INTRODUCTION

Over the past decade, a considerable number of studies have been made on atomic/molecular-scale device fabrication technology based on self-assembly. By utilizing the self-assembly, one-dimensional molecular lines aligned on a Si(001) surface have been produced. One-dimensional molecular lines were formed on the H-terminated Si(001)-(2×1) surface by a radical chain reaction. We found that pyrazine, which contains two nitrogen atoms of a six-membered ring, tends to align linearly along the dimer row on the bare Si(001)-(2×1) surface at room temperature. Scanning tunneling microscopy and photoelectron diffraction measurements revealed that pyrazine molecules attach between two Si dimer rows on the surface by forming two N-Si bonds. This structure is shown left top in Fig. 1 and called as inter-dimer-bridging (IDB) model. Recently, we also found that the 1D pyrazine lines over 20 nm in lengths can be obtained at elevated substrate temperatures (60-170 ºC). This ordering of the molecule on the surface indicates that the molecules migrate on the surface at that temperature. The stability of pyrazine adsorption has been studied theoretically and found that the inter-dimer-bridging model was the most stable structure using a periodic slab model and the density functional theory calculations. However, there are no theoretical studies of relation between two adjacent molecules, which is important for formation of the 1D molecular chain during migration and electronic structures.

EXPERIMENTAL

In this paper, formation process and electronic structure of the self-directed linear chains of pyrazine is studied by density functional theory calculations and angle-resolved photoelectron spectroscopy.

Key Words: Density functional theory, Pyrazine, Silicon, Surface science.
Perdew-Burke-Ernzerhof functional (GGA-PBE)\textsuperscript{15} using the PHASE code\textsuperscript{16} with an ultrasoft pseudo potential (a plane-wave cutoff of 25 Ry). The (2 \times 2) structure is assumed for the pyrazine-saturated surface\textsuperscript{8}.

The angle-resolved photoelectron spectroscopy experiments were performed in the ultrahigh vacuum system with a base pressure of 10\textsuperscript{-8} Pa at the 18A beam line, KEK-PF synchrotron in Tsukuba, Japan. A Si(001) sample was cleaned by a few cycles of flashing at 1250 \degree C in an ultrahigh vacuum condition. After the flashing, clear (2\times1) low-energy electron diffraction pattern with a low-background was obtained. The clean surface was then exposed to pyrazine vapour \textit{in situ} at ca. 60 \degree C.

### RESULTS AND DISCUSSION

Theoretically optimized cluster models with two pyrazine adsorbates are shown in Fig. 1. The first pyrazine molecule is fixed at the inter-dimer-bridging configuration as the left top model. The second pyrazine location is changed as in the Fig. 1 and total energies were calculated. We assumed side-bridge (SB), nitrogen end-on (EO), cycloaddition (CA) models as well as the inter-dimer-bridging models. Since steric hindrance prevents additional molecules accessing the Si dimers adjacent to the pyrazine adsorbate on the same dimer row, impossible models were excluded. In Table-1, adsorption energies (\(\Delta E_{ads}\)) in kcal/mol for the second pyrazine molecule on the single-pyrazine-adsorbed cluster are listed. For the second pyrazine, minimum total energy was obtained with the IDB1 model. Interestingly, the adsorption energy clearly increases with the IDB2 model, in which the second adsorbate is misaligned from the 1D chain growth direction. This means that presence of pyrazine adsorbates in the inter-dimer-bridging sites singularly is not energetically favourable and thus, pyrazine adsorbates align linearly to decrease the structural energy. The adsorption energy of the EO1 model is almost equal to that of IDB1. At both ends of the 1D molecular chain, the EO1 structure can be formed. In this case, pyrazine adsorbate will revert to the IDB1 structure since the adsorption energy of the SB1 model that is considerable structure from EO1 is clearly higher than that of IDE1. On the other hand, the IDB2 model will be changed...
### Table-1

<table>
<thead>
<tr>
<th>Models</th>
<th>$\Delta E_{ads}$ (in kcal/mol)</th>
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<th>$\Delta E_{ads}$ (in kcal/mol)</th>
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</thead>
<tbody>
<tr>
<td>IDB1</td>
<td>-28.3</td>
<td>SB2</td>
<td>17.6</td>
<td>EO3</td>
<td>-25.4</td>
</tr>
<tr>
<td>IDB2</td>
<td>-12.2</td>
<td>EO1</td>
<td>-28.2</td>
<td>EO4</td>
<td>-17.3</td>
</tr>
<tr>
<td>SB1</td>
<td>-16.6</td>
<td>EO2</td>
<td>-23.1</td>
<td>CA</td>
<td>-13.2</td>
</tr>
</tbody>
</table>

To the more stable EO3 model. If sufficient thermal energy is provided to change from EO3 to SB1, the adsorbate will fall into the IDB1 structure. The IDB1 structure can also be formed from the cicroaddition structure through the EO2 structure. Thus, the molecular chain could extend with embedding neighbour adsorbates migrating on the surface.

Then, by comparing electronic structure obtained by the angle-resolved photoelectron spectroscopy experiment with that obtained theoretically, we discuss the electronic structure of the pyrazine-adsorbed surface. Fig. 2 shows a band dispersion map obtained by taking the second differential of angle-resolved photoelectron spectroscopy datasets for a pyrazine-chemisorbed surface. Because the sample surface was in a double domain, angle-resolved photoelectron spectroscopy data contains information about the electronic states in both the [110] and [-110] directions. The angle-resolved photoelectron spectroscopy spectra for a clean 2x1 surface (data not shown) contain a strong peak that corresponds to the Si dimer observed with a high intensity at $E_F - 0.7$ eV at the G point. After adsorption of pyrazine, the Si dimer peak disappeared and an energetically flat surface state was observed at about $E_F - 1.4$ eV in the bulk band gap region. Thus, the surface is clearly semi-conducting. Another electronic state is located at about $E_F - 3.5$ eV with a high intensity. The low dispersions of these peaks indicate that these electronic states are geometrically localized.

![Fig. 1. Structural models of the second pyrazine adsorption on the single-pyrazine-adsorbed Si$_5$H$_6$ cluster](image1)

![Fig. 2. A band dispersion map of ARPES spectra for a pyrazine chemisorbed Si(001) surface along [110]/[-110] direction](image2)
We now discuss these electronic states in terms of the partial density of states obtained by density functional theory calculations. Fig. 3 shows partial density of states iso surfaces. Energies are written relative to the valence band maximum. Difference between the Fermi level and the valence band maximum is expected to be ca. 1.0 eV by the band structure of the clean surface. The partial density of states image for the energy range -1 to 0 eV shows that the electronic states are mainly localized on the Na atom of the chemisorbed molecule. The partial density of states image for -3 to -2 eV shows that the \( \pi \) electronic states of the molecule are localized on the C=C double bonds. Thus, the electronic states at about \( E_F -1.4 \) and -3.5 eV in Fig. 2 respectively correspond to the N dangling bond and C=C \( \pi \) bond states of the pyrazine adsorbate. Because there are well-ordered \( \pi \) bond states, the pyrazine-saturated surface can be considered to be an interface between the Si substrate and organic thin films that have \( \pi \) electronic states perpendicular to the molecular plane.

Conclusion

The formation process and electronic structure of a pyrazine 1D molecular chain formed on the Si(001)-(2×1) surface were studied by density functional theory calculations and angle-resolved photoelectron spectroscopy. It was found by the density functional theory cluster simulation with two pyrazine molecules adsorbed on the Si substrate that the most stable structure is obtained with linearly arranged inter-dimer-bridging pyrazine adsorbates (the IDB1 model in Fig. 1). Through the nitrogen end-on, side-bridge and cicroaddition structures, the molecular chain could extend with embedding neighbor adsorbates migrating on the surface. The angle-resolved photoelectron spectroscopy measurements and the density functional theory calculations reveal that the pyrazine-saturated surface is semiconducting. In the angle-resolved photoelectron spectroscopy band map, the N dangling bond and C=C \( \pi \) bond states of the pyrazine adsorbates were observed.

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REFERENCES