Electronic Supplementary Information (ESI)

Real-space observation of local anisotropic correlation between buckled dimers on Si(100) induced by a bidentate adsorbed molecule

Md. Zakir Hossain,[a] Kozo Mukai,[b] Yoshiyuki Yamashita,[c] Hiroshi Kawai[d] and Jun Yoshinobu*[b]

[a] *Faculty of Engineering, Gunma University, Kiryu City, Gunma, Japan*
[b] *The Institute for Solid State Physics, The University of Tokyo, Kashiwa, Japan; E-mail: yoshinobu@issp.u-tokyo.ac.jp*
[c] *National Institute for Materials Science, SPring-8, Sayo, Japan*
[d] *Faculty of Sciences, Kyushu University, Hakozaki, Fukuoka, Japan*

Experimental procedure: The Si(100) substrate was obtained from a cut of a Si-wafer (phosphorous doped, resistivity = 0.05 Ω cm). The clean surface was prepared by repeated flashing to 1500 K under UHV (ultrahigh vacuum) with a base pressure better than 1.5 x 10^{-8} Pa. Thus prepared clean surfaces contain < 1 % defects. The sample was cooled down to 65 K using liquid N_2 followed by pumping, which solidified the N_2. The liquid TMEDA (N,N,N′N′-tetramethylethylenediamine) was purified by several cycles of freeze-pump-thaw method. Gaseous TMEDA molecules were introduced into the UHV chamber through an electronically controlled pulse-valve dosing system. STM measurements were carried out using a JEOL SPM-4500.

Theoretical simulation: The thermal fluctuation of buckling arrangement of dimers around adsorbed TMEDA molecules was investigated with Monte Carlo simulation. The real system of dimers is projected onto the Ising spin model, in which the two degrees of freedom of an Ising spin correspond to the two possible tilting angles of the buckled dimer.[1,2] The Ising spin Hamiltonian consists of the coupling between neighboring dimers along the dimer row (V) and that of across the row (H, D).[1,2] The values of the coupling coefficients are obtained on the basis of first principles calculation as V=-51.9 meV, H=6.6 meV, D=3.6 meV.[1] In the present Monte Carlo simulation, the tilting angles of the buckled dimer with adsorbed TMEDA are fixed at the angles dominated by TMEDA.

The critical temperature T_c of the phase transition between buckled and non-buckled dimer structures on the Si(001) surface is observed to be around 220 K ~ 250 K by

LEED.[3] Whereas the phase transition temperature obtained by the Monte Carlo simulation is about 310 K. The discrepancy in temperature between experimental and theoretical results is related to the insufficient description of the real system. In the Ising model, the freedom of local structure on the Si(001) surface is reduced to two degrees.[1,2] This reduction of freedom causes the underestimation of entropy in the system, which results in an upward shift of the critical temperature. Indeed the improvement in theoretical model is required to solve the large discrepancy, but it is still difficult. At 300 K, the dimers in STM images and Monte Carlo simulation are in the non-buckled and buckled phase, respectively. Direct comparison between the results obtained by STM measurement and Monte Carlo simulation at the same temperature (300 K) is not proper. We performed Monte Carlo simulations at several temperatures, and we found that the calculations at 400 K reproduce the characterstics of STM images at 300 K. It is noted that the calculated results reproduce most of the aspects in the exerimental data if the temperature is scaled with T_c.[1] Thus, in the present study, the experimental results at 300 K are compared with the results of Monte Carlo simulation at 400 K, because the critical temperature for phase transition obtained from the Monte Carlo simulation is about ~1.3 times higher than that observed by experiments.

Valence photoelectron spectroscopy (PES) studies: TMEDA has two tertiary amino groups, having a lone pair on each N atom, separated by the -CH_2-CH_2- unit. To see the bonding nature of TMEDA molecule on the Si(100) surface, we carried out valence photoelectron spectroscopy (PES) of the surface. Figure ESI 1 shows a series of valence PES spectra of the Si(100) surface as a function of TMEDA coverage at 90 K. These coverage dependent evolutions of PES spectra are similar to that observed for trimethylamine (TMA) on Si(100).[4] In the case of multilayer TMEDA, an occupied state peak at 4.3 eV is ascribed to the lone pair state of the amino group.[4] At lower coverage, this N-lone pair peak does not appear. Thus the PES spectra indicate that similar to the cases of TMA and 2-dimethylaminopropyne on Si(100),[4,5,6] the chemisorption of TMEDA on Si(100)c(4 x 2) involves the interaction of N lone pair with the electron deficient down atom of the buckled dimer. This bonding configuration is in agreement with a recent report about ethylenediamine on the Si(100)-(2x1) surface.[7]

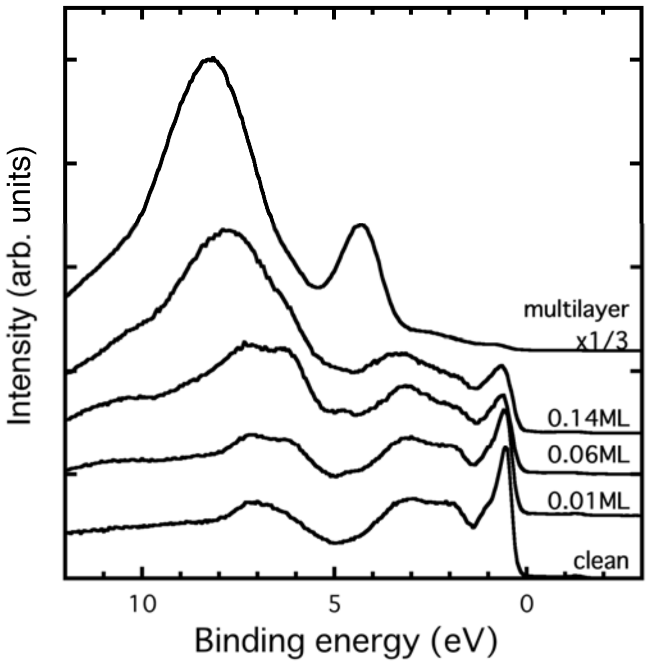

Figure ESI 1. Valence photoelectron spectra of clean and TMEDA adsorbed Si(100) surfaces at 90 K. hν = 21.2 eV (He I).

References

---

[1] K. Inoue, Y. Morikawa, K. Terakura and M. Nakayama, *Phys. Rev. B*, 1994, **49**, 14774.

[2] Y. Nakamura, H. Kawai and M. Nakayama, *Phys. Rev. B*, 1995, **52**, 8231.

[3] T. Tabata, T. Aruga and Y. Murata, *Surf. Sci.* 1987, **179**, L63.

[4] M.Z. Hossain, S. Machida, Y. Yamashita, K. Mukai and J. Yoshinobu, *J. Phys. Chem. B*, 2004, **108**, 4837.

[5] M.Z. Hossain, Y. Yamashita, K. Mukai and J. Yoshinobu, *Chem. Phys. Lett.*, 2004, **388**, 27.

[6] M.Z. Hossain, S. Machida, Y. Yamashita, K. Mukai and J. Yoshinobu, *J. Am. Chem. Soc.*, 2003, **125**, 9252.

[7] C. Mathieu, X. Bai, J. –J. Gallet, F. Bournel, S. Carniato, Rochet, E. Magnano, F. Bondino, R. Funke, U. Kohler and S. Kubsky, *J. Phys. Chem. C*, 2009, **113**, 11336.