Directionality of *o*-Phthalaldehyde adsorbed onto H-passivated Si(100) Surface Characterized by NEXAFS and HRPES

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The electronic and adsorption structure of *o*-phthalaldehyde (OPA) on the H-Si(100) surface was investigated by using Near Edge X-ray Fine Structure (NEXAFS) and high resolution photoemission spectroscopy (HRPES). We confirmed that the OPA grown on the H-Si(100) surface showed good dependency with about 60 degree tilting angle using NEXAFS and a single O 1s peak by using HRPES. Hydrogen atom passivated on the Si(100) surface was found to be a seed for making one dimensional organic line that uses a chain reaction as the H-Si(100) surface was compared with the hydrogen free Si(100) surface.

Key Words: *o*-Phthalaldehyde, H-Si(100), HRPES, NEXAFS, 1-D Organic molecular line

Introduction

For several decades, the fabrication of organic nanostructures and their self-assembling control on silicon surfaces has been intensively studied because of their versatile potential application as a silicon-based electronic components as well as the connecting wire in a variety of molecular scale devices.[1-6] Especially, the manipulation of one-dimensional (1D) organic nanostructures on the hydrogen terminated Si(100) (H-Si(100)) surface has been researched not only for industrial applications but also for academic interest.[4,7]

Generally, to make one-dimensional (1D) organic nanostructures, the radical species must succeed in abstracting a hydrogen atom from an adjacent Si-H surface site through chain reactions. As a result, it must generate a stable chemisorption between the organic molecule and the consecutive chain reactions using radical included in hydrogen atom.[8] The organic layers and lines on silicon surfaces have been a very interesting research subject from both scientific and technological points of view. The hybrid between the organic materials and the chain reactions is of particular interest since 1D line growth might provide the connecting wire in molecular devices and in the patterning of molecular nano scale devices. A density functional calculation revealed that *o*-phthaladehyde (OPA) grows 1D molecular lines self-directly on the H-terminated Si(001) surface.

Recently, Cho *et al.* have reported an interesting theoretical results that OPA (C$_8$H$_6$O$_2$) molecule on H-Si(100) can be formed into 1D organic molecular line using a chain reaction[9] and the mechanism of it.[10] To clarify the formation of 1D organic molecular line that uses OPA, we performed a near edge x-ray adsorption fine structure (NEXAFS) and high resolution photoemission spectroscopy (HRPES) experiment using synchrotron radiation.

Experimentals

An n-type Si(100) sample with a resistivity of 0.1 Ω cm was cleaned by repetitive heating to 1200 °C after outgassing at 600 °C for 12 hours; the cleanliness of the Si(100)-2×1 surface was confirmed by HRPES. We used hydrogen plasma dozer to prepare H-terminated Si(100) surface. We maintained the temperature of Si(100)-2×1 to room temperature and back filled the hydrogen gas to the base pressure was 5×10^{-8} Torr during 2 min at the filament temperature of 1580 °C. And then we confirmed the formation of H-Si bond through the Si 2*p* core level spectra. OPA (C$_8$H$_6$O$_2$: see Figure 1) was purchased from SIGMA ALDRICH (> 99.0% purity) and further purified through several freeze-pump-thaw cycles to remove all dissolved gases before being exposed to clean Si(100)-2×1. The purity of OPA was verified using *in situ* mass spectrometry in a vacuum chamber. OPA was exposed onto Si(100)-2×1 at room temperature through a direct doser controlled by a variable leak valve. The pressure during OPA exposure was determined from the uncorrected ion gauge reading. The exposure unit is Langmuir (L) (1 L= 1×10^{-6} Torr·sec).

C 1*s*, O 1*s* and Si 2*p* core level spectra were measured using the photon energy of 330, 635, 135 eV at 8A2 HR-PES beamline in the Pohang accelerator laboratory (PAL). The binding energy and the spectral resolution of C 1*s*, O 1*s* and Si 2*p* were calibrated by measuring the Au 4$f_{7/2}$ core level and the Au Fermi edge. The base pressure of the chamber was maintained below 2.0×10^{-10} torr. All the spectra were recorded in the normal emission mode. The photoemission spectra were carefully analyzed by using a standard nonlinear least squares fitting
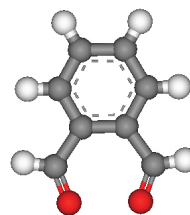
Figure 1. The structure of *o*-phthaladehyde molecule. Each gray, white, red colored ball indicates carbon (C), hydrogen (H), and oxygen (O), respectively.
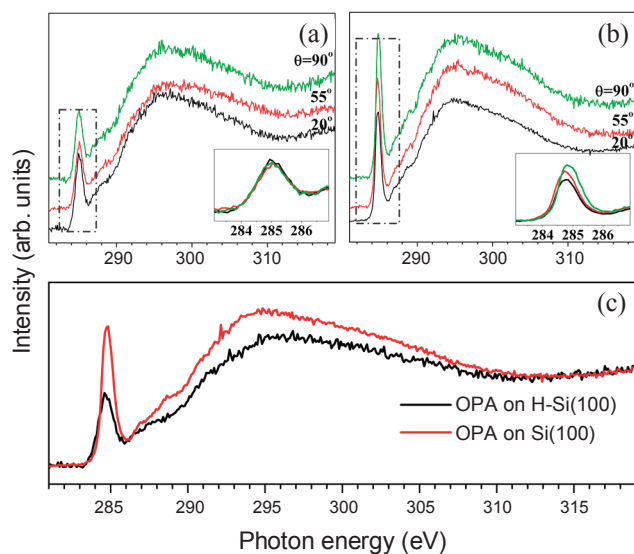
Figure 2. NEXAFS C K-edge spectra of (a) 100 L OPA/Si(100) and (b) 100 L OPA/H-Si(100) surface. (c) Comparison of the intensities of samples prepared under different conditions.
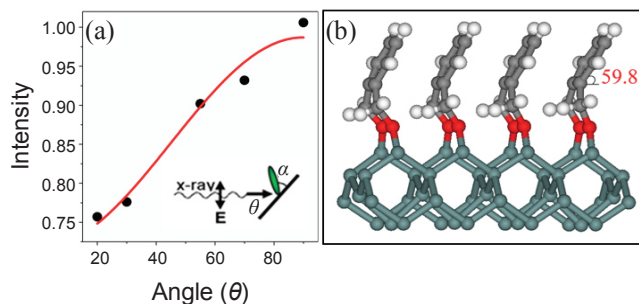

Figure 3. (a) Intensity of the π* (C=C) resonance of OPA on H-Si(100)-2×1 as a function of the incidence angle. (b) Schematic diagram of the OPA adsorbed onto the H-Si(100) surface. Gray, white, red, and dark cyan colored balls correspond, respectively, to carbon (C), hydrogen (H), oxygen (O), and the Si(100) surface.

procedure with Voigt functions.[11]

The NEXAFS spectra were measured at 2B1 PES beamline in the partial electron yield (PEY) detection mode with a retarding voltage of −210 V and an accelerating voltage of 1.6 kV.[12] Molecular bonding information for the top few layers of the multilayer films was obtained from the PEY mode NEXAFS spectra by considering probing depths of less than 10 Å.[13] The photons had a degree of polarization of about 85%, with an incident photon energy resolution of 350 meV near the carbon K-edge region.

Data and Results

First, C K-edge NEXAFS spectra were acquired. Figure 2(a) displays C K-edge spectra for the OPA adsorbed onto the Si(100) surface, and Figure 2(b) shows the C K-edge spectra for the OPA adsorbed onto the hydrogen-passivated Si(100) surfaces using a different incidence angle.

An OPA molecule adsorbed onto the hydrogen-free Si(100) surface, as shown in Figure 2(a), was distinctly different in structure from an OPA molecule adsorbed onto the H-Si(100) surface. The intensity of the C=C π* was found to be independent of the incident angle θ. In contrast, OPA molecules adsorbed onto the H-Si(100) surface, shown in Figure 2(b), showed an angular dependence of the C=C π* intensity at a photon energy of 285 eV. The insets of Figures 2(a) and 2(b) show the intensity variations as a function of photon incident angle θ. The inset of Figure 2(b) in particular shows good angular dependence, indicating that the OPA molecules were uniformly oriented on the H-Si(100) surface. Figure 2(c) compares the intensity variations of C=C π* at θ = 20°. As shown, the intensity obtained from OPA on H-Si(100) decreased to almost 52.2 % of the intensity observed from the OPA adsorbed onto the hydrogen-free Si(100) surface. Due to the presence of the reactive Si=Si dimer on the Si(100)-2×1 surface, OPA adsorbed with random orientations onto the Si(100)-2×1 surface.

The OPA C=C π* intensity on the H-Si(100) surface clearly showed an angular dependence (Figure 2(b)). The average tilt angle between the double bonds of the OPA and the Si(100)-2×1 substrate was determined using an analytical solution to the NEXAFS intensity problem. The relationship between the photoelectron intensity and the incident photon beam angle can be expressed by the equation.[13,14]

$$I_v = C[\frac{P}{3}\{1+\frac{1}{2}(3\cos^2\theta-1)(3\cos^2\alpha-1)\}+\frac{(1-P)}{2}\sin^2\alpha] \quad (1)$$

where α and θ are the angle between the molecular axis and the surface normal and the angle between the light polarization vector (E-vector) and the surface normal, respectively, and P is the degree of polarization.

For this experiment, we assumed a polarization factor of P = 0.85. Moreover, the tilting angle of the OPA molecules adsorbed onto the H-Si(100) surface was calculated using the experimentally measured relative intensity of the 285.0 eV π* (C=C) resonance as a function of the polarization vector angle.

Figure 3(a) shows the intensity of the π* (C=C) resonance of OPA on H-Si(100)-2×1 surfaces as a function of the incidence angle. Quantitative analysis revealed an average tilt angle of 59.8°. Figure 3(b) illustrates the adsorption geometry obtained from the two distinct spectra.

HRPES spectra were acquired to characterize the mechanism of 1D molecular growth on the H-terminated Si(100) surface. A single or double oxygen peak in the HRPES spectrum would be characteristic of an autocatalytic chain reaction. The left panel shows the Si 2p core-level spectra for samples of 1D organic nanostructures prepared by a variety of methods. The Si 2p peak of the clean Si(100)-2´1 surface was decomposed into four peaks that reflected the surface states of the dangling bond (S_u), the second layer (S), components originating from defects (D), and bulk (B). After confirming the clean Si 2p core-level spectrum (see Figure 4(a)), atomic hydrogen was deposited using a plasma hydrogen doser to terminate the Si(100) surface. As shown in Figure 4(b), the peak corresponding to Si-H appeared at a higher binding energy (100.1 eV), and the surface peak (marked as S_u) disappeared completely, indicating that the
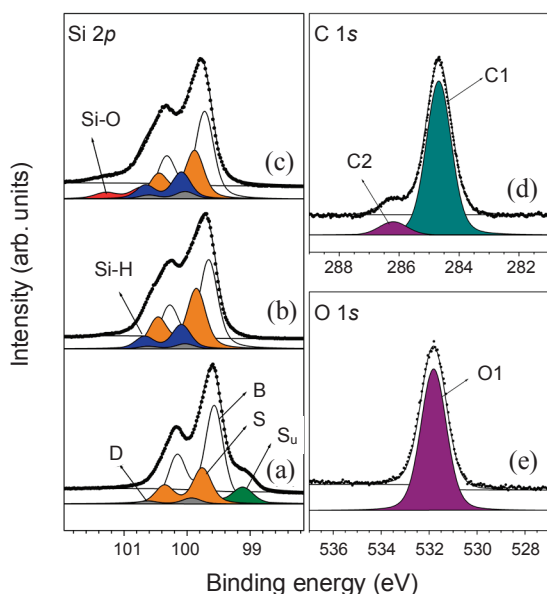
Figure 4. High resolution photoemission spectra. Left panel: Si 2*p* core level spectra (a) clean, (b) 100 L of hydrogen dosing, (c) 100 L OPA deposition on H-Si(100) surface. Right panel: (d) C 1s and (e) O 1s core-level spectrum obtained after OPA on H-Si(100) surface.

Si(100) surface was completely covered with hydrogen. Finally, the OPA was deposited onto the H-terminated Si(100) surface to study the autocatalytic chain reaction. Figure 4(c) shows the Si 2*p* core-level spectrum obtained after OPA deposition on the H-Si(100) surface. The Si-O related peak was observed at a binding energy of 100.7 eV.

The focus of this study was the growth of 1D organic molecular nanostructures aligned along a dimer row. Therefore, the C 1*s* and O 1*s* peaks of OPA also required examination. Figure 4(d) shows the C 1*s* core-level spectrum obtained after OPA deposition. As expected, two distinct carbon peaks were observed: one peak corresponded to the phenyl ring at 284.7 eV and the other peak originated from the carbonyl group at 286.1 eV. Figure 4(e) shows the O 1*s* core-level spectrum. As mentioned, the oxygen peak was the most important feature required for confirmation of the OPA chain reaction. As shown in this figure,

a single oxygen peak at 531.8 eV indicated the chain reaction, as expected. These findings suggested that OPA growth on the H-Si(100) surface was accompanied by the simultaneous formation of Si-O due to radical transformation.

Conclusion

We investigated the growth and structure of a 1D organic molecular nanostructure on a H-terminated Si(100) surface *via* OPA chain reaction using NEXAFS and HRPES characterization methods. Two important experimental results were obtained: 1) NEXAFS showed that the OPA molecule grew on the H-Si(100) surface with a 59.8° molecular tilting angle , and 2) the structure was immobilized *via* an autocatalytic chain reaction, as confirmed by the single oxygen peak observed in HRPES.

References

1. Collier, C. P. *et al. Science* **1999**, *285*, 391.
2. Tans, S. J.; Verschueren, A. R. M.; Dekker, C. *Nature* **1998**, *393*, 49.
3. Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413.
4. Lopinski, G. P.; Moffatt, D. J.; Wayner, D. D. M.; Walkow, R. A. *Nature* **1995**, *392*, 909.
5. Bent, S. F. *Surf. Sci.* **2002**, *500*, 879.
6. Hamers, R. J. *Nature* **2001**, *412*, 489.
7. Hossain, Md. Z.; Kato, H. S.; Kawai, M. *J. Am. Chem. Soc.* **2005**, *127*, 15030.
8. Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1995**, *117*, 3145.
9. Choi, J. H.; Cho, J. H. *Phys. Rev. Lett.* **2007**, *98*, 246101.
10. Choi, J. H.; Cho, J. H. *Phys. Rev. Lett.* **2009**, *102*, 166102.
11. Schreier, F. *J. Quant. Spectros. Radiat. Transfer* **1992**, *48*, 743.
12. Lee, H.-K.; Han, J.-H.; Kim, K.-J.; Kamg, T.-H.; Kim, B. *Surf. Sci.* **2007**, *601*, 1456.
13. Stöhr, J. *NEXAFS Spectroscopy*; Springer: New York, 1992.
14. Stöhr, J.; Outka, D. A. *Phys. Rev. B* **1987**, *36*, 7891.