C. *Adv. Mat. Lett* **2011**, *2(2)*, 90. **DOI**: 10.5185/amlett.2011.1211
6. Chang, W.H.; Chou, S.H.; Lin, J.J.; Chen, W.C.; Sheng, Y.J. *J. Chem. Phys.* **2010**, *132*, 21490401. **DOI**: 10.1063/1.3428761
7. Tanaka, K.; Okui, N.; Sakai, T. *Thin solid films.* **1991**, *196*, 137. **DOI**: 10.1016/0040-6090(91)90181-V
8. Fukao, K.; Kawamoto, H.; Horiuchi, T.; Matsushige, K. *Thin Solid Films.* **1991,** *197*, 157. **DOI**: 10.1016/0040-6090(91)90228-P
9. Yamamoto, T; Nozaki, K; Yamaguchi, A; Urakami, N. *J. Chem. Phys.* **2007**, 127, 154704 **DOI:** 10.1063/1.2781390
10. Nozaki, K; Saihara, R; Ishikawa, K; Yamamoto, T. *Jpn. J. Appl. Phys.* **2007**, 46, 761 **DOI**: 10.1143/JJAP.46.761
11. Li, H.Z.; Yamamoto, T. *J. Chem. Phys.* **2001**, *114*, 5774. **DOI**: 10.1063/1.1351162
12. Li, H.Z.; Yamamoto, T. *J. Phy. Soci. Jap.* **2002**, *71*, 1083 **DOI**: 10.1143/JPSJ.71.1083
13. Steele, W. A. *Surf. Sci.* **1973** , *36*, 317. **DOI**:10.1016/0039-6028(73)90264-1
14. Balasubramnian, S.; Klein, M.; Siepmann, J. I. *J. Chem. Phys.* **1995**, *103*, 3184. **DOI**: 10.1063/1.470251
15. Yamamoto, T. *J. Chem. Phys.* **1998,** *109*. 4638. **DOI**: 10.1063/1.477068

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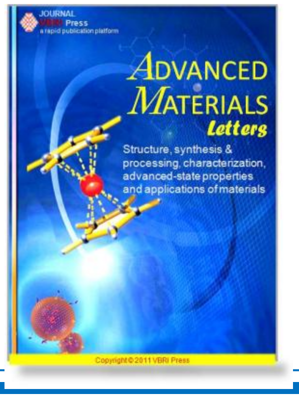

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