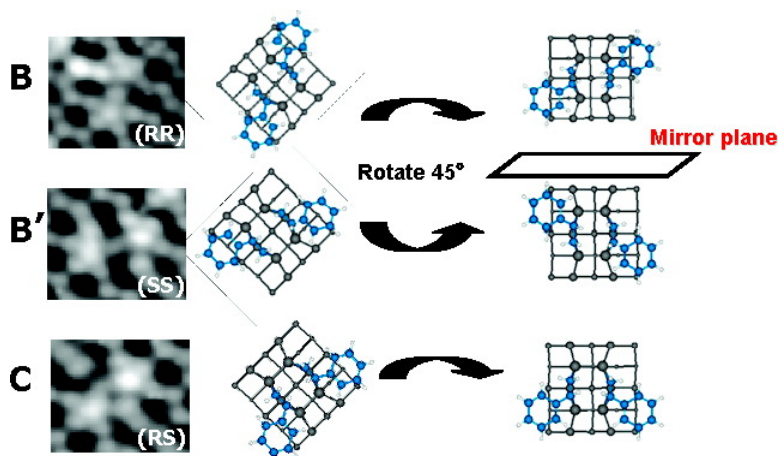


Chiral Attachment of Styrene Mediated by Surface Dimers on Ge(100)

Yun Jeong Hwang, Ansoon Kim, Eunkyung Hwang, and Sehun Kim

J. Am. Chem. Soc., **2005**, 127 (14), 5016-5017 • DOI: 10.1021/ja050234o • Publication Date (Web): 19 March 2005

Downloaded from <http://pubs.acs.org> on March 25, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 3 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Chiral Attachment of Styrene Mediated by Surface Dimers on Ge(100)

Yun Jeong Hwang, Ansoon Kim, Eunkyung Hwang, and Sehun Kim*

Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea

Received January 13, 2005; E-mail: sehun-kim@kaist.ac.kr

Stereochemistry has been intensively studied due to the discovery that most biological reactions are enantiospecific, as well as the finding that only single enantiomers of chiral molecules naturally exist in living organisms. Understanding of enantioselective antibody recognition and asymmetric enzyme reaction is indispensable for pharmaceutical industries.¹ The chirality of organic molecules on surfaces has been successfully investigated using scanning tunneling microscopy (STM) in order to monitor stereoselective reaction mechanisms at the single molecular level.^{2,3} Such chiral studies on the surface are also attractive in view of heterogeneous asymmetric catalysis, chiral separation, and chemical sensing. Until now, most studies have concentrated on metals,^{2a-e} highly ordered pyrolytic graphite,^{2f-h} or intrinsically chiral surfaces.^{2i-k} On the other hand, a few studies have focused on chiral adsorption on semiconductor surfaces,³ which is important for potential application to silicon-based molecular devices, biosensors, and nanolithography.

Fascinating and plentiful organic–semiconductor surface interactions have been studied on the (100) surfaces of diamond, silicon, and germanium, which reconstruct to form similar surface X=X dimers (X = C, Si, Ge).⁴ All chiral configurations observed on the Si(100) surface have been based on [2 + 2] and [4 + 2] cycloaddition between one alkene molecule and a surface dimer.³ However, more variable and adaptable routes to fabricate the chiral configuration should be explored to design stereoselective processes on a semiconductor surface. Recent studies of unsaturated hydrocarbon molecules on Si(100) and Ge(100) show that two molecules adsorb in the paired end-bridge (PEB) between two adjacent surface dimers within the same dimer row, as well as on the top (OT) of a surface dimer via a [2 + 2] cycloaddition forming di- σ bonds.⁵ We expect that styrene (C₆H₅–CH=CH₂) molecules on Ge(100) may adsorb in the OT and PEB configurations at room temperature. The OT configurations produce the (*R*) and (*S*) chiral products. The PEB configurations are divided into three kinds of PEB configurations according to the orientation of the phenyl ring of each styrene molecule: the diastereomeric (*R,S*) and the enantiomeric (*R,R*) and (*S,S*) configurations. The dimeric adsorption of styrene is mediated by Ge surface dimers; after one styrene adsorbs in one end-bridge, highly reactive unsaturated Ge atoms react with a second styrene.^{5a,f} Such dimeric chiral adsorption is formed in a different way from that on metal surfaces where the dimerization is produced by the interaction between the adsorbed molecules, such as hydrogen bonding after annealing the sample.^{2a,b}

Here, we present a novel method for achiral molecules to produce dimeric enantiomers and diastereomers covalently bonded to the Ge(100) surface. We have investigated the chiral adsorption configurations of styrene on Ge(100) using STM. Styrene was employed as a prochiral molecule that becomes a chiral species after reaction with the Ge(100) surface.

Figure 1a shows a filled-state STM image of styrene adsorbed onto the Ge(100) surface. The image exhibits various adsorption

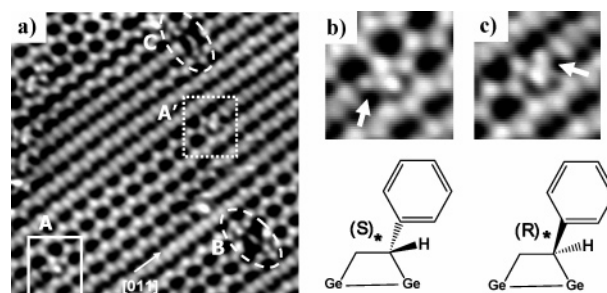


Figure 1. (a) Filled-state STM image ($12 \times 12 \text{ nm}^2$, $V_s = -1.0 \text{ V}$, $I_t = 0.1 \text{ nA}$) of styrene adsorbed onto a Ge(100) surface at a coverage of 0.02 ML. Enlarged images indicate (b) features A and (c) A', which reveal (*S*) and (*R*) chiral OT configurations, respectively.

features denoted as A, A', B, and C. Panels b and c of Figure 1 show the enlarged images of features A and A'. The spots marked with arrows are distinguished from bare Ge dimers (shown as bean or hexagon shapes) by narrowing of the bright spots. We can more clearly distinguish these spots when they are imaged dark in the empty-state STM image due to the elimination of π electronic states of Ge dimers (Supporting Information Figure S1). On the basis of several STM studies of unsaturated hydrocarbons on the semiconductor surfaces, we expect that these spots are associated with reacted vinyl groups of styrene with the Ge dimer via di- σ bonding. Each of the features of A and A' has an extra bright spot located on the lower Ge atom of the adjacent dimer within the same dimer row; this bright spot is attributed to the phenyl ring of styrene. The phenyl ring preserving the aromaticity is imaged bright since the π -bonding states of the aromatic ring located near the Fermi level elevate the tunneling current. Therefore, the most appropriate adsorption geometries for features A and A' are the OT configuration that has been studied in reactions of styrene on the (100) surface of group IV.^{4b,6} The reduced symmetry of adsorbed styrene induces a chiral center, and the (*S*) or (*R*) chiral OT configuration can be determined by the attack direction of styrene to the Ge dimer.^{3a} Reactions at the *Si* and *Re* faces lead to configurations with (*S*) and (*R*) chirality, respectively. Figure 1b,c illustrates that feature A is the mirror image of feature A', and features A and A' can be assigned to the (*S*) and (*R*) chiral OT configurations, respectively.

On the other hand, there are other adsorption features denoted as B and C. Figure 2 shows a high-resolution STM image measured at -1.8 V of sample bias. We can expect that all adsorption geometries are formed via the reaction between the vinyl group of styrene and Ge dimers due to the low reactivity of benzene on Ge(100) at room temperature.⁷ Similar to the previous adsorption study of ethylene, which has a reactive vinyl group, on Ge(100), features B, B', and C can be assigned as the structures of two styrene molecules reacted with two Ge dimers since the features are 2-fold as large as feature A and have two bright spots associated with the phenyl rings. Therefore, the most possible configurations for

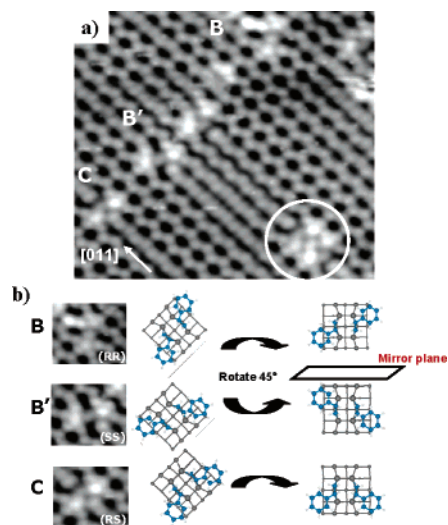


Figure 2. Stereoisomers of paired adsorbed styrene configurations at a coverage of 0.02 ML; (a) filled-state STM image ($12 \times 11 \text{ nm}^2$, $V_s = -1.8 \text{ V}$, $I_t = 0.1 \text{ nA}$) of styrene adsorbed onto a Ge(100) surface, and (b) enlarged STM images and schematic illustration of the (*R,R*)-, (*S,S*)-, and (*R,S*)-PEB configurations.

features B, B', and C are PEB configurations, as shown in the schematic illustrations of Figure 2b. The features B and B' are associated with PEB configurations, where the axis running through the two phenyl rings is oriented diagonally to the dimer row direction (*trans*-PEB). On the other hand, feature C shows the *cis*-PEB configuration, where the axis running through the two phenyl rings is oriented perpendicularly to the dimer row direction.^{6a} Each styrene in the PEB configuration has a chiral center, resulting in the (*R,R*)-, (*S,S*)-, and (*R,S*)-PEB configurations. The *trans*-PEB configurations can be classified into the enantiomeric (*R,R*) and (*S,S*) configurations whose mirror plane is $\sigma_v = (0-1 1)$. On the other hand, the (*R,S*)-*cis*-PEB configuration becomes a meso compound whose configuration is superimposable on its mirror image even though it contains chiral centers.

The population of each PEB configuration reflects the relative stability or energy barrier height in the adsorption pathway of each PEB configuration. The average ratio of the PEB configuration populations is 1:1.4:1.4 (*cis*-PEB:(*R,R*)-*trans*-PEB:(*S,S*)-*trans*-PEB) at 0.1 ML of styrene. Therefore, we expect that the *trans*-PEB configurations are more stable than the *cis*-PEB configuration. We suggest that the dimeric adsorption of styrene on Ge(100) has a certain degree of diastereoselectivity, but no preference between the *trans*-PEB (*S,S*) and the *trans*-PEB (*R,R*) configurations is observed. It is reasonable that styrene adsorbs diastereoselectively on an optically inactive Ge(100) surface on the basis of organic chemical knowledge; diastereomers have different chemical properties, whereas enantiomers have identical chemical properties toward optically inactive reagents.

Previous studies have elucidated that the PEB configuration is more favorable than the OT configuration under thermodynamic control processes.⁵ Therefore, a surface with only PEB configurations can be obtained after selective desorption of the OT configuration by annealing the surface at the appropriate temperature (Supporting Information Figure S2).⁸ In addition, two adjoining *cis*-PEB configurations (circle) are shown in Figure 2a, suggesting

the possibility for the formation of an ordered PEB phase along the dimer row. The ordered phase has the potential for a carrier channel due to the high conductivity of styrene molecules.

In conclusion, we have presented that a prochiral styrene molecule produces chiral structures when reacted with the Ge(100) surface. Specifically, we have shown that dimerization of styrene molecules on Ge(100) produces the enantiomeric (*R,R*) and (*S,S*) configurations. Because the PEB configuration has been observed when unsaturated hydrocarbon molecules are adsorbed on Si(100) and Ge(100) surfaces,⁵ the reaction can be used for producing chirality on these surfaces using acetylene or ethylene derivatives. Therefore, we anticipate that chiral configuration by dimeric adsorption will provide chiral organic hybrid systems on semiconductor surfaces for chemical reactions and silicon-based molecular devices.

Acknowledgment. This research was supported by grants from KOSEF through the Center for Nanotubes and Nanostructured Composites, the Brain Korea 21 Project, and National R&D Project for Nano Science and Technology.

Supporting Information Available: Experimental details, filled- and empty-state STM images, and TPD spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Sheldon, R. A. *Chirotechnology*; Marcel Dekker: New York, 1993; pp 39–72. (b) Cline, D. B. *Physical Origin of Homochirality in Life*; Woodbury: New York, 1996; pp 17–49.
- (2) (a) Chen, Q.; Richardson, N. V. *Nat. Mater.* **2003**, *2*, 324–328. (b) Kuhnle, A.; Linderoth, T. R.; Hammer, B.; Besenbacher, F. *Nature* **2002**, *415*, 891–893. (c) Raval, R. *J. Phys.: Condens. Mater.* **2002**, *14*, 4119–4132. (d) Ohtani, B.; Shintani, A.; Uosaki, K. *J. Am. Chem. Soc.* **1999**, *121*, 6515–6516. (e) Lorenzo, M. O.; Baddeley, C. J.; Mury, C.; Raval, R. *Nature* **2000**, *404*, 376–379. (f) Yablon, D. G.; Giancarlo, L. C.; Flynn, G. W. *J. Phys. Chem. B* **2000**, *104*, 7627–7635. (g) Wei, Y.; Kannappan, K.; Flynn, G. W.; Zimmt, M. B. *J. Am. Chem. Soc.* **2004**, *126*, 5318–5322. (h) Sowerby, S. J.; Heckl, W. M.; Petersen, G. B. *J. Mol. Evol.* **1996**, *43*, 419–424. (i) Erwin, S. C.; Baski, A. A.; Whitman, L. J. *Phys. Rev. Lett.* **1996**, *77*, 687–690. (j) Horvath, J. D.; Koritnik, A.; Kamakoti, P.; Sholl, D. S.; Gellman, A. J. *J. Am. Chem. Soc.* **2004**, *126*, 14988–14994. (k) Ahmadi, A.; Attard, G.; Feliu, J.; Rodes, A. *Langmuir* **1999**, *15*, 2420–2424.
- (3) (a) Lopinski, G. P.; Moffatt, D. J.; Wayner, D. D. M.; Wolkow, R. A. *Nature* **1998**, *392*, 909–911. (b) Lopinski, G. P.; Moffatt, D. J.; Wayner, D. D. M.; Zgierski, M. Z.; Wolkow, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 4532–4533. (c) Lopinski, G. P.; Moffatt, D. J.; Wayner, D. D. M.; Wolkow, R. A. *J. Am. Chem. Soc.* **2000**, *122*, 3548–3549. (d) Teague, L. C.; Boland, J. J. *J. Phys. Chem. B* **2003**, *107*, 3820–3823.
- (4) (a) Bent, S. F. *Surf. Sci.* **2002**, *500*, 879–903. (b) Filler, M. A.; Bent, S. F. *Prog. Surf. Sci.* **2003**, *73*, 1–56. (c) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413–441. (d) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271–1308.
- (5) (a) Kim, A.; Choi, D. S.; Lee, J. Y.; Kim, S. *J. Phys. Chem. B* **2004**, *108*, 3256–3261. (b) Cho, J. H.; Kleinman, L. *J. Chem. Phys.* **2003**, *119*, 2820–2824. (c) Miotto, R.; Ferraz, A. C.; Srivastava, G. P. *Surf. Sci.* **2002**, *507*, 12–17. (d) Lu, X.; Zhu, M. P. *Chem. Phys. Lett.* **2004**, *393*, 124–127. (e) Silvestrelli, P. L.; Pulci, O.; Palumbo, M.; Sole, R. D.; Ancilotto, F. *Phys. Rev. B* **2003**, *68*, 235306. (f) Lu, X.; Zhu, M. *Chem. Phys. Lett.* **2004**, *393*, 124–127.
- (6) (a) Schwartz, M. P.; Ellison, M. D.; Coulter, S. K.; Hovis, J. S.; Hamers, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 8529–8538. The authors suggested that styrene attaches to the Si(100) surface in only OT configuration. However, the re-examination of STM images of styrene on Si(100) in Figure 2c of ref 6a shows the paired bright features similar to the paired end-bridge (PEB) configuration observed in this study, which may provide the possibility for the dimeric chiral adsorption of styrene on Si(100), as well. (b) Zhang, Y. P.; Yang, L.; Lai, Y. H.; Xu, G. Q.; Wang, X. S. *Appl. Phys. Lett.* **2004**, *84*, 401–403. (c) Guisinger, N. P.; Greene, M. E.; Basu, R.; Baluch, A. S.; Hersam, M. C. *Nano Lett.* **2004**, *4*, 55–59.
- (7) Fink, A.; Menzel, D.; Widdra, W. *J. Phys. Chem. B* **2001**, *105*, 3828–3837.
- (8) Hwang, Y. J.; Hwang, E.; Kim, A.; Kim, S. In preparation.

JA050234O